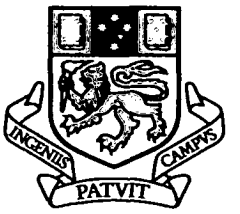

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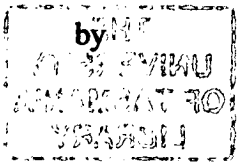
The Role of Organopalladium(IV) Species in Carbon-Oxygen and Carbon-Selenium Bond Forming Reactions



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Submitted in fulfilment of the requirements for the Degree of

Doctor of Philosophy

School of Chemistry
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September, 2003

Declaration

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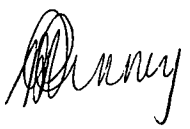

Melanie C. Denney

September 2003

Abstract

The role of palladium in carbon-oxygen and carbon-selenium bond forming processes has been investigated with particular emphasis on the postulated intermediacy of organopalladium(IV) species.

Reactions of the diorganopalladium(II) complexes $PdMeR(L_2)$ [R = Me, 4-tolyl (Tol); L_2 = 2,2'-bipyridine (bpy), *N,N,N',N'*-tetramethylethylenediamine (tmeda)] with diaroyl peroxides $(ArCO_2)_2$ [Ar = Ph, 4-$CF_3C_6H_4$ (Ar_F)] were investigated using variable temperature ^1H NMR spectroscopy, revealing a complex series of reactions. The complexes $Pd^{II}MeR(L_2)$ are predicted to undergo initial oxidative addition of $(ArCO_2)_2$ to give an unobserved Pd(IV) intermediate, '$Pd^{IV}(O_2CAr)_2MeR(L_2)$', which immediately takes part in an exchange reaction with the reagents $Pd^{II}MeR(L_2)$ to form the observed intermediates $Pd^{II}(O_2CAr)R(L_2)$ and $Pd^{IV}(O_2CAr)Me_2R(L_2)$ (except in the case of R = Tol and L_2 = tmeda, where no Pd(IV) intermediate was observed). Decomposition of $Pd^{IV}(O_2CAr)Me_2R(L_2)$ then occurred *via* reductive elimination of carbon-carbon bonds with absence of carbon-oxygen coupling. Carbon-oxygen coupling to form $R\text{-}O_2CAr$ occurred from the reaction of monoorganopalladium(II) species $Pd^{II}(O_2CAr)R(L_2)$ with $(ArCO_2)_2$, with concurrent formation of $Pd^{II}(O_2CAr)_2(L_2)$. The exception was the reaction of $Pd^{II}(O_2CAr)Tol(tmeda)$ with $(ArCO_2)_2$, which proceeded in a 2:1 ratio of reactants to form 4,4'-bitolyl and $Pd^{II}(O_2CAr)_2(tmeda)$. Observed Pd(II) and Pd(IV) intermediates and products of the reactions were also prepared by independent syntheses. Attempts to prepare $Pd^{IV}(O_2CAr)_2MeR(bpy)$ were unsuccessful.

The use of palladium and platinum complexes incorporating an intramolecularly coordinating 'NCN-pincer' ligand, $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$, as a potential means of preparing stable models for Pd(IV) intermediates has been investigated. No reaction was observed between $Pd^{II}(O_2CPh)(NCN)$ and $(PhCO_2)_2$, while the reaction with the platinum analogue resulted in formation and isolation of the stable complex *mer*-$Pt^{IV}(O_2CPh)_3(NCN)$. The reactions of $M^{II}(O_2CPh)(NCN)$ (M = Pd, Pt) with iodomethane resulted in formation of $M^{II}I(NCN)$ and $Me\text{-}O_2CPh$ in a 1:1 ratio. Low temperature ^1H NMR spectroscopic studies revealed the intermediacy of a Pt(IV) species, *cis*-$Pt^{IV}(O_2CPh)_2Me(NCN)$, but Pd(IV) intermediates were not observed.

The complex *cis*-$Pt^{IV}(O_2CPh)_2Me(NCN)$ has been isolated from the reaction of $Pt^{II}(O_2CPh)(NCN)$ with excess $Ag[O_2CPh]$ and iodomethane, and was found to decompose *via* first-order kinetics to form $Pt^{II}(O_2CPh)(NCN)$ and $Me\text{-}O_2CPh$. The reaction of $Pt^{II}Tol(NCN)$ with $(PhCO_2)_2$ led to the formation of *cis*-$Pt^{IV}(O_2CPh)_2Tol(NCN)$. This species has been isolated from the reaction of $PtI_2Tol(NCN)$ with $Ag[O_2CPh]$ and found to be resistant to decomposition. Studies of the analogous palladium chemistry were not feasible due to the instability of $Pd^{II}Tol(NCN)$.

Carbon-selenium bond-forming reactions at palladium were studied as potential models for carbon-oxygen coupling. The complexes $Pd^{II}MeAr(bpy)$ [Ar = Tol, 4-anisyl (Anis)] were found to react with bis(4-chlorophenyl) diselenide $[(ClC_6H_4Se)_2]$ to form *trans*-$Pd^{IV}(SeC_6H_4Cl)_2MeAr(bpy)$, in a rare example of reversible oxidative addition. The Pd(IV) intermediate decomposed by both carbon-carbon and methyl-selenium coupling, with the absence of aryl-selenium coupling. Reactions of $Pd^{II}MeR(tmeda)$ (R = Me, Tol) with $(ClC_6H_4Se)_2$ led to the formation of products arising from both carbon-carbon and carbon-selenium coupling. Palladium(IV) species are postulated as intermediates but have not been observed. Reactions of $Pd^{II}MeR(dmpe)$ [R = Me, Tol; dmpe = 1,2-bis(dimethylphosphino)ethane] with $(ClC_6H_4Se)_2$ resulted in carbon-selenium coupling only. The reaction of $Pd^{II}MeTol(dmpe)$ with one equivalent of $(ClC_6H_4Se)_2$ gave $Me\text{-}SeC_6H_4Cl$ and $Pd^{II}(SeC_6H_4Cl)Tol(dmpe)$ as the major products. However, addition of a second equivalent of $(ClC_6H_4Se)_2$ resulted in aryl-selenium coupling, from the reaction of $Pd^{II}(SeC_6H_4Cl)Tol(dmpe)$ with $(ClC_6H_4Se)_2$.

X-ray structural studies are reported for $Pd(O_2CPh)_2(bpy)$, $Pd(O_2CAr)_2(tmeda)$ (Ar = Ph, Ar_F), $Pd(O_2CPh)Tol(bpy)$, $M(O_2CPh)(NCN)$ (M = Pd, Pt), $Pt(O_2CPh)_3(NCN)$, $Pt(O_2CPh)_2R(NCN)$ (R = Tol, Me) and $Pd(SeC_6H_4Cl)Me(dmpe)$.

Observations of the reactivity of M(II) and M(IV) (M = Pd, Pt) complexes have led to a better understanding of the possible role of Pd(IV) in carbon-oxygen bond forming processes in reactions catalysed by palladium complexes.

Acknowledgements

Throughout my PhD candidature, I have had support and encouragement from many different people and I thank them all. While I believe this to be a comprehensive list of these people, if I have neglected to mention anyone, I am truly sorry.

To my supervisor, Prof Allan Canty, thank you for your constant support and enthusiasm, and many words of wisdom throughout my candidature. I feel privileged to have been part of your research group.

Special thanks to Dr Thomas Rodemann and Dr Jim Patel. You have not only been wonderful teachers and mentors, especially in the laboratory, but have also been great friends. You have both made the lab a fun and enjoyable place to work. Thank you also to other members and visitors to the Canty research group.

To the collective research groups of Prof Allan Canty, Dr Michael Gardiner, Dr Jason Smith, Dr Vicki-Anne Tolhurst and Dr Brian Yates, I have greatly appreciated the excellent forum for discussion of ideas and problems provided by our group meetings.

Prof dr Gerard van Koten, thank you for your contribution to our collaborative project and the opportunity and funding to spend time in your research group. It truly helped me to grow as a chemist. Thank you also to the staff and students of the Debye Institute, Department of Homogeneous Catalysis and Metal-Mediated Synthesis at the University of Utrecht for making my stay so enjoyable.

(Ik zou Prof. Dr van Koten hartelijk willen bedanken voor zijn bijdrage aan onze samenwerking, en voor het bieden van de mogelijkheid en financiering om enige tijd door te brengen in zijn onderzoeksgroep. Het heeft me werkelijk geholpen door te groeien als chemicus. Tevens zou ik zowel de staf als de studenten van het Debye

Instituut, afdeling Katalyse en Metaalgemedieerde Synthese, Universiteit Utrecht willen bedanken voor het zeer aangenaam maken van mijn verblijf in Nederland.)

Thank you Prof dr Rudi van Eldik for the opportunity and funding to spend time in your research group and Joanna Procelewska for contributions to our collaborative project.

Thank you to the staff of the Central Science Laboratory for analysis of samples and for providing expert technical advice. In particular, thank you Dr Noel Davies, Mr Marshall Hughes, Dr Evan Peacock and Dr Graham Rowbottom.

Thank you Prof Allan White and Dr Brian Skelton of the University of Western Australia for X-ray structure determinations.

Thanks to the Australian Research Council and University of Tasmania for project and scholarship funding.

To the staff and students of the School of Chemistry, it has been wonderful being surrounded by such a friendly and supportive bunch of people for the last few years. Thank you all.

Finally, my biggest thank you to my family, and especially my husband Guy, who have been the greatest source of love, support and motivation anyone could ask for. Thank you for always believing in me and helping me to believe in myself.

Abbreviations

Anis	4-methoxyphenyl
Ar	aryl
Ar_F	4-(trifluoromethyl)phenyl
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
bpy	2,2'-bipyridine
Bu^t	*tert*-butyl
Bu^tbpy	4,4'-bis(*tert*-butyl)-6,6'-bipyridine
Bz	benzyl
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
dba	*trans,trans*-dibenzilideneacetone
dmpe	1,2-bis(dimethylphosphino)ethane
dmphen	2,9-dimethyl-1,10-phenanthroline
dppbz	1,2-bis(diphenylphosphino)benzene
dppe	1,2-bis(diphenylphosphino)ethane
DPPF	1,1'-bis(diphenylphosphino)ferrocene
GC	gas chromatography
IR	infrared
Me	methyl
MS	mass spectrometry
NCN	2,6-bis[(dimethylamino)methyl]phenyl
NMR	nuclear magnetic resonance
Ph	phenyl
phen	1,10-phenanthroline
phenyl-BIP	9,10-bis(phenylimino)-9,10-dihydrophenanthroline
Pr^i	*iso*-propyl
pz	pyrazol-1-yl
THF	tetrahydrofuran
tmeda	N,N,N',N'-tetramethylethylenediamine
Tol	4-methylphenyl
4-Tol-BIAN	bis(4-tolylimino)acenaphthalene
Tol-BINAP	2,2'-bis(di-4-tolylphosphino)-1,1'-binaphthyl

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CHAPTER TWO: Carbon-Oxygen Coupling at Palladium Centres

CHAPTER ONE

The Role of Palladium in Carbon-Oxygen and Carbon-Selenium Bond Forming Processes and Related Organopalladium(IV) Chemistry: An Overview

1.1 Introduction

Palladium has emerged as one of the most widely studied and versatile of the transition metals due, at least partly, to its ability to mediate and catalyse a variety of organic processes.[1-7] It is commonly used in both homogenous and heterogeneous catalysis and the vast majority of reactions involve palladium in its 0 or +II oxidation state. The more recent development of organopalladium(IV) chemistry has opened new avenues for the involvement of palladium in organic synthesis, and has led to the mechanisms of some reactions being revisited. The research contained in this thesis investigates the involvement of organopalladium(IV) complexes in carbon-oxygen and carbon-selenium coupling reactions and considers the potential role of such species as intermediates in catalytic reactions.

This chapter reviews the involvement of palladium in carbon-oxygen and carbon-selenium coupling processes (Section 1.2) and discusses aspects of palladium(IV) chemistry and its role in catalytic reactions. Sections 1.3-1.4 consider early suggestions of organopalladium(IV) species and review the basic principles and characteristics of organopalladium(IV) chemistry most relevant to the research described in following chapters. Section 1.5 surveys a selection of proposals for the

involvement of organopalladium(IV) in catalysis that are of considerable current interest, and Section 1.6 examines related organoplatinum(IV) chemistry.

1.2 Palladium(0)/(II) Catalysed Carbon-Oxygen and Carbon-Selenium Bond Formation

Palladium has long been known to catalyse a number of processes in which carbon-oxygen bonds are formed. Such reactions include the oxidation of olefins, nucleophilic substitution of a vinylic substrate, the acetoxylation of benzene and alkylbenzenes and the oxidation of alcohols.[5,7]

One of the earliest and most well-known examples of carbon-oxygen bond formation catalysed by palladium is the oxidation of ethene to acetaldehyde, commonly known as the Wacker reaction (Scheme 1.1).[3-5,7] It is a three-step process involving initial coordination of ethene and nucleophilic attack of water on this palladium-bound ethene (eq 1.1). This is followed by oxidation of palladium(0) by $CuCl_2$ back to the active palladium(II) species (eq 1.2), and oxidation of CuCl by O_2 (eq 1.3). This process can also be applied to higher alkenes to produce ketones.

Scheme 1.1: The Wacker reaction.[3-5,7]

$$CH_2{=}CH_2 + H_2O + PdCl_2 \rightarrow CH_3CHO + 2\,HCl + Pd(0) \quad (1.1)$$

$$Pd(0) + 2\,CuCl_2 \rightarrow PdCl_2 + 2\,CuCl \quad (1.2)$$

$$2\,CuCl + \tfrac{1}{2}\,O_2 + 2\,HCl \rightarrow 2\,CuCl_2 + H_2O \quad (1.3)$$

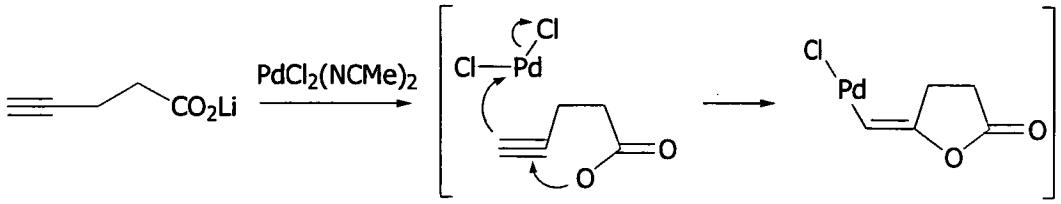
Overall:

$$CH_2{=}CH_2 + \tfrac{1}{2}\,O_2 \rightarrow CH_3CHO \quad (1.4)$$

Cyclisation reactions between carboxylic acids or alcohols and alkynes are also catalyzed by palladium(II) complexes.[3] However, in these cases carbon-oxygen bond formation does not occur directly at the palladium centre, but rather as a result of oxypalladation of the triple bond as shown in Scheme 1.2.[3] Similarly, palladium

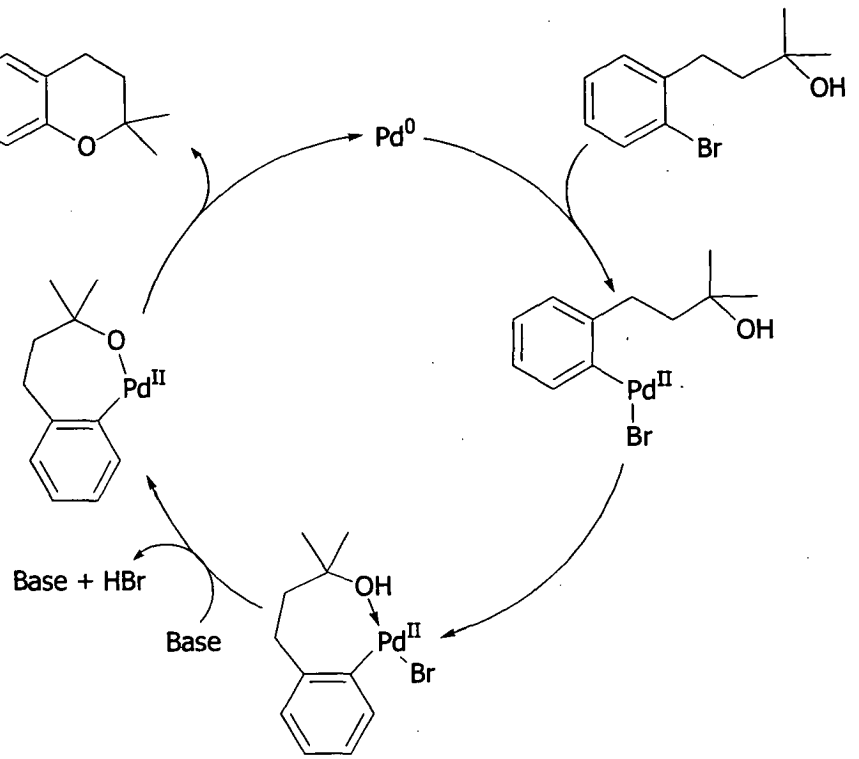
can catalyse cyclisation of olefinic diols, 2-allylphenols and γ,δ-unsaturated alcohols.[5]

Scheme 1.2: Carbon-oxygen bond formation *via* oxypalladation of a triple bond.[3]



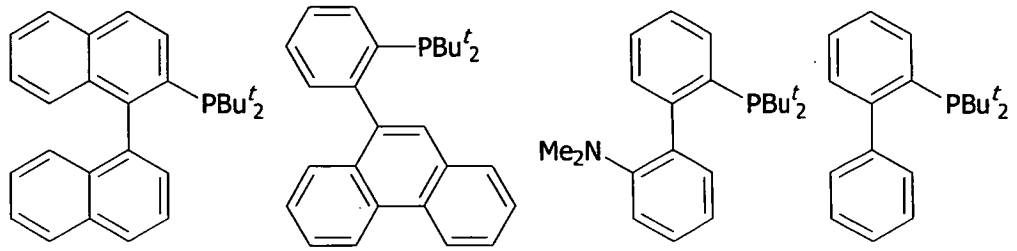
Formation of the carbon-oxygen bond of ethers was reported almost simultaneously by Buchwald and Hartwig in 1996,[8,9] and from this point the field evolved rapidly.[8-21] The initial process, developed by Buchwald and coworkers, involved the synthesis of cyclic aryl ethers *via* an intramolecular *ipso* substitution of an aryl halide with an alcohol. It was proposed to proceed by a Pd(0)/Pd(II) catalytic cycle (Scheme 1.3)[8] similar to that suggested for palladium catalysed aryl amination reactions.[22,23] The use of $Pd(O_2CMe)_2$ as precatalyst in conjunction with either 1,1'-bis(diphenylphosphino)ferrocene (DPPF) or (*S*)-(-)-2,2'-bis(di-4-tolylphosphino)-1,1'-binaphthyl (Tol-BINAP) as bidentate ligand, and K_2CO_3 or $NaOBu^t$ as base in toluene at 80-100 °C were found to be the optimal conditions for this system.

Scheme 1.3: Proposed mechanism for the palladium catalysed synthesis of cyclic aryl ethers. Phosphine ligands are omitted for clarity.[8]



Extension to include primary and secondary alcohols was largely unsuccessful owing to the ease of β-hydrogen elimination, which led to the formation of ketones or aldehydes.[8] However, development of ligands which resulted in a rate of reductive elimination from palladium(II) intermediates that was far greater than β-hydrogen elimination (Figure 1.1) brought about the successful intramolecular cyclisation of primary and secondary alcohols.[24] Of these, the binaphthyl ligand was shown to provide the most generally applicable catalyst system.[24] In addition, these ligands were able to be used in the preparation of heterocycles containing multiple heteroatoms in the constructed ring, and in the cyclisation of optically active alcohols to optically active cyclic ethers.[24] Similar binaphthyl ligands, with moderately large substituents (NMe_2, Ph or cyclohexyl) in the 2' position of the distal naphthyl group, were also very effective as ligands in the intermolecular coupling of primary alcohols and aryl halides.[25]

Figure 1.1: Ligands effective in the cyclisation of primary and secondary alcohols.[24]



The first account of palladium catalysed *intermolecular* carbon-oxygen bond forming reactions between aryl halides and alcohols followed soon after Buchwald's initial report.[9,17] In 1996, Mann and Hartwig tested a range of bidentate phosphine ligands with $Pd(dba)_2$ (dba = *trans,trans*-dibenzilideneacetone) or $Pd(PPh_3)_4$ as precatalysts in the catalytic formation of aryl ethers from aryl halides and sodium *tert*-butoxide.[9] The most effective ligand tested was determined to be DPPF,[9] and subsequent studies found that modification of the electronic properties of this ligand had a dramatic effect on product yields.[10] Nevertheless, none of those ligands tested led to systems effective in the coupling of sodium alkoxides containing β-hydrogens.[9,10] It was not until 2001 that a system able to catalyse coupling of aryl halides with primary alcohols was reported.[25] This method utilised the disubstituted binaphthyl ligands described earlier, and was only efficient for reactions between aryl bromides or chlorides and primary alcohols.[25]

Mechanistic studies of these aryl ether forming reactions led to the first direct observations of aryl-oxygen reductive elimination from palladium(II) centres.[9,18] Mann and Hartwig reported formation of the aryl ether 4-Bu^{t}OC$_6$H$_4$CHO from Pd(OBu^t)(4-C$_6$H$_4$CHO)(DPPF),[9] while Buchwald and coworkers observed a similar reductive elimination from a series of aryl(alkoxo)palladium(II) complexes, Pd(OR)(4-C$_6$H$_4$CN)(L$_2$) [R = CH_2CMe_3, $CHMe_2$, CMe_3; L$_2$ = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), Tol-BINAP, DPPF].[18] The latter reactions were accompanied by biaryl formation.[18] Widenhoefer and Buchwald also found that carbon-oxygen reductive elimination was facilitated by the presence of substituents on the palladium-coordinated aryl that were able to delocalise negative charge (*e.g.* 4-CN, 4-NO_2).[19] Furthermore, very recent studies by

Hartwig and coworkers have shown that steric properties of the ligand can dramatically affect the rate of reductive elimination.[16]

In contrast to the rapidly expanding field of carbon-oxygen bond formation, palladium catalysed carbon-selenium bond formation has remained relatively unexplored. In a rare example, $Pd(PPh_3)_4$ was shown to catalyse the addition of diaryl diselenides to terminal alkynes in a stereoselective manner.[26] Nickel catalysed carbon-selenium bond formation has also been reported.[27] After testing a range of dibromonickel(II) complexes, Cristau *et al.* found that $NiBr_2(bpy)_2$ (bpy = 2,2'-bipyridine) showed good catalytic efficiency in the reaction of various aryl, pyridyl and thienyl iodides or bromides with sodium phenylselenolate. The products were the corresponding aryl phenyl selenides, pyridyl phenyl selenides and thienyl phenyl selenides.[27]

1.3 Synthesis and Structural Aspects of Organopalladium(IV) Complexes

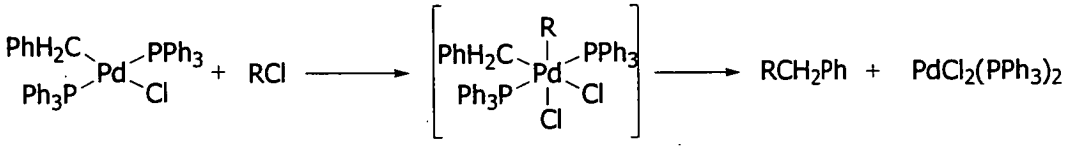
While the organometallic chemistry of palladium(IV) has developed rapidly over the past two decades, it is still a relatively 'young' field when compared with the extensive and well-established area of organoplatinum(IV) chemistry. The isolation of the first organopalladium(IV) complexes were reported in the 1970's with the preparation of a number of mono- and bis(pentafluorophenyl)palladium(IV) species from the oxidation of pentafluorophenylpalladium(II) complexes with chlorine.[28,29]

1.3.1 Early Evidence for Organopalladium(IV) Complexes

Much of the early interest in organopalladium(IV) chemistry stemmed from suggestions that undetected alkylpalladium(IV) species existed as reaction intermediates.[30-37] In their studies on the oxidative addition of alkyl halides to zero-valent palladium complexes, Stille and Lau reported that the palladium(II) products of benzyl halide oxidative addition, *e.g.*

benzyl(chloro)bis(triphenylphosphine)palladium(II), underwent further reactions with benzyl chloride, acyl chlorides and hydrogen chloride.[30] The products of these reactions (bibenzyl, benzyl alkyl ketones and toluene) were consistent with reductive elimination from an unstable palladium(IV) intermediate (Scheme 1.4).[30]

Scheme 1.4: Postulated involvement of Pd(IV) in the reaction of $PdCl(CH_2Ph)(PPh_3)_2$ with benzyl chloride, acyl chlorides and hydrogen chloride.[30]

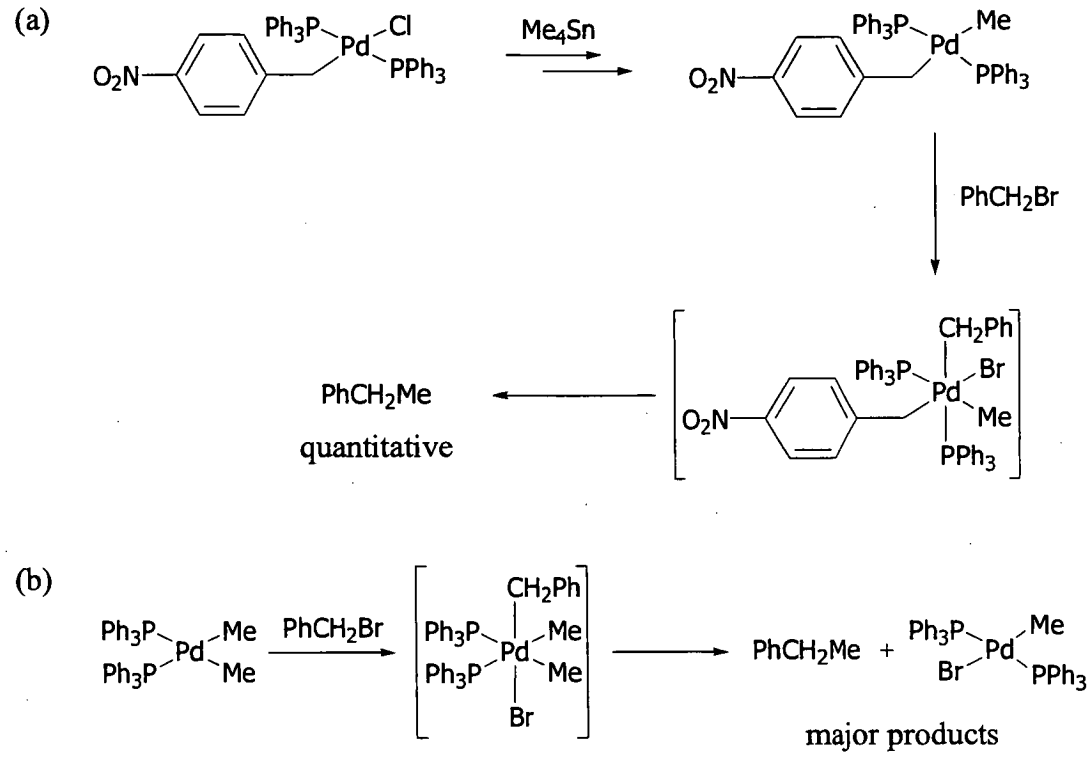


R = $PhCH_2$, CH_3CO, $PhCH_2CO$, H

These observations led to the investigation of a series of reactions by Stille and coworkers in which palladium(IV) species were implicated as probable intermediates.[31-35] Unlike palladium catalysed reactions of benzyl chloride with methyllithium or methylmagnesium bromide, which yield predominantly the homocoupling product bibenzyl, palladium catalysed reactions of organic halides with tetraorganotin complexes (in the presence of excess organic halide) leads to the formation of mainly cross-coupled products.[31,32] This cross coupling was thought to arise from reaction of a dialkylpalladium(II) intermediate with excess organic halide. Strong support for the involvement of a palladium(IV) intermediate in this process was observed when the reaction of 4-nitrobenzyl(chloro)bis(triphenylphosphine)palladium(II) with tetramethyltin, in the presence of benzyl bromide, resulted in quantitative formation of ethylbenzene and no 4-nitroethylbenzene.[31] In order to achieve this result, benzyl bromide is assumed to undergo oxidative addition to palladium as shown in Scheme 1.5a. Further evidence for palladium(IV) intermediates came from the observation that the major products from the reaction between *cis*-dimethylbis(triphenylphosphine)palladium(II) and benzyl bromide were ethylbenzene and methyl(bromo)bis(triphenylphosphine)palladium(II) (Scheme 1.5b).[31] Kinetic studies of reactions of *cis*-dimethylbis(phosphine)palladium(II) (phosphine = PPh_3, $PMePh_2$) with iodomethane gave second order rate constants

consistent with a mechanism involving rate determining oxidative addition of iodomethane to give unstable $Pd^{IV}IMe_3(phosphine)_2$, followed by the immediate reductive elimination of ethane.[35]

Scheme 1.5: Postulated involvement of Pd(IV) intermediates in the reactions of benzyl bromide with (a) $PdCl(CH_2C_6H_4NO_2\text{-}4)(PPh_3)_2$ and tetramethyltin, and (b) $PdMe_2(PPh_3)_3$.[31]



1.3.2 Synthesis of Organopalladium(IV) Complexes

Canty and coworkers reported the first hydrocarbylpalladium(IV) complex and first X-ray structure of an organopalladium(IV) complex in 1986 with the isolation of $PdIMe_3(bpy)$ from the reaction of $PdMe_2(bpy)$ with iodomethane.[38]

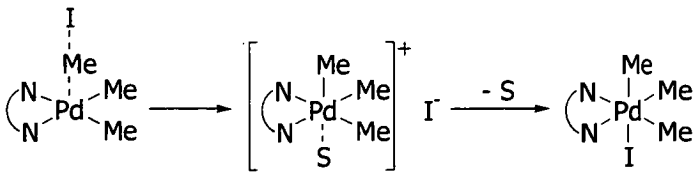
The majority of organopalladium(IV) complexes characterised to date have been prepared by oxidative addition to a square planar palladium(II) substrate incorporating a chelating ligand, and have led to formation of coordinatively saturated octahedral palladium(IV) species. Oxidants have included organyl (sp^3) halides, halogens, diorganyl dichalcogenides, peroxides and water.[39] A notable

exclusion from this list are aryl halides, which undergo reactions in the presence of palladium(II) complexes but not with detectable palladium(IV) intermediates. In a small number of cases, octahedral palladium(IV) species have been generated by ligand exchange at existing palladium(IV) centres.[40,41] The majority of characterised palladium(IV) complexes have been triorgano- species. There are now also a number of examples of isolated diorganopalladium(IV) complexes, but the formation of monoorganopalladium(IV) species sufficiently stable for characterisation is still rare.[42-45]

1.3.2.1 Mechanism of Oxidative Addition

Several kinetic and spectroscopic studies into the mechanism of oxidative addition of alkyl halides to dialkylpalladium(II) complexes have been completed.[46-51] In each case results indicated operation of a S_N2 mechanism and implicated the participation of cationic palladium(IV) intermediates.[46-51] Kinetic studies of the reactions of $PdMe_2(L_2)$ (L_2 = bpy, phen) with iodomethane revealed second order rate constants, rate dependence on solvent and large negative values for $\Delta S^{\ddagger}$, typical of a S_N2 mechanism.[46,47] The NMR detection of cationic species, $[PdMe_3(CD_3CN)(bpy)]^+$,[46] $[PdMe_2(CD_3)\{(CD_3)_2CO\}(bpy)]^+$,[48,49] $[PdMe_2(CH_2COAr)\{(CD_3)_2CO\}(L_2)]^+$ (Ar = phen, 4-C_6H_4Br; L_2 = bpy, phen),[48,49] and $[PdMe_3(CD_3CN)(tmeda)]^+$ [52] are also supportive of a S_N2 mechanism *via* a cationic intermediate. Volume profile studies of the reaction between $PdMe_2(bpy)$ and iodomethane suggest that cation formation is subsequent to an end-on interaction between the two reagents (Scheme 1.6).[51] The neutral species forms on reassociation of the halide (Scheme 1.6).

Scheme 1.6: Proposed mechanism for oxidative addition of iodomethane (and other alkyl halides) to diorganopalladium(II) complexes.[51]



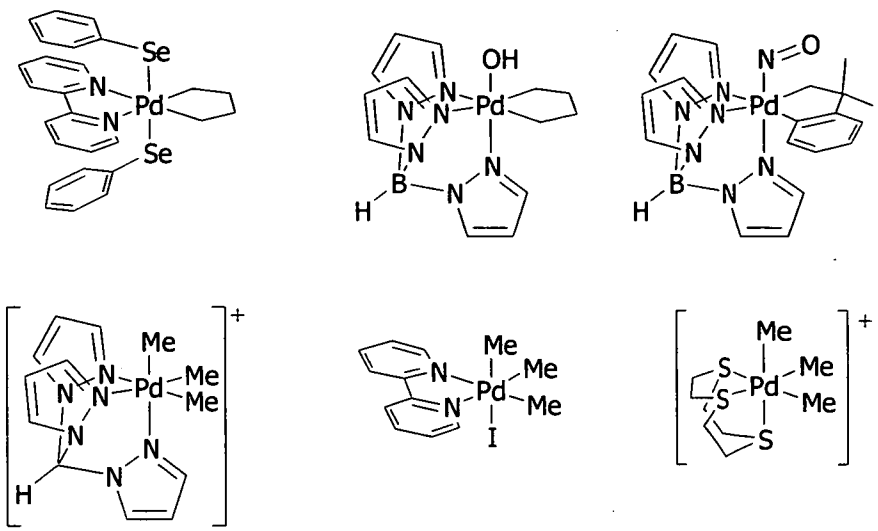
S = solvent

The mechanism of oxidative addition of group 16 E-E bonds (E = O, S, Se) to palladium(II) and platinum(II) is unknown. Addition of $(PhSe)_2$ to $MMe_2(L_2)$ (M = Pd, Pt; L_2 = bpy, phen) and $Pd(CH_2CH_2CH_2CH_2)(bpy)$ leads exclusively to the *trans* addition product, as does the reaction of $PtMe_2(phen)$ with H_2O_2.[53,54] Reactions of $PtMe_2(phen)$ with $(PhCO_2)_2$ and $(RS)_2$ (R = Ph, Me),[54] and the reactions of $PtAr_2(L_2)$ (L_2 = bpy, phen) with $(PhCO_2)_2$[55] predominantly generate the *trans* addition product, but in these cases minor amounts of the *cis* isomer are also identifiable.[54,55] Kinetic studies by Rashidi *et al.* excluded S_N2 and radical mechanisms for the oxidative addition of $(PhCO_2)_2$ to $PtAr_2(L_2)$.[55] While the strong preference for formation of the *trans* isomer does not appear to be consistent with a concerted three-centred mechanism, it is possible that generation of a kinetically favoured *cis* addition product is followed by rapid isomerisation to a thermodynamically preferred *trans* isomer.[55]

1.3.3 Structural Characteristics of Organopalladium(IV) Complexes

Of those complexes that have been characterised crystallographically, diorganopalladium(IV) complexes have the organic groups in a mutually *cis* arrangement in the equatorial plane,[53,56,57] while triorganopalladium(IV) species have a *facial* arrangements of organic ligands.[38-41,48,56,58-64] Figure 1.2 shows several examples of diorgano- and triorganopalladium(IV) complexes.

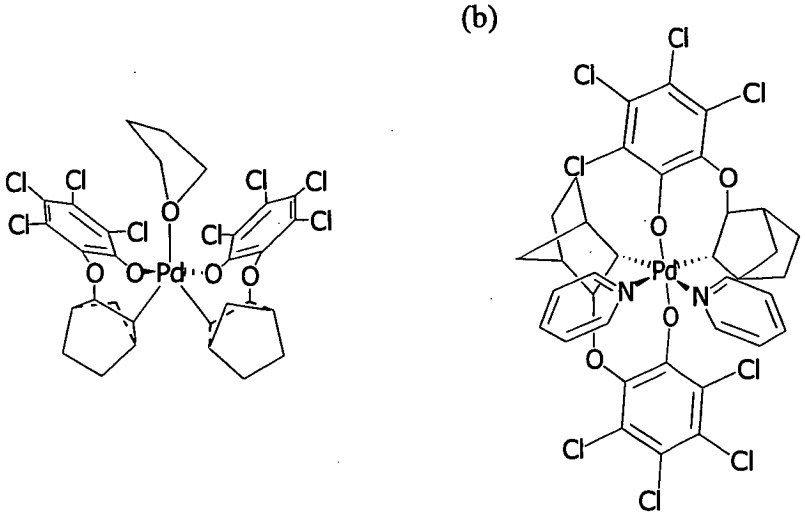
Figure 1.2: Some examples of diorgano- and triorganopalladium(IV) complexes.[38,53,56,57,61,65]



There are a few notable departures from these generally observed structural trends. In a recent report, an ambient temperature reaction of $Pd_2(dba)_3$ with tetrachloro-1,2-benzoquinone and bicyclo[2.2.1]hept-2-ene (norbornene) directly formed a spirocyclic dialkylpalladium(IV) complex with a coordinated diethyl ether molecule.[66] Treatment of the latter complex with tetrahydrofuran (THF) led to the displacement of the diethyl ether to give the species shown in Figure 1.3a. Crystallographic studies of this complex revealed trigonal bipyramidal geometry with C_2-symmetry. The observed spirocyclic framework is probably a result of tandem oxidative cyclisation between the tetrachloro-1,2-benzoquinone and norbornene at the palladium(0) centre.[66] Reaction of this complex with pyridine resulted in formation of a *cis*-bispyridine complex with distorted octahedral geometry (Figure 1.3b).

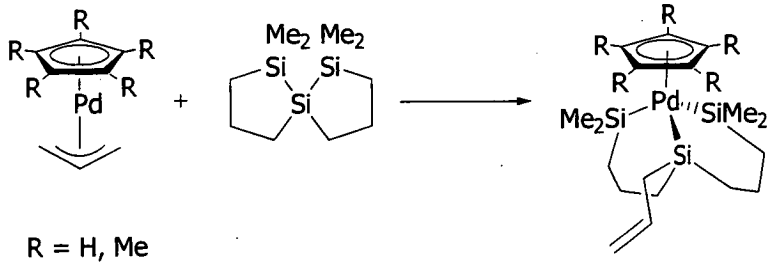
Figure 1.3: Spirocyclic dialkylpalladium(IV) complexes.[66]

(a) (b)



The formation of half-sandwich palladium(IV) complexes was observed during the investigation of silicon-silicon bond activation by palladium(II) complexes.[67,68] The reaction of a spirocyclic trisilane with palladium(II) complexes bearing an allyl group and either a cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) ligand resulted in the formation of stable palladium(IV) complexes as shown in Scheme 1.7.[67,68]

Scheme 1.7: Reactions of $PdCp^{(*)}(CH_2CH{=}CH_2)$ with 1,1,6,6-tetramethyl-1,5,6-trisilaspiro[4.4]nonane.[67,68]



R = H, Me

1.4 Reactions of Organopalladium(IV) Complexes

1.4.1 Reductive Elimination

It is not surprising that the reactions of palladium in its highest oxidation state, +IV, are dominated by processes leading to its reduction to lower oxidation states. Unlike their platinum(IV) analogues, palladium(IV) complexes generally undergo reduction under mild conditions, thus providing a good opportunity for the determination of product distribution from facile reactions.

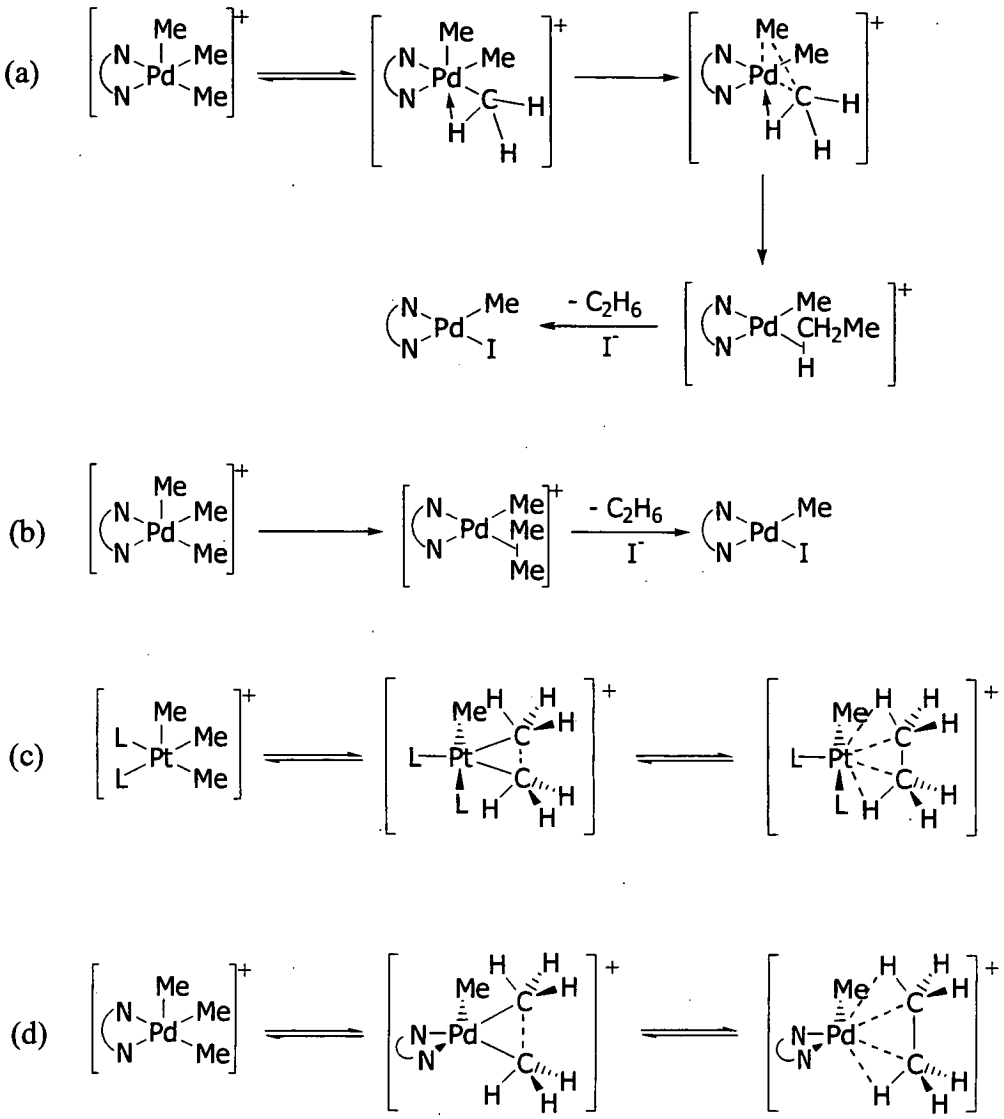
1.4.1.1 Mechanism of Reductive Elimination

In 1988, Byers *et al.* reported detailed studies into the mechanism involved in reductive elimination of ethane from $PdIMe_3(bpy)$.[46] Although reductive elimination of ethane did occur, to some extent, directly from neutral $PdIMe_3(bpy)$, the majority of the decomposition (97.7 %) proceeded *via* a cationic intermediate, $[PdMe_3(bpy)]^+$ or $[PdMe_3(S)(bpy)]^+$ (S = solvent).[46] Considerable support exists for the involvement of a cationic species. The rate of reductive elimination was dependent on both the presence of excess iodide and on the polarity of the solvent. The rate of decomposition was faster in more polar solvents.[46] This is expected as more polar solvents are anticipated to assist in stabilising a cationic intermediate. Excess iodide in the reaction led to a significant decrease in the rate of reductive elimination, presumably by causing the majority of the palladium(IV) to be present as the neutral species, $PdIMe_3(bpy)$, rather than the cationic species required for facile reductive elimination. Further support for cationic intermediates in palladium(IV) chemistry is provided by the observation of several solvated organopalladium(IV) cations by ^1H NMR, obtained during oxidative addition processes. These have included $[PdMe_3(CD_3CN)(bpy)]^+$,[46] $[PdMe_2(CD_3)\{(CD_3)_2CO\}(bpy)]^+$,[48,49] $[PdMe_2(CH_2COAr)\{(CD_3)_2CO\}(L_2)]^+$ (Ar = phen, 4-C_6H_4Br; L_2 = bpy, phen),[48,49] and $[PdMe_3(CD_3CN)(tmeda)]^+$.[52] Studies of activation volumes suggest that in their ground state, palladium(IV) intermediates

will be six-coordinate, although reductive elimination is most likely to occur from a five-coordinate species (*vide infra*).[51]

The intramolecular nature of decomposition of $PdIMe_3(bpy)$, along with the finding that the activation energy in both acetone and methanol is lower than the estimated Pd-Me bond strength, indicates that reductive elimination must be a concerted process.[46] There is considerable current interest in exploring mechanisms of reductive elimination *via* theoretical approaches. Byers *et al.* proposed two mechanisms based on literature views of mechanisms pertaining at the time (1988).[46,58] The first involves carbon-carbon bond formation following agostic interaction of an α-hydrogen of an equatorial methyl group with the metal centre (Scheme 1.8a).[46] Alternatively, direct carbon-carbon coupling could occur from the cationic intermediate in a process analogous to that proposed for reductive elimination from platinum(IV) (Scheme 1.8b).[46] A subsequent theoretical study of reductive elimination from platinum(IV) complexes has led to the proposal shown in Scheme 1.8c, which can be viewed as an elaboration of (b).[64,69] Thus, a scheme showing this for palladium and a bidentate nitrogen ligand is shown in Scheme 1.8d.

Scheme 1.8: Possible mechanisms for reductive elimination from proposed cationic palladium(IV) and platinum(IV) intermediates.[46,64,69]



1.4.1.2 Selectivity of Reductive Elimination

For triorganopalladium(IV) complexes, decomposition occurs almost solely by carbon-carbon bond formation. The most commonly observed triorganopalladium(IV) complexes are those incorporating three methyl groups.[38,46,48,59,60,63,70-76] All of these complexes form ethane and a monomethylpalladium(II) product and, in almost all instances, this is the only decomposition pathway.

In situations where more than one type of organic group is present on the metal, selectivity in coupling can be investigated.[41,47,50,76-80] The preferential formation of thermodynamically favoured products seems to have the largest influence on the selectivity of these reductive elimination reactions. This is reflected in the general preference for formation of bonds according to their bond dissociation energies (Ph-Me > Me-Me > $PhCH_2$-Ph > $PhCH_2$-Me) (Table 1.1).[50] There are, however, a number of other factors that can have an effect on selectivity including the identities of the organic groups, halogen (or pseudohalogen) and ancillary ligands, and the ease of rearrangement of the organic groups around the metal centre. For example, rigidity of the ancillary ligand has an inverse relationship with the selectivity of the coupling observed (Table 1.1), that is, as the rigidity of the ligand increases reductive elimination becomes less selective.

An example where the thermodynamically favoured product is not formed preferentially is the selective formation of Me-Me bonds (80 %) rather than Ph-Me bonds (20 %) from $PdIMe_2Ph(bpy)$ (random distribution would give 33 % Me-Me and 67 % Ph-Me).[50] A possible explanation for this is that the arrangement of ligands in the proposed cationic intermediate may be less favourable for Me-Ph bond formation. It would be of interest to explore this process using the thoeretical approaches of Hill and Puddephatt (Scheme 1.8c)[69] for elimination from a dimethyl(aryl)metal(IV) species.

Table 1.1: Selectivity in carbon-carbon bond formation from $PdXMeR(CH_2Ph)(L_2)$ complexes.

$PdXMe_2(CH_2Ph)(L_2) \rightarrow a$ [$PdX(CH_2Ph)(L_2)$ + Me-Me] + b [$PdXMe(L_2)$ + $PhCH_2$-Me]

L_2	X	*a*	*b*	Ref.
tmeda	Br	≥ 0.95	≤ 0.05	[78]
bpy	Br	0.8	0.2	[47]
bpy	Br	1	0	[41]
bpy	N_3	1	0	[41]
bpy	SCN	1	0	[41]
bpy	O_2CPh	1	0	[41]
bpy	F	~ 0.9	~ 0.1	[41]
bpy	Cl	~ 0.9	~ 0.1	[41]
bpy	I	~ 0.9	~ 0.1	[41]
bpy	OCN	~ 0.9	~ 0.1	[41]
bpy	SeCN	~ 0.9	~ 0.1	[41]
bpy	O_2CCF_3	~ 0.9	~ 0.1	[41]
phen	Br	0.5	0.5	[47]
4-Tol-BIAN [a]	Br	0.6	0.4	[76]

$PdXMeAr(CH_2Ph)(L_2) \rightarrow a$ [$PdX(CH_2Ph)(L_2)$ + Ar-Me] + b [$PdXMe(L_2)$ + $PhCH_2$-Ar]

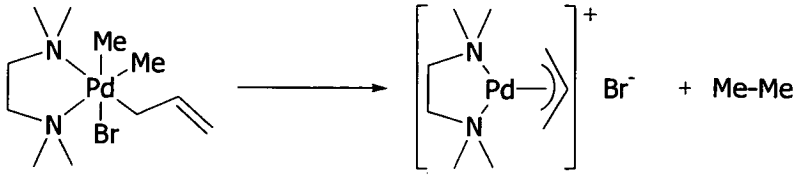
L_2	Ar	X	*a*	*b*	Ref.
tmeda	Ph	Br	1	0	[50]
tmeda	Ph	I	1	0	[50]
bpy	Ph	Br	1	0	[50,77]
bpy	Ph	I	1	0	[50]
bpy	4-Tol	Br	1	0	[77]
bpy	4-$MeOC_6H_4$	Br	1	0	[77]
phen	Ph	Br	~ 0.8	~ 0.2	[77]
phen	4-Tol	Br	~ 0.9	~ 0.1	[77]
phen	4-$MeOC_6H_4$	Br	~ 0.9	~ 0.1	[77]
phen	3-$MeOC_6H_4$	Br	~ 0.9	~ 0.1	[77]

[a] 4-Tol-BIAN = bis(4-tolylimino)acenaphthalene

Decomposition of the allylpalladium(IV) complex $PdBrMe_2(CH_2CH{=}CH_2)$(tmeda) leads to the formation of ethane and a cationic η^3-allylpalladium(II) complex (Scheme 1.9).[78] The vacant coordination site of the

proposed five-coordinate intermediate provides an opportunity for the allyl group to take on strong η^3 bonding mode which could favour ethane elimination.[78]

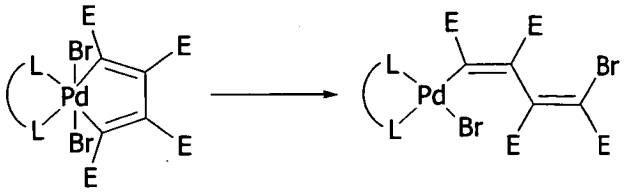
Scheme 1.9: Selective reductive elimination of a triorganopalladium(IV) complex with a η^1-allyl group.[78]



There are a few examples of methyl halide elimination from triorganopalladium(IV) species, but in each case this proved to be only a minor decomposition pathway.[48,76] Reductive elimination from $PdIMe_3$(4-Tol-BIAN) is somewhat unselective when compared with other trimethylpalladium(IV) species which decompose *via* ethane formation only (*vide supra*).[76] While ethane is still the major decomposition product, iodomethane (10-20 %) is also formed, *i.e.* the initial oxidative addition of iodomethane is reversible.[76] In another example of alkyl halide elimination, but not from a reversible reaction, bromomethane was observed in addition to ethane on the decomposition of $PdBrMe_2\{CH_2C(O)Ph\}(L_2)$ (L_2 = bpy, phen).[48]

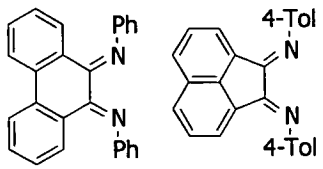
Reductive elimination from diorganopalladium(IV) complexes can lead to the formation of carbon-carbon and carbon-heteroatom bonds. The complexes $PdI_2Me_2(L_2)$ [L_2 = 4-Tol-BIAN, bis(phenylimino)camphane] display lower stability than triorganopalladium(IV) complexes with the same ligands.[76] Reductive elimination from these species is unselective, with both ethane and iodomethane observed along with an insoluble palladium complex.[76] By contrast, decomposition of related dibromopallada(IV)cyclopentadiene complexes with 4-Tol-BIAN and closely related 9,10-bis(phenylimino)-9,10-dihydrophenanthroline (phenyl-BIP) as ligands leads to the formation of a single σ-butadienylpalladium(II) product resulting from carbon-bromine coupling (Scheme 1.10).[44,45] No other products were formed in this reaction.

Scheme 1.10: Decomposition of a dibromopallada(IV)cyclopentadiene complex.[44,45]



$E = CO_2CH_3$

$L_2 =$



phenyl-BIP 4-Tol-BIAN

The decomposition of a variety of diorganopalladium(IV) complexes incorporating bpy, phen and tris(pyrazol-1-yl)borate $\{[(pz)_3BH]^-\}$ as ancillary ligands and PhE^- (E = S, Se) have also been investigated.[53,70] Decomposition of the complexes $Pd(EPh)_2Me_2(L_2)$ (L_2 = bpy, phen) and $[Pd(EPh)Me_2\{(pz)_3BH\}]^-$ display both Me-Me and Me-EPh coupling.[53,70] Kinetic parameters for the reduction of $Pd(SePh)_2Me_2(L_2)$ are consistent with an analogous mechanism to the reduction of $PdIMe_3(bpy)$,[53] and carbon-carbon and carbon-selenium bond formation is expected to occur from a cationic intermediate formed by the dissociation of $PhSe^-$ or a polar intermediate with Pd···Se bond lengthening.[53] It should be noted that although decomposition of $Pd(O_2CPh)_2Me_2(L_2)$ has also been reported,[53] it has now been shown that this complex was incorrectly identified (see Chapter Two).

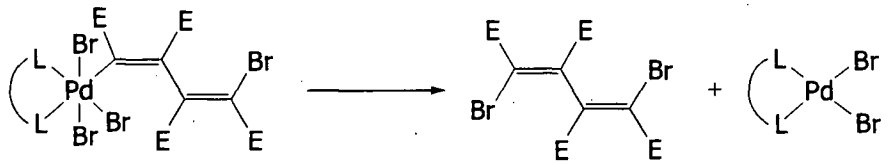
Decomposition studies of palladium(IV) complexes incorporating a palladacyclopentane ring also revealed formation of both carbon-carbon and carbon-chalcogen bonds.[53,70] The complexes $Pd(CH_2CH_2CH_2CH_2)(EPh)\{(pz)_3BH\}$ (E = S, Se) decompose by carbon-carbon bond formation to give cyclobutane and butenes, as well as by carbon-chalcogen coupling to form C_4H_9-EPh and C_4H_7-EPh. Butene products arise by β-hydrogen elimination from the palladium(II) species formed by reductive elimination. The complexes $Pd(CH_2CH_2CH_2CH_2)(EPh)_2(bpy)$

(E = O_2CPh, S) and $\overline{Pd(CH_2CH_2CH_2CH_2)}(O_2CPh)\{(pz)_3BH\}$ were too unstable to be observed, but the formation of analogous products suggests reaction *via* a similar mechanism.[53,70] Although the decomposition of the isolated complex $\overline{Pd(CH_2CH_2CH_2CH_2)}(SePh)_2(bpy)$ was not discussed,[53] it is assumed to decompose by a similar process.

Of the three known examples of monoorganopalladium(IV) complexes, the decomposition behaviour of two has been investigated.[42,45] A recent report described the characterisation of (σ-butadienyl)tribromopalladium(IV) complexes with 4-Tol-BIAN and phenyl-BIP ligands.[45] These complexes displayed lower stability than the related dibromopallada(IV)cyclopentadiene species (*vide supra*), and were observed to decompose cleanly to a 1,4-dibromobutadi-1,3-ene compound and a dibromopalladium(II) complex (Scheme 1.11a).[45] Similarly, the intramolecularly coordinated complex $PdCl_3(CNN')$ {CNN' = $[C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)\text{-}2]^-$} undergoes carbon-chlorine coupling to give a palladium(II) dichloride complex with a pendant, chlorine-substituted aryl group (Scheme 1.11b).[42]

Scheme 1.11: Decomposition of monoorganopalladium(IV) trihalide complexes.[42,45]

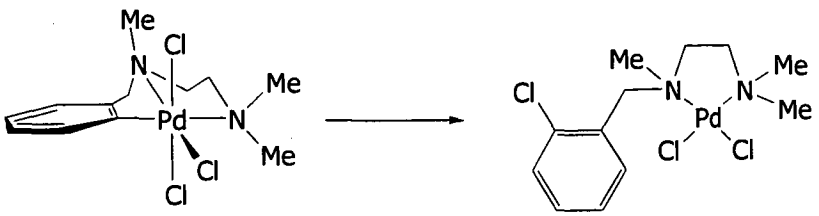
(a)



E = CO_2CH_3

L_2 = phenyl-BIP, 4-Tol-BIAN

(b)



1.4.2 Alkyl Halide Transfer Reactions

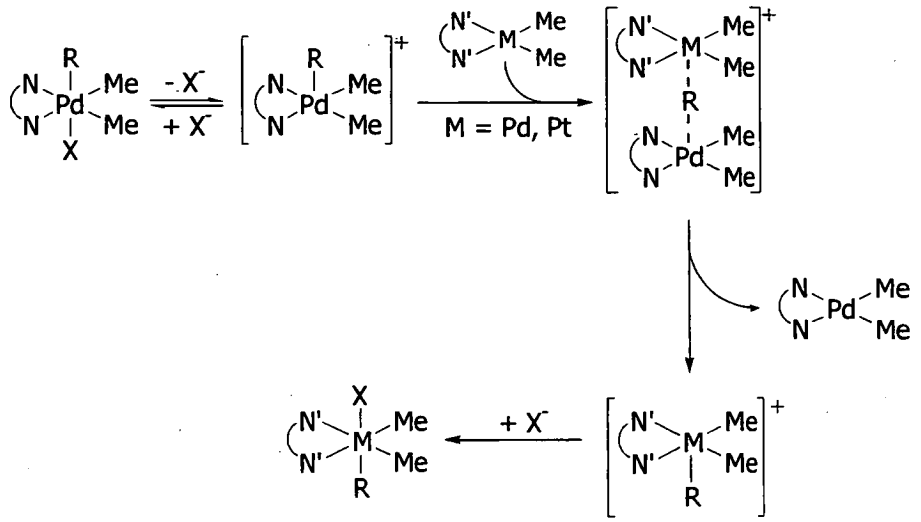
Another reaction which palladium(IV) commonly undergoes is the transfer of alkyl halide groups to palladium(II) or platinum(II) complexes to form metal(IV) complexes of higher stability.[47,50,70,77] In 1989, it was shown that the reactions of $PdIMe_3(L_2)$ (L_2 = bpy, phen) and $PdBrMe_2(CH_2Ph)(L_2)$ with $PtMe_2(L_2)$ led to the formation of more stable platinum(IV) and palladium(II) complexes through the transfer of a methyl (or benzyl) and a halogeno group.[47] Kinetic studies of these processes gave results indicative of reaction *via* a S_N2 mechanism.[47] The reactions followed good second order kinetics and had activation parameters consistent with a S_N2 process. Retardation in the presence of free iodide was observed, implying initial halide dissociation.[47] In terms of mechanism, these results suggest that preliminary halide dissociation from palladium(IV) is followed by nucleophilic attack by the platinum(II) complex on the axial organic group of the palladium(IV) cation. Association of the halide to the newly formed platinum(IV) cation results in the observed neutral platinum(IV) and palladium(II) species. An observed preference for benzyl group transfer is rationalised by the faster rate of nucleophilic attack on $PhCH_2$-X than CH_3-X.[47]

Similar transfer reactions are also observed between palladium species. The reactions between $PdIMe_2Ph(bpy)$ and $PdMe_2(bpy)$ to give PdMePh(bpy) and $PdIMe_3(bpy)$, and between $PdBrMe(CH_2Ph)Ar(bpy)$ and $PdMe_2(phen)$ to give PdMeAr(bpy) and $PdBrMe_2(CH_2Ph)(phen)$, are consistent with the occurrence of an identical mechanism to that described above.[50,77] A similar reaction has also been suggested as the reason for the formation of $PdMe_3\{(pz)_3BH\}$ and $PdMe(PPh_3)\{(pz)_3BH\}$ in the reaction of $[PdMe_2\{(pz)_3BH\}]^-$ with $(PhCO_2)_2$ and PPh_3.[70] Undetected $Pd(O_2CPh)Me_2\{(pz)_3BH\}$ is expected to undergo $PhCO_2^-$ dissociation followed by nucleophilic attack at a $Pd^{IV}Me$ group by $[PdMe_2\{(pz)_3BH\}]^-$ resulting in the transfer of a methyl group.[70]

A representative mechanism for these reactions is shown in Scheme 1.12. The reactions can be considered as reversible, where attack of the more nucleophilic

species, $MMe_2(N'N')$, results in the formation of the more stable M(IV) products $MXMe_2R(N'N')$.

Scheme 1.12: Representative proposed mechanism for alkyl halide transfer from palladium(IV) complexes to palladium(II) and platinum(II).



1.5 The Role of Palladium(IV) in Catalytic Reactions

Palladium(IV) species have been proposed as intermediates in a variety of palladium mediated reactions, and assessments of these proposals have been reported.[39,58,81-83] Spectroscopic evidence for the involvement of organopalladium(IV) species is rare, and consequently, mechanisms involving palladium(II) and palladium(0) intermediates are often proposed as alternatives for many of these reactions.

1.5.1 The Heck Reaction

A classic example of the debate involving palladium(IV) intermediates in catalysis concerns the Heck reaction. The issue of whether palladium(IV) species play a role in the Heck reaction remains a point of debate between some researchers, and has been recently reviewed.[39,81,82] Traditionally, the Heck reaction is considered to involve a Pd(0)/Pd(II) cycle as represented, in simplified form, in Scheme 1.13.

There are several examples of catalysts for which a Pd(II)/Pd(IV) cycle is considered a distinct possibility.[84-87] Ohff *et al.* reported some palladium(II) complexes with PCP-pincer ligands to be highly active catalysts for the Heck reaction (Figure 1.4).[81,85] The involvement of a palladium(0) complex as the active species was considered unlikely. This is largely due to the presence of two strongly chelating rings, which they considered would most likely not allow palladium-aryl bond dissociation during the reaction. The formation of an anionic palladium(0) complex without such chelate opening is improbable.[85]

Scheme 1.13: The classical mechanism for the Heck reaction involving a Pd(0)/Pd(II) cycle (L = ligand; B = base).

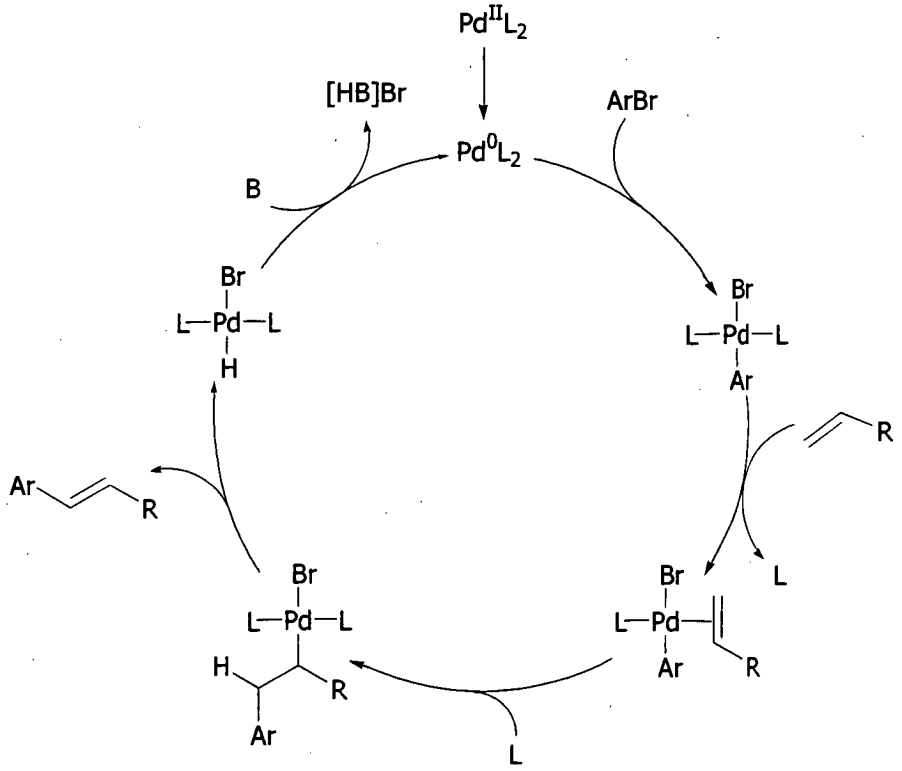
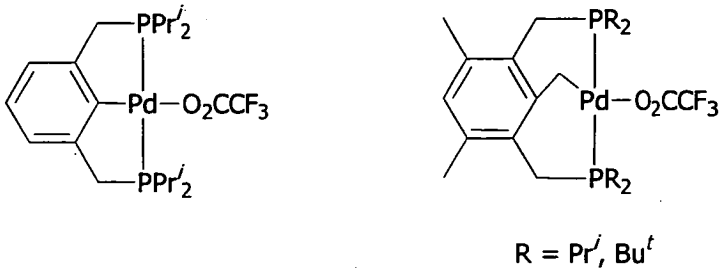
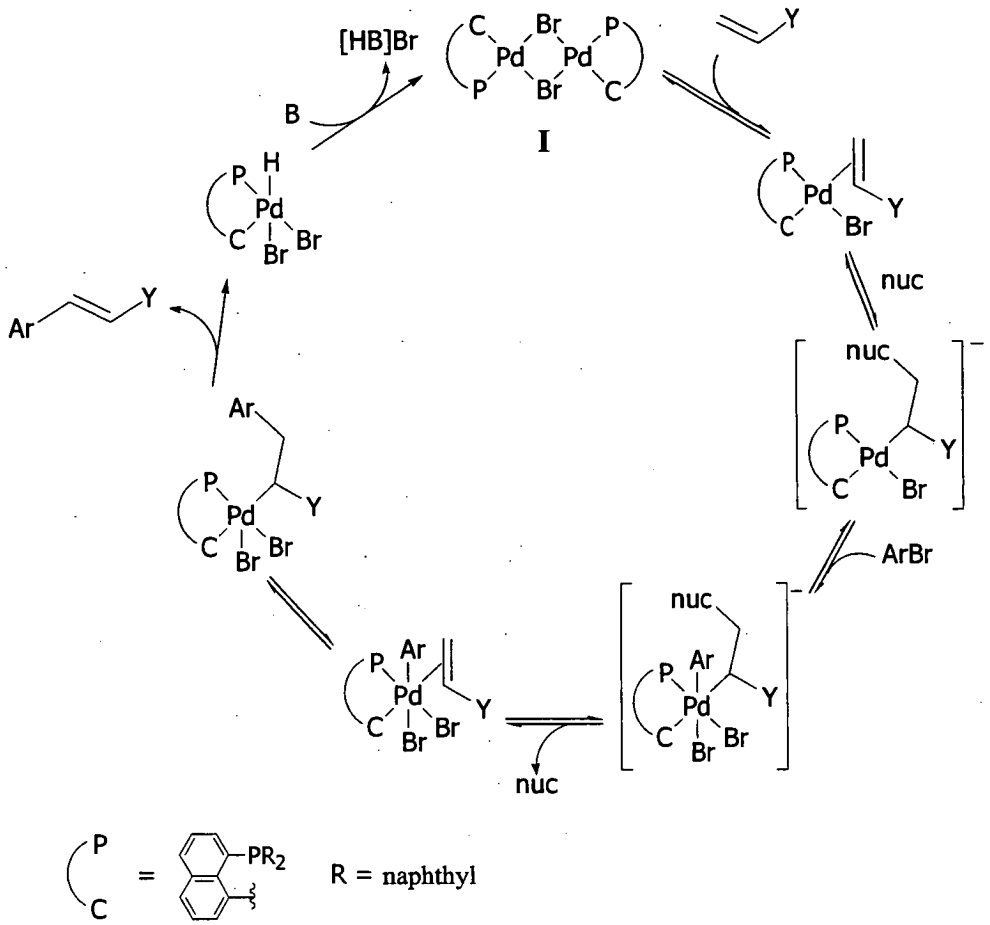


Figure 1.4: Examples of Pd^{II}(PCP) catalysts active in the Heck reaction.



Other palladacyclic complexes active as Heck catalysts have also been proposed to proceed *via* a Pd(II)/Pd(IV) cycle.[86-88] Shaw and coworkers have prepared several palladium(II) complexes incorporating chelating diphosphine,[87] chelating monophosphine[86] or phosphine free ligands.[88] In each case, a Pd(II)/Pd(IV) cycle such as that shown in Scheme 1.14 is proposed for the Heck reaction. The proposed mechanism involves alkene coordination to species **I** followed by reversible attack by a nucleophile such as $MeCO_2^-$, $acac^-$, OH^-, Br^- or I^-. The resulting anionic diorganopalladium(II) species, which is expected to support oxidation to palladium(IV), undergoes oxidative addition by an aryl halide followed by the loss of the nucleophile to reform the coordinated alkene. Migration of the aryl group to the alkene and subsequent β-hydrogen elimination releases the product, ArCH=CHY; and elimination of HBr by the base regenerates the catalyst (**I**).[86]

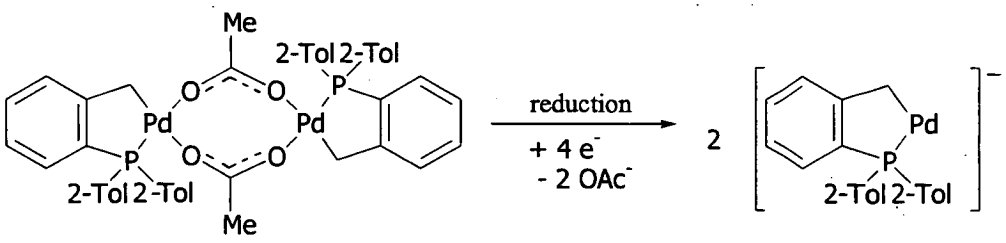
Scheme 1.14: Proposed mechanism for the Heck reaction using a palladacycle and an aryl bromide.[86]



In contrast to the views of Milstein and Shaw and coworkers, other researchers have suggested that palladium(IV) intermediates do not take part in Heck reactions.[39,82,83,89] Böhm and Herrmann observed departure from the 'classical' Pd(0)/Pd(II) mechanism for the Heck reaction (Scheme 1.13) when the phosphapalladacycle $[\overline{PdCH_2C_6H_4}P(2\text{-Tol})_2(O_2CMe)]_2$ (Scheme 1.15) was used as catalyst.[89] While a Pd(II)/Pd(IV) cycle was initially proposed as a possible explanation,[84] subsequent experiments suggested the involvement of palladium(IV) intermediates was unlikely.[89] Along with this, Louis and Hartwig were able to prove that this phosphapalladacyle could be reduced to an active palladium(0) catalyst *via* reduction with $HNEt_3$.[82,90] Although such reagents are not present in the Heck reaction, palladium(II) species are very susceptible to reduction. The observed deviation from classical behaviour of this catalyst in the Heck reaction was

attributed, by Böhm and Herrmann, to possible reduction of the catalyst to the highly active cyclometallated anionic palladium(0) species shown in Scheme 1.15.[89]

Scheme 1.15: A phosphapalladacycle catalyst and its proposed reduction to a highly active Pd(0) anionic intermediate.[89]



Alternative mechanisms, not involving palladium(IV) intermediates, have also been discussed for palladium(II) complexes incorporating PCP-pincer ligands (*e.g.* Figure 1.4).[83] Beletskaya and Cheprakov have suggested that these complexes may, in fact, be activated by heat induced disassembly of the two palladacyclic rings.[83] Labilisation of one phosphine arm of the ligand could occur in order to alleviate the strained geometry of the complexes (P-Pd-P angles as small as 152°), and the high temperatures used (140-160 °C) may promote further dechelation and reduction of the complex to palladium(0).[83] The recovery of intact catalyst at the end of the reaction could be attributed to a reassembly of the bispalladacyclic structure following the full consumption of all reagents.[83]

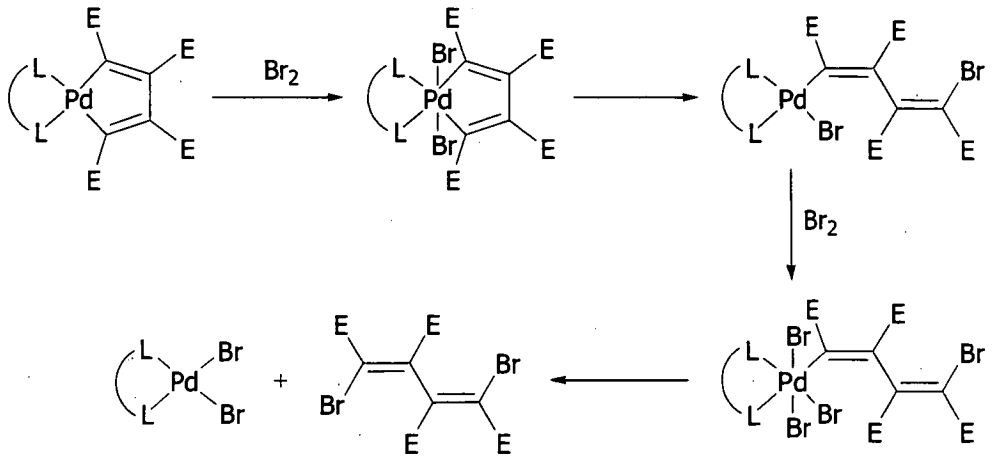
Although debate as to the mechanism of the Heck reaction continues, all researchers agree that further mechanistic studies are required before either pathway is conclusively excluded.

1.5.2 The Synthesis of Conjugated Dienes

Studies by Elsevier and coworkers on the direct synthesis of conjugated dienes from alkynes mediated by palladium compounds with ancillary, rigid, bidentate nitrogen ligands have led to the demonstrated involvement of palladium(IV) intermediates.[44,45] The room temperature reaction of 2,3,4,5-tetrakis(carbomethoxy)palladacyclopentadiene bearing the rigid bidentate

ligands 4-Tol-BIAN and phenyl-BIP, with excess X_2 (X = Cl, Br, I) resulted in complete conversion to $PdX_2(L_2)$ and the respective 1,4-dihalo-1,2,3,4-tetrakis(carbomethoxy)-1,3-butadienes.[44,45] When the same reactions with bromine were carried out stoichiometrically at –70 °C, palladium(IV) species with bromide ligands positioned mutually *trans* were observed by ^{1}H NMR spectroscopy. Raising the temperature led to conversion of the palladium(IV) species to a (σ-butanedienyl)bromopalladium(II) complex (Scheme 1.16).[44,45] Subsequent reaction of the latter palladium(II) species with bromine resulted in the observation of a (σ-butanedienyl)tribromopalladium(IV) complex which decomposed cleanly to $PdBr_2(L_2)$ and 1,3-dibromobuta-1,3-diene (Scheme 1.16).[44,45]

Scheme 1.16: Mechanism for the formation of 1,3-dibromobuta-1,3-diene from the reaction of bromine with a palladacyclopentadiene complex.[44,45]



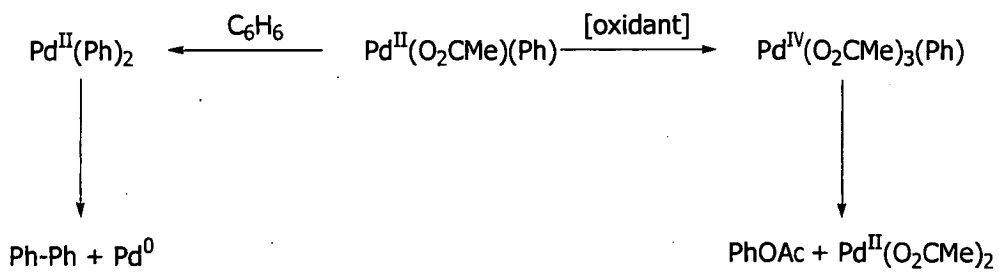
E = CO_2CH_3
L_2 = 4-Tol-BIAN, phenyl-BIP

1.5.3 The Acetoxylation of Arenes

Palladium(IV) intermediates have also been proposed in carbon-oxygen bond forming catalytic cycles such as the acetoxylation of arenes.[91-93] In 1971, Henry observed that, in the absence of oxidant, the reaction of benzene with $Pd(O_2CMe)_2$ yielded biphenyl as the sole product.[91] By contrast, when the same reaction was carried out in the presence of the oxidant $K_2Cr_2O_7$, phenyl acetate was formed while biphenyl formation was inhibited.[91] It was in these reactions that palladium(IV)

species were first proposed as feasible reaction intermediates. In 1981, kinetic isotope effect studies by Stock *et al.* suggested that a phenylpalladium(II) species was a common intermediate that could either react with benzene to form diphenylpalladium(II) or undergo oxidation in the presence of dichromate (and acetic acid) to form an unstable phenylpalladium(IV) compound.[92] Subsequent reductive elimination from these intermediates would yield biphenyl and phenyl acetate, respectively (Scheme 1.17).[92] Support for this mechanism came from investigations by Yoneyama and Crabtree into the use of $PhI(O_2CMe)_2$ as oxidant for this reaction.[93] In agreement with previous studies, they found that carbon-oxygen bond formation occurred in the presence of an oxidant with concurrent suppression of biaryl formation. It was also shown that addition of some ligands, such as picolinic acid, could further suppress biaryl formation, presumably by stabilising the postulated palladium(IV) intermediate.[93] An alternative process for the formation of a $Pd^{II}Ph_2$ species may involve aryl group transfer between monophenylpalladium(II) species, as such transfer processes are well established.[94-96]

Scheme 1.17: The proposed formation of biphenyl and phenyl acetate *via* a common phenylpalladium(II) intermediate.[92,93] The number of ligands bonded to Pd(II) and Pd(IV) are arbitrarily set to two and four, respectively.



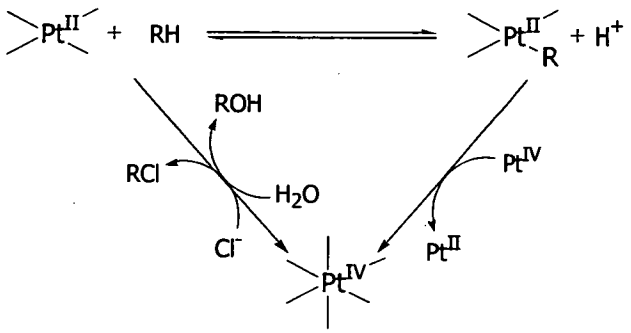
The process of oxidation and formation of MeO_2CPh is shown in more detail in Scheme 2.1 (Chapter Two) and the possible involvement of palladium(IV) in this process is explored in Chapters Two to Four.

1.6 Platinum(IV) as a Model for Palladium(IV)

The generally higher stability of organoplatinum(IV) complexes, and the propensity of platinum to undergo analogous reactions to palladium, renders organoplatinum(IV) complexes suitable, although not ideal, models for reactions expected to involve unstable palladium(IV) intermediates. Consideration of similar reactions involving platinum reagents can provide a valuable insight into potential reactions at palladium centres. As mentioned earlier, unlike organopalladium(IV) chemistry, organoplatinum(IV) chemistry is extensive. Therefore, only a few representative bodies of work are discussed.

A mechanism for carbon-oxygen bond formation by the platinum catalysed oxidation of alkanes was proposed by Shilov *et al.* in 1983.[97] It involves activation of the alkane by platinum(II) to form an alkylplatinum(II) species, which undergoes two-electron oxidation to generate an alkylplatinum(IV) intermediate. Reductive elimination of RX (X = Cl, OH) releases the oxidised alkane and reforms the platinum(II) catalyst (Scheme 1.18).[98] This is still considered to be the likely mechanism.[98,99] Detailed studies carried out by Luinstra *et al.* found that the oxidation of '$Pt^{II}R$' to '$Pt^{IV}R$' proceeds by electron transfer, and not by alkyl transfer, which was also considered a possibility.[100,101] Luinstra *et al.*, and others, also carried out investigations into the mechanism involved in reductive elimination of the oxidised alkane.[98,101,102] Water soluble platinum(IV) salts $[PtCl_5R][NMe_4]_2$ (R = CH_3, CH_2CH_2OH), which were postulated intermediates in the oxidation of methane and ethanol respectively, were isolated.[102] They were observed to decompose slowly in water to a mixture of either methanol and chloromethane, or ethylene glycol and 2-chloroethanol.[102] Kinetic studies, and the observation of inversion of stereochemistry at the platinum-bound carbon centre upon reduction, indicated the operation of a S_N2 mechanism *via* nucleophilic attack of water or chloride on the anionic platinum(IV) intermediate.[101,102]

Scheme 1.18: The proposed mechanism for the platinum catalysed oxidation of alkanes in aqueous solution.[98]



Catalytic carbon-oxygen bond formation involving platinum(IV) has also been reported in a high yield oxidative conversion of methane to a methanol derivative.[103] The complex $PtCl_2$(bpym) (bpym = 2,2'-bipyrimidine) reacts in H_2SO_4, *via* a similar mechanism as described above, to convert methane to methyl bisulfate (CH_3OSO_3H).[103] The reactions resulted in *ca.* 90 % conversion of methane with 81 % selectivity for methyl bisulfate formation.[103]

Carbon-oxygen bond formation has been directly observed from trimethylplatinum(IV) complexes bearing bidentate phosphine ligands.[104,105] Reductive elimination from $Pt(OR)Me_3(L_2)$ [R = aryl, acyl; L_2 = 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylphosphino)benzene] to form methyl esters and methyl aryl ethers occurs *via* OR^- dissociation followed by S_N2 attack of OR^- on a platinum-bound methyl group.[104,105] The formation of ethane was also observed from these complexes.[104,105] These reactions are discussed further in Chapter Two.

1.7 Scope of the Thesis

Palladium catalysed formation of carbon-heteroatom bonds can provide convenient and mild inroads to common functionalities that are often difficult to synthesise.[12] In view of this, and the proposals for palladium(IV) involvement discussed above, the research described in this thesis has focussed on attempting to

provide an insight into the role of palladium(IV) in carbon-oxygen bond forming processes. Recent developments in the field will be reviewed and current research described. Models for such systems will also be explored through the use of palladium and platinum incorporating a 'NCN-pincer' ligand and through the investigation of related carbon-selenium coupling processes.

1.8 References

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CHAPTER TWO:

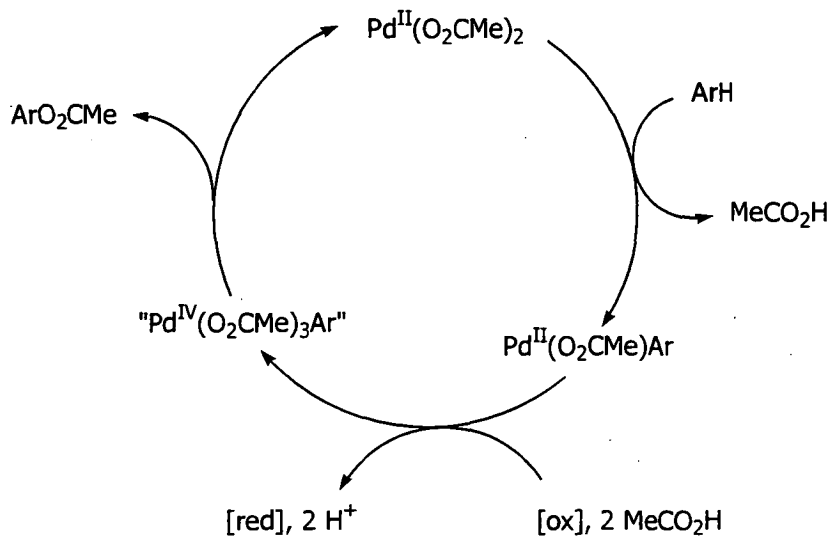
Carbon-Oxygen Coupling at Palladium Centres

2.1 Introduction

Carbon-oxygen bond formation at palladium centres is an important process currently attracting considerable attention due to its significance in homogeneous catalysis and potential in stoichiometric metal-mediated organic syntheses. Although this interest has focused predominantly on coupling occurring from palladium(II) centres,[1,2] organopalladium(IV) species have been postulated as intermediates in a variety of processes[3-11] including the acetoxylation of arenes (Scheme 2.1 and Section 1.5).[10,11] However, as yet, no spectroscopic evidence of such palladium(IV) intermediates in specific catalytic processes has been observed.

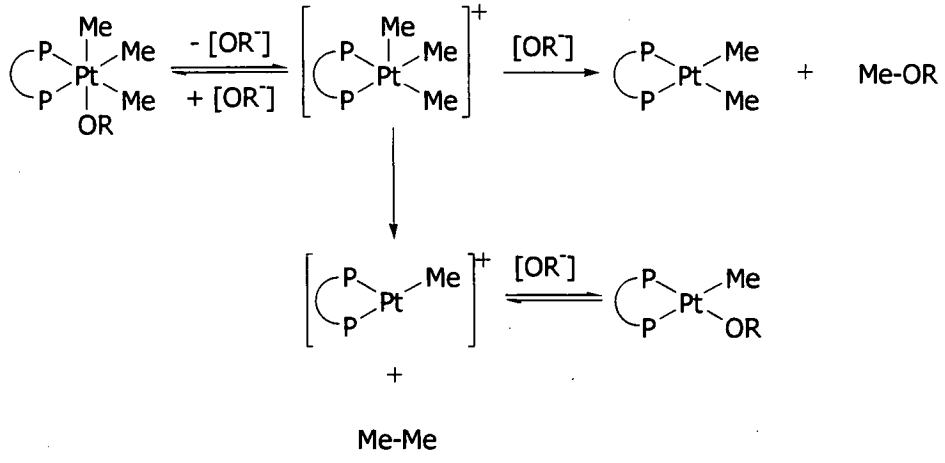
Scheme 2.1: The acetoxylation of arenes: reaction of arenes with acetic acid in the presence of $Pd^{II}(O_2CMe)_2$ and oxidising agents.[10,11] The number of ligands bonded to Pd(II) and Pd(IV) is arbitrarily set to two and four, respectively. Pd(II) and Pd(IV) species are assumed to have square planar and octahedral coordination, respectively, where the number of carboxylate ligands depends on their coordination mode in achieving these geometries.

$$ArH + MeCO_2H \longrightarrow ArO_2CMe + 2\,H^+ + 2\,e^-$$



An indication that organopalladium(IV) species may be involved in the formation of carbon-oxygen bonds at palladium centres is provided by studies of analogous, yet more stable, platinum(IV) systems. The reaction of $PtMe_2(phen)$ with dibenzoyl peroxide, $(PhCO_2)_2$, was shown to form predominantly the *trans,cis-* isomer of the diorganoplatinum(IV) complex, $Pt(O_2CPh)_2Me_2(phen)$,[12] while the reaction of $PtAr_2(L_2)$ [Ar = 4-tolyl (Tol), 3-tolyl, 4-anisyl (Anis); L_2 = bpy, phen] with dibenzoyl peroxide formed *cis,cis-* and *trans,cis*-$Pt(O_2CPh)_2Ar_2(L_2)$.[13] Furthermore, both carbon-carbon and carbon-oxygen coupling have been directly observed in reductive elimination from triorganoplatinum(IV) complexes of the form *fac*-$Pt(OR)Me_3(L_2)$ [L_2 = 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylphosphino)benzene (dppbz); OR = O_2CMe, O_2CCF_3, OTol and L = PMe_3, OR = OTol] (Scheme 2.2).[14,15] Reductive elimination occurs by preliminary dissociation of a ligand to give a five-coordinate intermediate. In the case of carbon-oxygen coupling, the dissociating ligand is OR^-. For carbon-carbon coupling, the dissociating group is OR^- for coupling from complexes containing a bidentate phosphine ligand, and is phosphine for complexes with monodentate phosphine ligands. This dissociation is followed by either nucleophilic attack of OR^- on a platinum(IV) bound methyl group to give Me-OR, or carbon-carbon coupling from the five-coordinate species to give ethane. The selectivity of this reaction has been demonstrated to be highly solvent dependent.[14,15]

Scheme 2.2: Reductive elimination from triorganoplatinum(IV) complexes with bidentate phosphine ligands.[14,15]



Preliminary studies into the reaction of $PdMe_2(bpy)$ with dibenzoyl peroxide found that, along with palladium(II) products, ethane, $Me\text{-}O_2CPh$ and $PhCO_2H$ (upon workup) were formed. It was postulated that the organic products were formed by direct reductive elimination from an undetected palladium(IV) species, '$Pd(O_2CPh)_2Me_2(bpy)$'.[16]

Although the main reason for interest in carbon-oxygen coupling at palladium(IV) was to investigate the formation of $C(sp^2)$-O bonds, the present study was initially confined to a reinvestigation of the reaction of $PdMe_2(bpy)$ with $(PhCO_2)_2$ in view of the predicted higher stability for the proposed dimethylpalladium(IV) intermediate compared with that expected for methyl(aryl)palladium(IV) species from the reaction with PdMeAr(bpy). However, the results of this reinvestigation, documented below, revealed a considerably more intricate process than was initially reported. Following the elucidation of the reaction sequence involved in this reaction, increased complexity was introduced by extending investigations to include methyl(aryl)palladium(II) systems. This allowed potential aryl-oxygen coupling to be explored and any selectivity in alkyl- and aryl-oxygen coupling to be considered. Solubility difficulties during these investigations led to the use of bis(4-trifluoromethyl)benzoyl peroxide, $(Ar_FCO_2)_2$, as an oxidant to enhance the solubility of intermediates and end products. *N,N,N',N'*-Tetramethylethylenediamine (tmeda) was included in the study as an aliphatic and more flexible ancillary ligand than bpy.

2.2 Results and Discussion

2.2.1 The Reaction of $PdMe_2(L_2)$ (L_2 = bpy, tmeda) with $(ArCO_2)_2$ (Ar = Ph, Ar_F)

2.2.1.1 ^1H NMR Studies

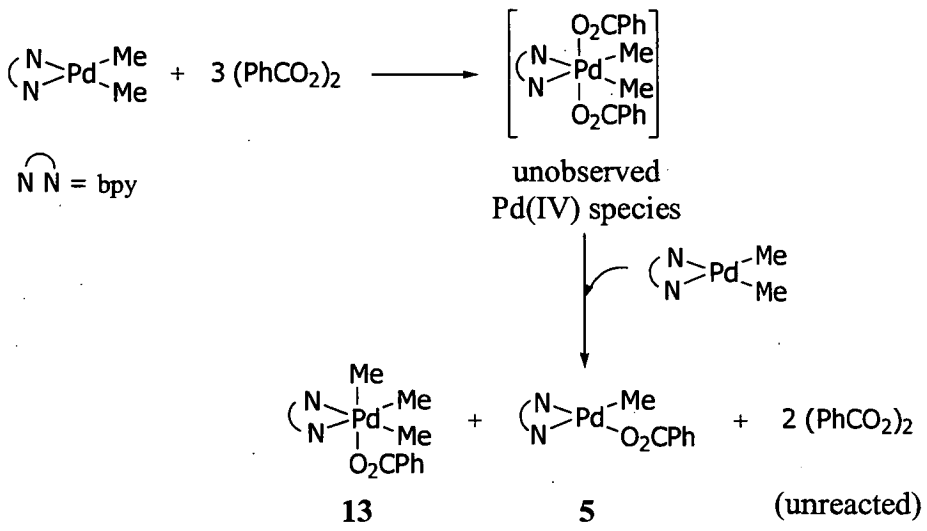
In the preliminary studies carried out on the reaction between $PdMe_2(bpy)$ and $(PhCO_2)_2$ discussed above, reagents were mixed in equimolar amounts at –70 °C and the reaction followed by ^1H NMR at –50 °C.[16] A species detected at this temperature was proposed to be $Pd^{IV}(O_2CPh)_2Me_2(bpy)$, which was then assumed to decompose at higher temperatures to ethane, Me-O_2CPh, $PhCO_2H$ and a yellow solid, tentatively characterised as $Pd(O_2CPh)_2(bpy)$.[16] However, as described below, on repeating this reaction it was found that the observed palladium(IV) intermediate was, in fact, the trimethylpalladium(IV) complex, $Pd^{IV}(O_2CPh)Me_3(bpy)$. Furthermore, a second palladium species, $Pd^{II}(O_2CPh)Me(bpy)$, was identified at both low and room temperature. It was also noted that if excess $(PhCO_2)_2$ was added to this reaction, the amount of $Pd(O_2CPh)Me(bpy)$ at room temperature decreased and the quantity of yellow precipitate increased. This prompted a complete reinvestigation of this system, using various reagent ratios and variable low temperature ^1H NMR spectroscopy to monitor reactions.

Only in the case of a 2:3 ratio of $PdMe_2(bpy)$:$(PhCO_2)_2$ did the reaction proceed with complete utilisation of both reagents. It was also noted that the reaction progressed in definite stages as the temperature was raised. Thus, variable temperature ^1H NMR studies of the reaction of $PdMe_2(bpy)$ with 1.5 equivalents of $(PhCO_2)_2$ revealed a complex series of reactions, which proceeded in the same manner in both acetone-d_6 and CD_2Cl_2.

At temperatures below –30 °C, two equivalents $PdMe_2(bpy)$ and three equivalents of $(PhCO_2)_2$ reacted to form $Pd(O_2CPh)Me_3(bpy)$ (**13**) and $Pd(O_2CPh)Me(bpy)$ (**5**) in a 1:1 ratio with 2 equivalents of unreacted peroxide remaining. Complex **13** is

believed to form by an exchange reaction between an undetected palladium(IV) species, '$Pd^{IV}(O_2CAr)_2Me_2(L_2)$', and $PdMe_2(bpy)$ (Scheme 2.3). Such reactions are often observed in palladium(IV) chemistry, resulting in formation of the most stable palladium(IV) species (section 1.4.2).[17,18] This process is discussed in more detail in Section 2.2.4.1.

Scheme 2.3: Reaction of $PdMe_2(bpy)$ with $(PhCO_2)_2$ in a 2:3 ratio at < -30 °C.

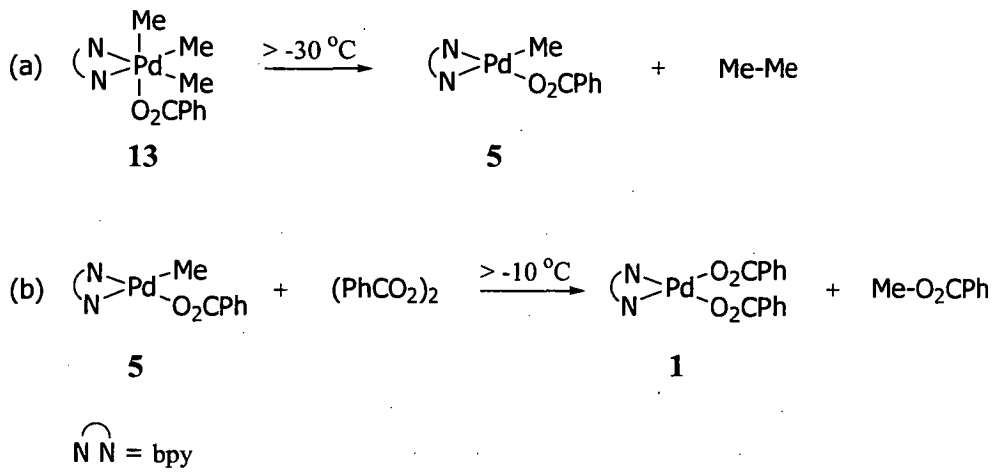


The presence of a palladium(IV) species was indicated by a significant downfield shift of the methyl and some bpy protons. Symmetry of the bpy ligand was maintained, indicating a *facial* arrangement of the methyl groups around the metal centre. When carried out in acetone-d_6, the protons of the two equatorial methyl groups were shifted 1.08 ppm downfield of the starting complex, while the axial methyl protons appeared 0.40 ppm downfield of the palladium(II) reagent. The H6 bpy proton was shifted 0.24 ppm downfield compared with the equivalent proton on the starting complex. The appearance of a set of asymmetric bpy protons along with a methyl signal at 0.74 ppm (-40 °C) was attributed to the formation of $Pd(O_2CPh)Me(bpy)$ (**5**). If kept at low temperature in acetone-d_6 for an extended time, **5** slowly precipitated from the reaction mixture.

Warming to –30 °C led to the slow decomposition of **13** accompanied by an increase in the amount of **5** and the formation of ethane (Scheme 2.4a). At

temperatures above –10 °C, the quantity of **5** decreased and the formation of methyl benzoate along with the precipitation of a yellow crystalline solid was observed. The latter was later demonstrated (Section 2.2.1.2) to occur by the reaction of **5** with $(PhCO_2)_2$ as shown in Scheme 2.4b. X-ray crystallographic studies and ^1H NMR confirmed the identity of the yellow crystalline solid as $Pd(O_2CPh)_2(bpy)$ (**1**). Details of these studies are presented in later sections.

Scheme 2.4: (a) The decomposition of $Pd(O_2CPh)Me_3(bpy)$ (**13**). (b) The reaction of $Pd(O_2CPh)Me(bpy)$ (**5**) with $(PhCO_2)_2$.



When $(Ar_FCO_2)_2$ was used in place of $(PhCO_2)_2$, the observed reaction sequence was the same as described above. However, carbon-oxygen coupling to form $Me\text{-}O_2CAr_F$ occurred at a lower temperature (-30 °C). The use of $(Ar_FCO_2)_2$ as oxidant had the advantages that the reactions occurred more rapidly (presumably due to the presence of the electron withdrawing CF_3 substituent, leading to a stronger oxidising ability), and that *para*-substitution of the phenyl group led to simpler aromatic regions in ^1H NMR spectra. Furthermore, unlike **1**, the inorganic product, $Pd(O_2CAr_F)_2(bpy)$ (**3**) was soluble, allowing the product distribution to be determined by NMR. Complex **3** and $Me\text{-}O_2CAr_F$ were present in approximately equal amounts at the end of the reaction. Ethane could not be quantified reliably by NMR due to its volatility.

The reaction of two equivalents of $PdMe_2$(tmeda) with three of $(PhCO_2)_2$ followed an identical series of reactions as observed for $PdMe_2$(bpy), with analogous intermediates identified. The appearance of methyl benzoate was noted at a slightly lower temperature (*ca.* –20 °C) than for the bpy analogue. The use of tmeda as ligand led to very simple aromatic regions in ^{1}H NMR spectra. However, complexity in the aliphatic region increased markedly. Organisation of the methyl groups on the palladium(IV) intermediate, $Pd(O_2CPh)Me_3$(tmeda) (**14**), was again shown to be *facial* by the retention of symmetry of the tmeda ligand. The inorganic product, $Pd(O_2CPh)_2$(tmeda) (**2**), was initially soluble and only crystallised slowly, allowing product ratios to be determined. Complex **2** and methyl benzoate were present in *ca.* 1:1 ratio at completion of the reaction. When $(Ar_FCO_2)_2$ was used as oxidant, analogous intermediates were detected and, as seen in the reaction of the bpy analogue, the formation $Me\text{-}O_2CAr_F$ was observed at the lower temperature of –30 °C.

These observations can be represented by eqs 2.1-2.4 in Scheme 2.5, with the overall reaction shown in eq 2.5. The only species not detected is '$Pd^{IV}(O_2CAr)_2Me_2(L_2)$'.

It is important to note that although products formed by carbon-oxygen coupling are observed in each case, they *do not* form by reductive elimination from the observed palladium(IV) complexes. Rather, coupling occurs in the reaction of monoorganopalladium(II) complexes with $(ArCO_2)_2$ as seen in eq 2.4. These and other related reactions are discussed in detail in Sections 2.2.1.2 and 2.2.4.

Scheme 2.5: Reaction of $Pd^{II}Me_2(L_2)$ (L_2 = bpy, tmeda) with $(ArCO_2)_2$ (Ar = Ph, Ar_F) in 2:3 ratio in acetone-d_6 and CD_2Cl_2.

(i) Up to ~ -30 °C (Ar = Ph and Ar_F):

$$Pd^{II}Me_2(L_2) + (ArCO_2)_2 \rightarrow \text{'}Pd^{IV}(O_2CAr)_2Me_2(L_2)\text{'} \quad (2.1)$$

$$\text{'}Pd^{IV}(O_2CAr)_2Me_2(L_2)\text{'} + Pd^{II}Me_2(L_2) \rightarrow Pd^{IV}(O_2CAr)Me_3(L_2) + Pd^{II}(O_2CAr)Me(L_2) \quad (2.2)$$

(ii) Above ~ -30 °C (Ar = Ph and Ar_F):

$$Pd^{IV}(O_2CAr)Me_3(L_2) \rightarrow Pd^{II}(O_2CAr)Me(L_2) + Me\text{-}Me \quad (2.3)$$

(iii) Above ~ -10 °C (Ar = Ph; L_2 = bpy); Above ~ -20 °C (Ar = Ph; L_2 = tmeda); Above ~ -30 °C (Ar = Ar_F; L_2 = bpy, tmeda):

$$Pd^{II}(O_2CAr)Me(L_2) + (ArCO_2)_2 \rightarrow Pd^{II}(O_2CAr)_2(L_2) + Me\text{-}O_2CAr \quad (2.4)$$

(iv) Overall reaction

$$2\ Pd^{II}Me_2(L_2) + 3\ (ArCO_2)_2 \rightarrow 2\ Pd^{II}(O_2CAr)_2(L_2) + 2\ Me\text{-}O_2CAr + Me\text{-}Me \quad (2.5)$$

2.2.1.2 Model Reactions

Studies described above were carried out in 2:3 mole ratio of palladium(II):peroxide and were followed to partial completion of the reaction at different low temperatures, and to full completion at room temperature. The individual steps in eqs 2.1-2.5 were subsequently studied in detail by carrying out a series of reactions that modeled the different stages of the reaction of $PdMe_2(L_2)$ with $(ArCO_2)_2$. Reagents were mixed in different ratios and kept at various temperatures in order to stop the reaction sequence at different points. In addition, intermediates were synthesised by independent methods (described in Section 2.2.5), and their subsequent reactions investigated.

When the reagents $PdMe_2(L_2)$ and $(ArCO_2)_2$ were mixed in a 2:1 ratio, and the reaction allowed to go to completion below -30 °C, $Pd(O_2CAr)Me_3(L_2)$ and $Pd(O_2CAr)Me(L_2)$ were observed in *ca.* 1:1 ratio and with all reagents consumed, in agreement with eqs 2.1 and 2.2. In the reaction involving $(PhCO_2)_2$, $Pd(O_2CPh)Me(bpy)$ (**5**) gradually precipitated, generating inaccuracy in the NMR determination of the product distribution. This was overcome by using CD_2Cl_2 as solvent. Solubility problems were not encountered when $(Ar_FCO_2)_2$ was used as the oxidant. Warming to temperatures above –30 °C led to the decomposition of $Pd(O_2CAr)Me_3(L_2)$ (eq 2.3), with $Pd(O_2CAr)Me(L_2)$ and ethane the only species observed at room temperature.

Eq 2.3 was investigated further by the *in situ* preparation of the palladium(IV) intermediates, $Pd(O_2CAr)Me_3(L_2)$, from $PdIMe_3(L_2)$ and $Ag[O_2CAr]$ (Section 2.2.5.3). Decomposition to $Pd(O_2CAr)Me(L_2)$ and ethane was observed from *ca.* –30 °C and products formed by carbon-oxygen coupling were notably absent. The complexes $Pd(O_2CAr)Me(L_2)$ were confirmed as intermediates in these reactions *via* their syntheses by independent methods (Section 2.2.5.3).

The reactions of $Pd(O_2CAr)Me(L_2)$ with $(ArCO_2)_2$ proceeded, above the temperatures outlined in Scheme 2.5(iii), forming $Pd(O_2CAr)_2(L_2)$ and carbon-oxygen coupling products, $Me\text{-}O_2CAr$. When a similar reaction was carried out using $Pd(O_2CPh)Me(bpy)$ and the *para*-substituted peroxide, $(Ar_FCO_2)_2$, a mixture of products including $Me\text{-}O_2CPh$ and $Me\text{-}O_2CAr_F$, in a ratio of *ca.* 1:4, as the only organic products was observed. Palladium(IV) intermediates have not been identified in these reactions but their involvement cannot be excluded, in particular for the latter reaction where carbon-oxygen bond formation from a '$Pd^{IV}(O_2CAr_F)_2(O_2CPh)Me(bpy)$' species could explain the mixture of products formed.

Attempts to prepare pure $Pd(O_2CPh)_2Me_2(bpy)$, in particular in the absence of $PdMe_2(bpy)$, and investigate its reactions failed (see Section 2.2.5.4). It was, therefore, not possible to confirm unequivocally that this species does, indeed, form

or undergo an exchange reaction with $PdMe_2(bpy)$. Moreover, the inability to detect $Pd(O_2CAr)_2Me_2(bpy)$ meant that it could not be determined whether carbon-oxygen coupling can occur directly from this species.

2.2.2 The Reaction of PdMeTol(bpy) with $(ArCO_2)_2$ (Ar = Ph, Ar_F)

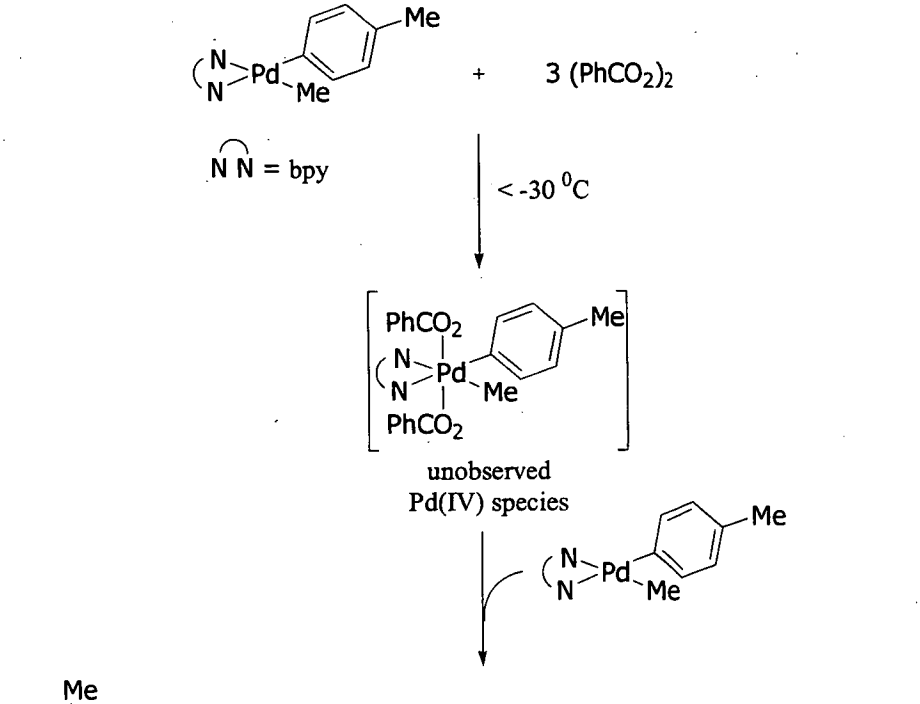
2.2.2.1 ^1H NMR Studies

The reaction of PdMeTol(bpy) with $(ArCO_2)_2$ displayed many close similarities to eqs 2.1-2.5 above. However, the presence of an aryl group in place of one methyl group introduced several new intermediates and, consequently, increased the complexity of the related ^1H NMR spectra. Changing solvent from acetone-d_6 to CD_2Cl_2 did not appear to affect the sequence of reactions. It did, however, change the ratio of structural isomers for $Pd(O_2CAr)Me_2Tol(bpy)$, and altered the distribution of products formed as a result of carbon-carbon coupling from these intermediates.

Initially, the reaction of PdMeTol(bpy) with $(PhCO_2)_2$ was studied in a 2:3 ratio in order to mimic the overall stoichiometry determined for the reaction between $PdMe_2(L_2)$ and $(PhCO_2)_2$. When this reaction was performed below –30 °C, a slow process to form $Pd(O_2CPh)Tol(bpy)$ (**9**) and two isomers of $Pd(O_2CPh)Me_2Tol(bpy)$ [**17a** (both Me groups equatorial) and **17b** (one Me group equatorial and one axial)] was observed (Scheme 2.6). The presence of two isomers is consistent with the reported formation of two isomeric forms of $PdIMe_2Ph(bpy)$.[18,19] With the reaction held at –40 °C in acetone-d_6, a ratio of *ca.* 1:1 **17a:17b** was observed with $\mathbf{17}_{total}$:**9**:$(PhCO_2)_2$ equal to 1:1:2, reflecting the reaction of one third of the $(PhCO_2)_2$ reagent. When the same reaction was carried out with CD_2Cl_2 as solvent, **17a**:**17b** was found to be *ca.* 1:2 and, as expected, the ratio of $\mathbf{17}_{total}$:**9**:$(PhCO_2)_2$ was again 1:1:2 (Scheme 2.6). A possible explanation for the difference in observed isomer ratios is discussed in Section 2.2.2.2.

Difficulties were encountered in assigning resonances due to the highly complex nature of the aromatic regions in these ^{1}H NMR spectra. However, some bpy signals characteristic of palladium(IV) species could be identified and two sets of $Pd^{IV}Me$ and $Pd^{IV}Tol$ protons were visible in the aliphatic region. It was found that comparison with ^{1}H NMR assignments of related known palladium(IV) complexes, $PdIMe_2Ph(bpy)$[18] and $Pd(O_2CPh)Me_2(CH_2Ph)(bpy)$,[20] aided in the identification of these palladium(IV) species. Ratios of the two isomeric forms of **17** were determined by comparison of the integrals of the H6 bpy signal of **17a** with H6' of **17b**. These signals were chosen as they occurred downfield of all other signals and were well-resolved (see Section 2.2.5.3 for more detail).

Scheme 2.6: Reaction of PdMeTol(bpy) with $(PhCO_2)_2$ at < -30 °C in 2:3 ratio.



	17a		**17b**		**9**		
in acetone-d_6	0.5	:	0.5	:	1	:	2
in CD_2Cl_2	0.33	:	0.67	:	1	:	2

Between –30 °C and –10 °C, the quantity of **17** decreased and ethane, 1,4-xylene and $Pd(O_2CPh)Me(bpy)$ (**5**) were detected. Above –10 °C, the appearance of methyl benzoate and $Pd(O_2CPh)_2(bpy)$ (**1**) was accompanied by a decrease in **5**. Further warming to ambient temperature led to the very slow appearance of 4-tolyl benzoate along with an increase in **1** and the slow disappearance of **9**.

When $(Ar_FCO_2)_2$ was used as oxidant, in both solvents, the reaction proceeded in the same manner as described above. The ratios of isomers of $Pd^{IV}(O_2CAr_F)Me_2Tol(bpy)$ [**18a** (both Me groups equatorial) and **18b** (one Me group equatorial and one axial)] were determined in the same way and gave similar values.

These observations are consistent with the reaction sequence shown as eqs 2.6-2.10 to give the overall reaction as eq 2.11.

Scheme 2.7: Reaction of $Pd^{II}MeTol(bpy)$ with $(ArCO_2)_2$ in 2:3 ratio in acetone-d_6 or CD_2Cl_2.

(i) Up to ~ -30 °C:

$$Pd^{II}MeTol(bpy) + (ArCO_2)_2 \rightarrow \text{'}Pd^{IV}(O_2CAr)_2MeTol(bpy)\text{'} \quad (2.6)$$

$$\text{'}Pd^{IV}(O_2CAr)_2MeTol(bpy)\text{'} + Pd^{II}MeTol(bpy) \rightarrow Pd^{IV}(O_2CAr)Me_2Tol(bpy) + Pd^{II}(O_2CAr)Tol(bpy) \quad (2.7)$$

(ii) Above ~ -30 °C:

$$Pd^{IV}(O_2CAr)Me_2Tol\ (bpy) \rightarrow n\ Pd^{II}(O_2CAr)Me(bpy) + n\ \text{Tol-Me} + (1\text{-}n)\ Pd^{II}(O_2CAr)Tol(bpy) + (1\text{-}n)\ \text{Me-Me} \quad (2.8)$$

(iii) Above ~ -10 °C:

$$n\ Pd^{II}(O_2CAr)Me(bpy) + n\ (ArCO_2)_2 \rightarrow n\ Pd^{II}(O_2CAr)_2(bpy) + n\ \text{Me-}O_2CAr \quad (2.9)$$

(iv) Room temperature:

$$(2\text{-}n)\ Pd^{II}(O_2CAr)Tol(bpy) + (2\text{-}n)\ (ArCO_2)_2 \rightarrow (2\text{-}n)\ Pd^{II}(O_2CAr)_2(bpy) + (2\text{-}n)\ Tol\text{-}O_2CAr \quad (2.10)$$

(v) Overall reaction:

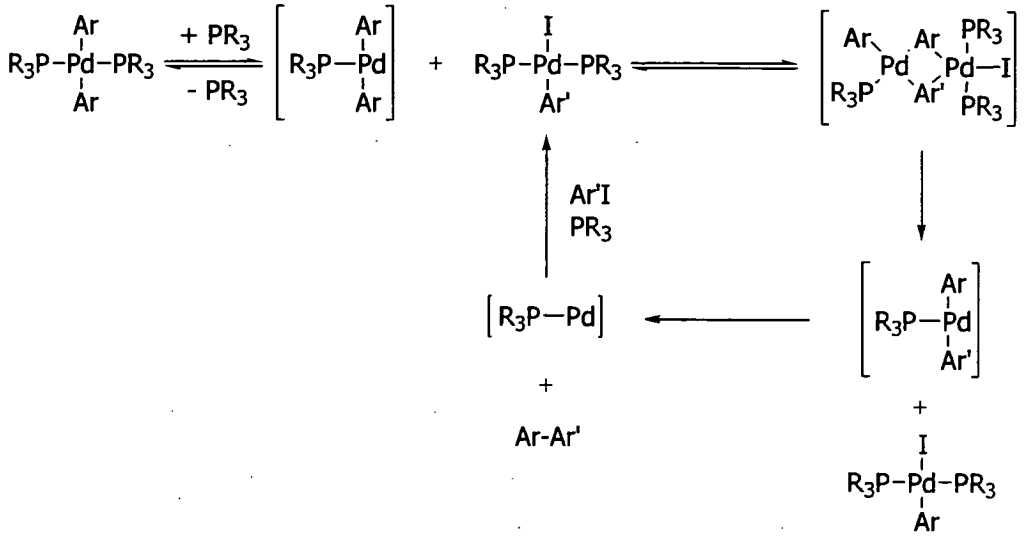
$$2\ Pd^{II}MeTol(bpy) + 3\ (ArCO_2)_2 \rightarrow 2\ Pd^{II}(O_2CAr)_2(bpy) + (2\text{-}n)\ Tol\text{-}O_2CAr + n\ Tol\text{-}Me + n\ Me\text{-}O_2CAr + (1\text{-}n)\ Me\text{-}Me \quad (2.11)$$

The value of n in eqs 2.8-2.11 was found to be dependent on the oxidant chosen and, to a lesser extent, on solvent. For reactions where Ar = Ph, n was 0.6 when carried out in acetone-d_6, while in CD_2Cl_2 it was found to be 0.5. When Ar = Ar_F, n was 0.4 in acetone-d_6 and 0.5 in CD_2Cl_2. Details of how n was calculated and used to predict the overall stoichiometry of the reactions can be found in Section 2.2.2.2.

In agreement with the reactions of $PdMe_2(L_2)$, carbon-oxygen coupling did not occur from the *observed* palladium(IV) intermediates. The reaction of monoorganopalladium(II) complexes with diaroyl peroxides did lead to carbon-oxygen coupling, but no palladium(IV) intermediates were observed.

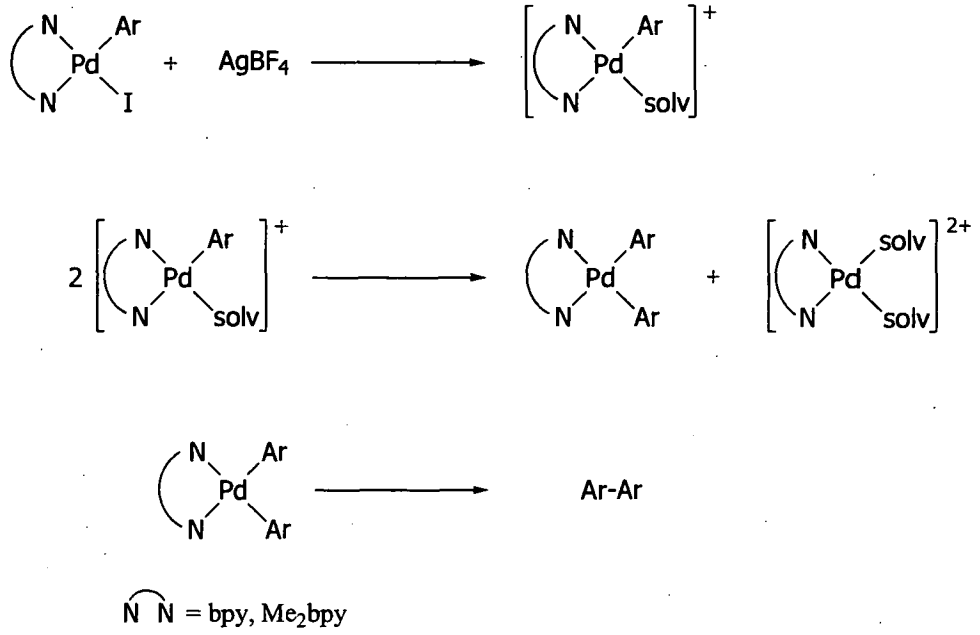
In several of the reactions carried out above, 4,4'-bitolyl was observed as a minor product. Its presence predominantly occurred in reactions carried out at room temperature and was largely suppressed in reactions performed at low temperature. The formation of biaryls as a product in palladium mediated reactions is common and several mechanisms for their formation have been proposed.[10,11,21-25] Yamamoto and coworkers suggested the involvement of a three-coordinate $Pd^{II}Ar_2$ species and a bimetallic intermediate for biaryl coupling from a phosphine system (Scheme 2.8).[24,25] It is unlikely that species directly analogous to this would be involved in the reactions described above because the presence of the rigid, bidentate bpy ligand would not allow for the proposed intermediate configuration leading to biaryl formation.

Scheme 2.8: Postulated mechanism for the formation of biaryls in a $PdAr_2(PR_3)_2$ system.[24,25]



More recent studies by Yamamoto and coworkers investigating biaryl coupling from complexes of the form $Pd^{II}IAr(L_2)$ (Ar = Ph, Anis, $C_6H_3Me_2$-3,5; L_2 = bpy, 4,4'-Me_2bpy) may provide an explanation for the observed coupling to form 4,4'-bitolyl.[21] In this model, biaryl formation takes place *via* the initial formation of a cationic intermediate, by reaction of $Pd^{II}IAr(L_2)$ with a silver(I) salt, followed by aryl group exchange and subsequent coupling of the aryl groups (Scheme 2.9).[21] The fate of the proposed $[Pd(solvent)_2(L_2)]^{2+}$ species was not discussed. Formation of similar intermediates in the system under consideration can be envisaged in which the benzoate group dissociates to allow formation of the proposed diarylpalladium(II) intermediate.

Scheme 2.9: Proposed pathway for biaryl coupling from $PdIAr(L_2)$.[21]



N N = bpy, Me_2bpy

2.2.2.2 Model Reactions

Eqs 2.6-2.11 were studied in more detail by carrying out a series of model reactions similar to those described for the reactions of $PdMe_2(L_2)$. When the reagents were mixed in a 2:1 ratio, and the reaction allowed to go to completion at -40 °C, all reagents were consumed and $Pd(O_2CAr)Me_2Tol(bpy)$ [two isomers; Ar = Ph (**17**), Ar_F (**18**)] and $Pd(O_2CAr)Tol(bpy)$ [Ar = Ph (**9**), Ar_F (**11**)] were observed in a 1:1 ratio, in accord with eqs 2.6 and 2.7. As seen in the previous section, the ratio of palladium(IV) isomers depends on the solvent that is used but not on the choice of oxidant, *i.e.* 1:1 in acetone-d_6, and 1:2 in CD_2Cl_2, for both **17a**:**17b** using $(PhCO_2)_2$ and **18a**:**18b** using $(Ar_FCO_2)_2$. In the case where this reaction mixture was allowed to warm slowly to ambient temperature, the products were those shown in eq 2.8.

The presence of nearly equal amounts of the palladium(IV) isomers in acetone-d_6 suggests that the two isomeric forms are similar in energy and that the equilibrium between the two is finely balanced. Therefore, it is likely that relatively small changes in the chemical environment could have an effect on the ratio. One such change would be the alteration of the solvent, resulting in different interactions with

the isomers since they are expected to have different charge distributions and solvation properties, *e.g.* aryl group axial or equatorial. However, interactions with solvent may be relatively unaffected on changing from Ar = Ph to Ar_F, perhaps accounting for the lack of difference in results on changing the oxidant.

As an additional model for eq 2.8, and in order to confirm the identities of the observed species, the suspected palladium(IV) intermediates were prepared *in situ* for NMR studies by an independent synthesis. ^{1}H NMR spectroscopy confirmed $Pd(O_2CAr)Me_2Tol(bpy)$ as the species observed and, in each case, indicated the presence of two isomeric forms (for details of synthesis and characterisation see Section 2.2.5.3). The ratio of isomers was dependent on the solvent used, and agreed with those reported above. The isomers persisted to *ca.* -30 °C, at which temperature they decomposed to give the products shown in eq 2.8.

Independently synthesised $Pd(O_2CPh)Tol(bpy)$ (**9**) (Section 2.2.5.2) was shown to react with dibenzoyl peroxide very slowly at ambient temperature to form 4-tolyl benzoate and $Pd(O_2CPh)_2(bpy)$ (**1**), in agreement with eq 2.10. Eq. 2.9 is identical to eq 2.4 and was discussed in Section 2.2.1.2.

As for $Pd(O_2CPh)_2Me_2(bpy)$, attempts to prepare $Pd(O_2CPh)_2MeTol(bpy)$ and investigate its reactions failed. This is discussed further in Section 2.2.5.4.

The value of *n*, seen in eqs 2.8-2.11, can be calculated by two methods, and allows the stoichiometry of the overall equation for the reaction of PdMeTol(bpy) with $(ArCO_2)_2$ (eq 2.11) to be predicted. Each method uses the relationship between ^{1}H NMR integrations of Tol-Me and $Pd(O_2CAr)Tol(bpy)$ in determining *n*. Theoretically, it would be equally valid to use integrations of $Pd(O_2CAr)Me(bpy)$ and Me-Me, but, in practice, Me-Me cannot be quantified reliably due to its volatility and $Pd(O_2CPh)Me(bpy)$ (**5**) precipitates from acetone-d_6. The complexes $Pd(O_2CAr)Tol(bpy)$ and Tol-Me also have the advantage that they display well-resolved resonances in ^{1}H NMR spectra and, consequently, can be easily integrated.

The first method for predicting *n* involves determining the distribution of products from the decomposition of independently prepared $Pd(O_2CAr)Me_2Tol(bpy)$ (eq 2.8). The term *n* can be calculated by comparing the integration per hydrogen for Tol-Me (abbreviated in the equations below to $Int_{(TolMe)}$) and $Pd(O_2CAr)Tol(bpy)$ (abbreviated to $Int_{(PdTol)}$) as shown below:

$$\frac{n}{1-n} = \frac{Int_{(TolMe)}}{Int_{(PdTol)}}$$

$$n = \frac{Int_{(TolMe)}}{Int_{(TolMe)} + Int_{(PdTol)}}$$

The second method is carried out in an analogous way to that described above. However, in this case, the reaction being considered is the one between $(ArCO_2)_2$ and two equivalents of PdMeTol(bpy) (eqs 2.6-2.8) at room temperature, which has the overall reaction shown in eq 2.12. By considering the same integrals as described above, *n* can be determined as shown below:

$$\frac{n}{2-n} = \frac{Int_{(TolMe)}}{Int_{(PdTol)}}$$

$$n = \frac{2\,Int_{(TolMe)}}{Int_{(TolMe)} + Int_{(PdTol)}}$$

$$2\ PdMeTol(bpy) + (ArCO_2)_2 \rightarrow n\ Pd(O_2CAr)Me(bpy) + n\ Tol\text{-}Me + (2\text{-}n)\ Pd(O_2CAr)Tol(bpy) + (1\text{-}n)\ Me\text{-}Me \quad (2.12)$$

Each of these analyses was carried out on a number of reactions, allowing average values of *n* to be calculated for reactions where Ar = Ph and Ar_F in acetone-d_6 and CD_2Cl_2. The combined results using both methods are shown in Table 2.1. Substitution of *n* into the overall equation (eq 2.11) allowed the overall stoichiometry of the reactions of two equivalents of PdMeTol(bpy) with three equivalents of $(ArCO_2)_2$ to be predicted. Consequently, the predicted overall equations for reactions in acetone-d_6 are those shown in eq 2.13 and 2.14 (Scheme 2.10). These

predicted values show good agreement with those observed experimentally for the 2:3 ratio of reagents that leads to complete consumption of reagents.

Table 2.1: Average calculated values of n for the reactions of PdMeTol(bpy) with $(ArCO_2)_2$ (Ar = Ph, Ar_F). The values shown were obtained using both methods with a total of at least three experiments each (except where indicated).

	Ph	Ar_F
acetone-d_6	0.59 ± 0.04	0.43 ± 0.08
CD_2Cl_2	0.52 ± 0.05	0.45^a

[a] One measurement only

Scheme 2.10: Predicted overall stoichiometry of the reaction of PdMeTol(bpy) with (a) $(PhCO_2)_2$ and (b) $(Ar_FCO_2)_2$ in acetone-d_6. These agree with values observed experimentally.

(a)

$$2\ Pd^{II}MeTol(bpy) + 3\ (PhCO_2)_2 \rightarrow 2\ Pd^{II}(O_2CPh)_2(bpy) + 1.4\ Tol\text{-}O_2CPh + 0.6\ Tol\text{-}Me + 0.6\ Me\text{-}O_2CPh + 0.4\ Me\text{-}Me \quad (2.13)$$

(b)

$$2\ Pd^{II}MeTol(bpy) + 3\ (Ar_FCO_2)_2 \rightarrow 2\ Pd^{II}(O_2CAr_F)_2(bpy) + 1.6\ Tol\text{-}O_2CAr_F + 0.4\ Tol\text{-}Me + 0.4\ Me\text{-}O_2CAr_F + 0.6\ Me\text{-}Me \quad (2.14)$$

2.2.3 The Reaction of PdMeTol(tmeda) with $(ArCO_2)_2$ (Ar = Ph, Ar_F)

2.2.3.1 ^{1}H NMR Studies

The reaction of PdMeTol(tmeda) with $(ArCO_2)_2$ presented some differences to the analogous bpy reactions. In view of the results for the bpy systems, reagents PdMeTol(tmeda) and $(PhCO_2)_2$ were mixed in a 2:3 ratio at –50 °C in acetone-d_6 and monitored by ^{1}H NMR spectroscopy as the temperature was increased slowly. No reaction occurred until approximately –30 °C when ethane and Pd(O_2CPh)Tol(tmeda) (**10**) began to form. No palladium(IV) intermediates were

observed, but support for their involvement exists through analogy with the related bpy system. Warming to –20 °C led to the appearance of 1,4-xylene, $Pd(O_2CPh)Me(tmeda)$ (**6**), methyl benzoate and $Pd(O_2CPh)_2(tmeda)$ (**2**). At ambient temperature, the reaction continued over several days forming 4,4'-bitolyl and further **2**, while **10** decreased. It was interesting to note that no 4-tolyl benzoate was formed. The final products, after several days at ambient temperature, were **2**, 1,4-xylene, methyl benzoate and 4,4'-bitolyl. Interestingly, not all of the peroxide was consumed during this reaction.

When $(Ar_FCO_2)_2$ was used as oxidant, the reaction appeared to occur *via* the same sequence as described above. However, reaction began at temperatures as low as –50 °C and was proceeding rapidly by the time the temperature reached –30 °C. As observed above, when the reaction was carried out with a 2:3 ratio of reagents, not all of the peroxide was consumed.

Based on results for the bpy systems, the initial stages of these reactions are anticipated to proceed as shown in eqs 2.15-2.18 (Scheme 2.11) below. Unlike the bpy analogue, in which $Pd(O_2CAr)Tol(bpy)$ reacts with one equivalent of $(ArCO_2)_2$, $Pd(O_2CAr)Tol(tmeda)$ appears to react with only half an equivalent of $(ArCO_2)_2$, as shown in eq 2.19. Consequently, the overall stoichiometry for complete consumption of reagents would not be a 2:3 ratio, but rather would require a reagent ratio of $2:\{(1+n) + [(2-n)/2]\} = 2:[2+(n/2)]$ (from eqs 2.15-2.20). Therefore, in order to predict the stoichiometry of the reaction, n would need to be determined from the product distribution of eq 2.17. Problems associated with this are discussed in the next section.

Scheme 2.11: Reaction of $Pd^{II}MeTol(tmeda)$ with $(ArCO_2)_2$ (Ar = Ph, Ar_F) in acetone-d_6.

(i) Above ~ -30 °C (Ar = Ph); Above ~ -50 °C (Ar = Ar_F):

$$Pd^{II}MeTol(tmeda) + (ArCO_2)_2 \rightarrow \text{'}Pd^{IV}(O_2CAr)_2MeTol(tmeda)\text{'} \quad (2.15)$$

$$\text{'}Pd^{IV}(O_2CAr)_2MeTol(tmeda)\text{'} + Pd^{II}MeTol(tmeda) \rightarrow \text{'}Pd^{IV}(O_2CAr)Me_2Tol(tmeda)\text{'} + Pd^{II}(O_2CAr)Tol(tmeda) \quad (2.16)$$

$$\text{'}Pd^{IV}(O_2CAr)Me_2Tol(tmeda)\text{'} \rightarrow n\ Pd^{II}(O_2CAr)Me(tmeda) + n\ Tol\text{-}Me + (1\text{-}n)\ Pd^{II}(O_2CAr)Tol(tmeda) + (1\text{-}n)\ Me\text{-}Me \quad (2.17)$$

(iii) Above ~ -20 °C (Ar = Ph); Above ~ -30 °C (Ar = Ar_F):

$$n\ Pd^{II}(O_2CAr)Me(tmeda) + n\ (ArCO_2)_2 \rightarrow n\ Pd^{II}(O_2CAr)_2(tmeda) + n\ Me\text{-}O_2CAr \quad (2.18)$$

(iv) Room temperature:

$$(2\text{-}n)\ Pd^{II}(O_2CAr)Tol(tmeda) + (2\text{-}n)/2\ (ArCO_2)_2 \rightarrow (2\text{-}n)\ Pd^{II}(O_2CAr)_2(tmeda) + (2\text{-}n)/2\ Tol_2 \quad (2.19)$$

(v) Overall reaction:

$$2\ Pd^{II}MeTol(tmeda) + (2 + n/2)\ (ArCO_2)_2 \rightarrow 2\ Pd^{II}(O_2CAr)_2(tmeda) + (1\text{-}n)\ Me\text{-}Me + n\ Tol\text{-}Me + n\ Me\text{-}O_2CAr + (2\text{-}n)/2\ Tol_2 \quad (2.20)$$

2.2.3.2 Model Reactions

Model reactions were carried out in a similar manner as described previously. In light of previous unsuccessful attempts to observe $PdIMe_2Ph(tmeda)$,[18] no attempt was made to synthesise the unobserved species '$Pd(O_2CPh)Me_2Tol(tmeda)$'. When PdMeTol(tmeda) and diaroyl peroxide were mixed in 2:1 ratio at temperatures *above* –30 °C, in order to simulate eqs 2.15-2.17, methyl aroate and $Pd(O_2CAr)_2(tmeda)$ were observed in addition to the expected products. This suggests that the reaction

of diaroyl peroxide with Pd(O_2CAr)Me(tmeda) (eq 2.18) is competitive with the reaction with PdMeTol(tmeda) (eq 2.15) at this temperature. Therefore, in order to try and achieve a true product distribution at room temperature, it was important to keep the process at low temperature for sufficient time for PdMeTol(tmeda) to be fully consumed before allowing it to warm to room temperature. It proved to be very difficult to obtain a reaction free of methyl aroate. This suggests that the reaction may be taking place slowly at a lower temperature than that reported above. Competition of this type was not seen in the reactions with PdMeTol(bpy).

As expected, Pd(O_2CAr)Me(tmeda) reacted with diaroyl peroxide (above *ca.* –20 °C for Ar = Ph and –30 °C for Ar = Ar_F) to form Me-O_2CAr and Pd(O_2CAr)$_2$(tmeda) (eq 2.18). In contrast to bpy analogues, the reaction of Pd(O_2CAr)Tol(tmeda) with (ArCO_2)$_2$ did not give rise to aryl-oxygen coupling products. Instead, 4,4'-bitolyl was observed as the sole organic product along with Pd(O_2CAr)$_2$(tmeda) (eq 2.19). When the reaction was carried out using equal amounts of reagents full consumption of Pd(O_2CAr)Tol(tmeda) was observed, yet only half of the peroxide reacted. Full consumption of both reagents occurred when the reaction was carried out using a 2:1 ratio of Pd(II):(ArCO_2)$_2$, *i.e.* $n = 0$ in eq 2.19. The mechanism by which this reaction occurs is not clear and no intermediates are detected.

The formation of 4,4'-bitolyl has also been shown to occur from the reaction of Pd(O_2CAr)Tol(tmeda) with PdMeTol(tmeda) and Pd(O_2CAr)Tol(tmeda) with Pd(O_2CAr)Me(tmeda). However, the absence of 4,4'-bitolyl at low temperatures suggests that these reactions are suppressed at such temperatures. Therefore, when the overall reaction is followed by slowly raising the temperature, it is expected that both PdMeTol(tmeda) and Pd(O_2CAr)Me(tmeda) will be fully consumed before they are able to react with Pd(O_2CAr)Tol(tmeda). Nevertheless, contribution of these reactions to the product distribution cannot be completely discounted. Further to this, 4,4'-bitolyl was found to form very slowly from a sample of Pd(O_2CPh)Tol(tmeda), with no other reagents present. Although this reaction proceeded at a considerably slower rate than the reaction with dibenzoyl peroxide,

this reaction could be making a minor contribution to product distribution. The latter may occur by a similar mechanism to that discussed in Section 2.2.2.1 (see Scheme 2.9).

Unlike the analogous bpy reactions, the value of *n*, and therefore the overall reaction stoichiometry, could not be obtained reliably. The main reason for this was the difficulty in obtaining reliable product distributions. As discussed above, there are a number of competing reactions that can potentially interfere with the accurate determination of *n*. The best method of determining *n* would be from the product distribution resulting from the reaction of 2:1 Pd(II):$(ArCO_2)_2$. However, as discussed previously, it is difficult to monitor this reaction without the unwanted appearance of Me-O_2CAr.

2.2.4 Mechanistic Considerations

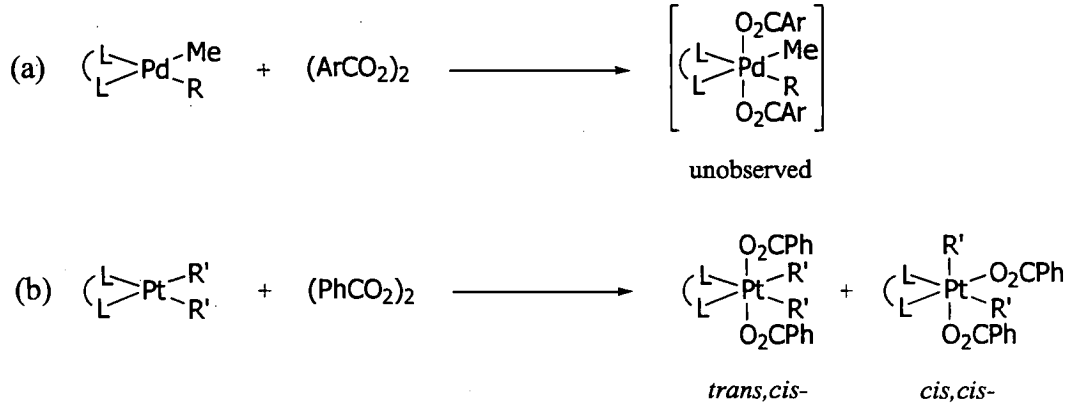
Diaroyl peroxides react with $PdMe_2(L_2)$ and $PdMeTol(L_2)$ in a complex series of reactions affording a combination of carbon-carbon and carbon-oxygen coupling products along with bis(carboxylato)palladium(II) species. Each of the complexes reacts *via* similar pathways, according to the reactions in Schemes 2.5, 2.7 and 2.11. The process involved is considerably more complicated than a simple reductive elimination from $Pd(O_2CAr)_2MeR(L_2)$ that might have been expected by direct analogy with related palladium mediated carbon-selenium bond formation (see Chapter Four).[16]

2.2.4.1 Oxidative Addition and Exchange Reactions

Diorganopalladium(II) reagents are expected to undergo an initial oxidative addition to form an undetected '$Pd^{IV}(O_2CAr)_2MeR(L_2)$' intermediate (Scheme 2.12a). The configuration of the unobserved palladium(IV) species is shown as the *trans,cis-* isomer, but may well be *cis,cis-* or a combination of the two.[12,13,26] Evidence for such reactions can be seen in the addition of dibenzoyl peroxide to

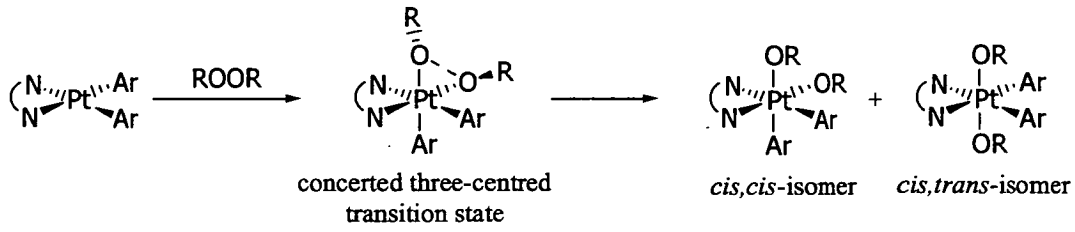
$PtR'_2(L_2)$ (R' = Me; L_2 = phen and R' = Ph, Tol, 3-tolyl, Anis; L_2 = bpy, phen) to form *cis,cis*- and *trans,cis*-$Pt^{IV}(O_2CPh)_2R'_2(L_2)$ (Scheme 2.12b).[12,13] Further support is seen in the oxidative addition of diphenyl diselenide, $(PhSe)_2$, to a range of platinum(II)[12,27] and palladium(II)[16,28] species. Reaction of diphenyl diselenide with $PtMe_2$(phen), Pt(Anis)R(Bu^{t}bpy) [Bu^{t}bpy = 4,4'-bis(*tert*-butyl)-6,6'-bipyridine; R = $CH(CO_2Me)_2$, $CH(CO_2Et)_2$, $CH(CO_2Pr^i)_2$] and $PdMe_2$(bpy) gives $Pt^{IV}(SePh)_2Me_2$(phen), $Pt^{IV}(SePh)_2$(Anis)R(Bu^{t}bpy) and $Pd^{IV}(SePh)_2Me_2$(bpy), respectively.[12,16,27,28] The relationship between carbon-oxygen and carbon-selenium bond formation will be discussed in more depth in Chapter Four.

Scheme 2.12: (a) The expected reaction of $PdMeR(L_2)$ (R = Me, Tol; L_2 = bpy, tmeda) with $(ArCO_2)_2$. (b) Known reactions of $PtR'_2(L_2)$ (R' = Me; L_2 = phen and R' = Ph, Tol, 3-tolyl or Anis; L_2 = bpy, phen) with dibenzoyl peroxide.[12,13]



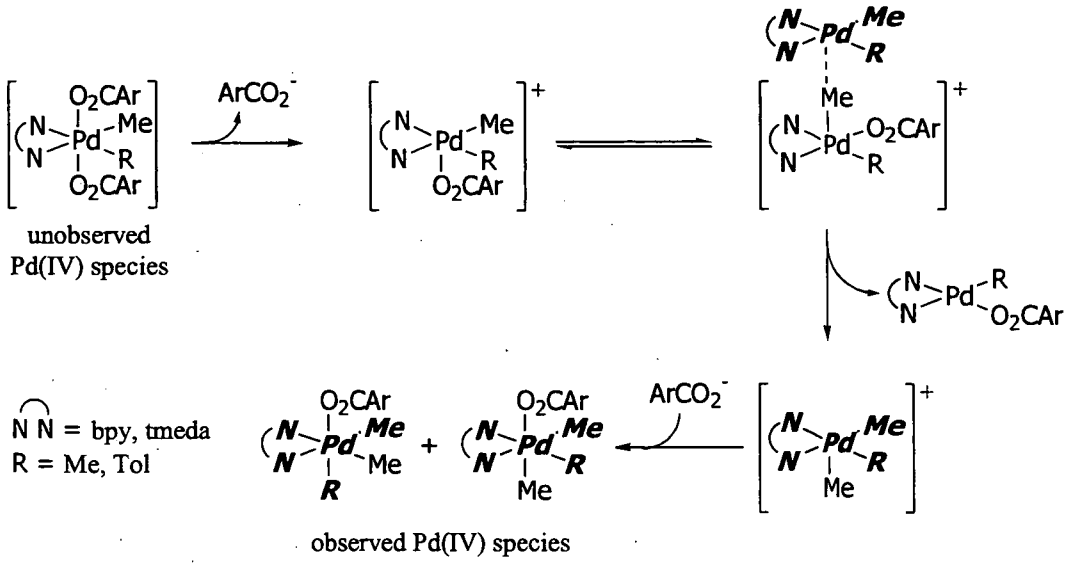
The mechanism by which dibenzoyl peroxide oxidatively adds to a d^8 metal(II) centre has not been established. However, kinetic studies carried out by Rashidi *et al.* on the addition of $(PhCO_2)_2$ to $PtAr_2(L_2)$ are consistent with *cis* addition *via* the formation of a concerted three-centre transition state (Scheme 2.13).[13] Rapid isomerisation could then occur to give the *trans* addition product. Such a mechanism could feasibly be responsible for the mixture of products observed in the reaction of $Pd(O_2CPh)Me$(bpy) with $(Ar_FCO_2)_2$ (Section 2.2.1.2).

Scheme 2.13: Proposed mechanism for the oxidative addition of peroxides to $PtAr_2(L_2)$.[13]



Unobserved '$Pd^{IV}(O_2CPh)_2MeR(L_2)$', from the reaction of $PdMeR(L_2)$ with $(ArCO_2)_2$, is thought to immediately be involved in an exchange reaction with remaining palladium(II) starting complex to form the detected triorganopalladium(IV) species and a monoorgano(benzoato)palladium(II) complex (Scheme 2.14). Related reactions have been observed on several occasions in palladium(IV) chemistry (Section 1.4.2).[17,18] By analogy with reported reactions, initial dissociation of one benzoate moiety from '$Pd(O_2CAr)_2MeR(L_2)$' would result in the formation of a five-coordinate intermediate, which may undergo isomerisation leading to a methyl group occupying an axial position. Nucleophilic attack by the diorganopalladium(II) reagent at an axial methyl group of the five-coordinate palladium cation would follow, forming a new cationic palladium(IV) species and the palladium(II) species $Pd(O_2CAr)R(L_2)$ on transfer of the methyl group. Association of the benzoate anion with the newly formed palladium(IV) cation would then lead to the observed, more stable, palladium(IV) intermediate, $Pd(O_2CAr)Me_2R(L_2)$. The configuration of the cationic intermediates are unknown, although it is of interest to note that a related neutral five-coordinate organoplatinum(IV) species, $PtMe_3(L)$ ($L^- = [\{(1,2\text{-}^iPr_2C_6H_3)NC(CH_3)\}_2CH]^-$), has been fully characterised and shown to have a square pyramidal geometry.[29]

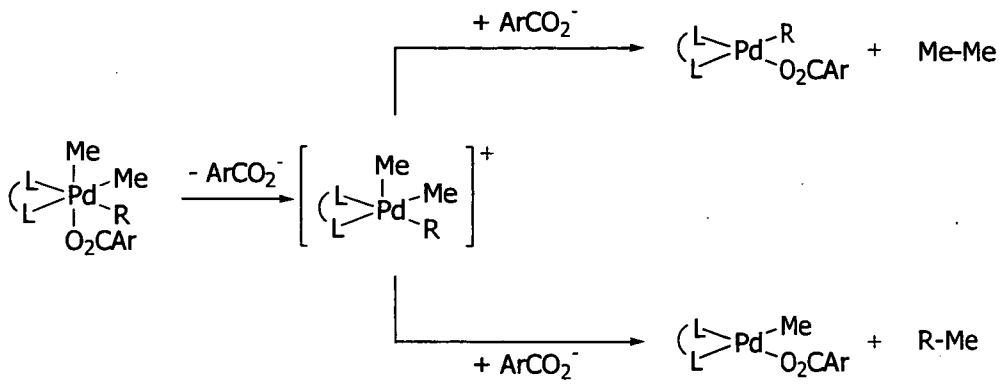
Scheme 2.14: Exchange reaction between the unobserved Pd(IV) species, '$Pd(O_2CPh)_2MeR(L_2)$', and the reagent, $PdMeR(L_2)$.



2.2.4.2 Reductive Elimination

Decomposition of the observed palladium(IV) species by reductive elimination follows the exchange reaction, forming monoorganopalladium(II) species and carbon-carbon coupling products. Reductive elimination is assumed to proceed by an initial dissociation of the benzoate group followed by reductive elimination of two organic groups from a cationic palladium(IV) intermediate (Scheme 2.15). Support for such a mechanism has been documented from kinetic studies of $PdIMe_3(bpy)$ (Section 1.4.1),[17,30,31] and evidence for the existence of cationic palladium(IV) species is provided by the detection of complexes such as $[PdMe_2(CD_3)\{(CD_3)_2CO\}(bpy)]^+$, $[PdMe_3\{(CD_3)_2CO\}(bpy)]^+$ and $[PdMe_3(CD_3CN)(tmeda)]^+$ in ^1H NMR studies of oxidative addition reactions.[32-35]

Scheme 2.15: Reductive elimination of carbon-carbon coupling products from $Pd(O_2CAr)Me_2R(L_2)$ (Ar = Ph, Ar_F; R = Me, Tol; L_2 = .bpy, tmeda)



It is important to note that carbon-oxygen coupling did not occur from the *observed* palladium(IV) species, but rather from the reaction of monoorganopalladium(II) species with diaroyl peroxide. This is in contrast to a related platinum(IV) system investigated by Goldberg and coworkers in which both carbon-carbon and carbon-oxygen coupling were observed directly from $PtMe_3(OR)(L_2)$ [L_2 = dppe, dppbz; OR = O_2CMe, O_2CCF_3, OTol] (Section 2.1).[14,15]

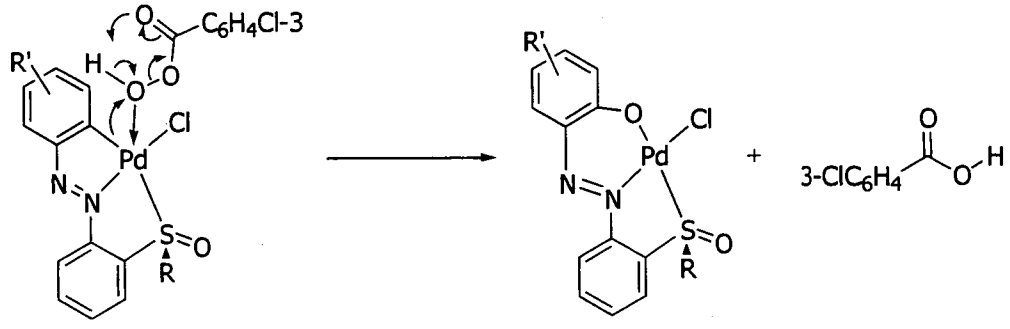
2.2.4.3 Carbon-Oxygen Bond Formation

The reaction of diaroyl peroxides with transition metal complexes is an area that is largely unstudied. Although the reactions of $Pd(O_2CAr)Tol(bpy)$ and $Pd(O_2CAr)Me(L_2)$ with $(ArCO_2)_2$ to give R-O_2CAr (R = Tol, Me) and inorganic palladium(II) is clearly related to the oxidative addition/reductive elimination steps in the proposed mechanism for the acetoxylation of arenes (Scheme 2.1), no reaction intermediates have been observed. As such, the proposal of a possible mechanism for these reactions has proved challenging.

The formation of carbon-oxygen bonds at palladium centres has been shown to occur in numerous examples and by a variety of proposed mechanisms. A large body of work has focussed on the reaction of percarboxylic acids and hydroperoxides.[3-5,7-9,36-45] Bandyopadhyay and coworkers demonstrated that

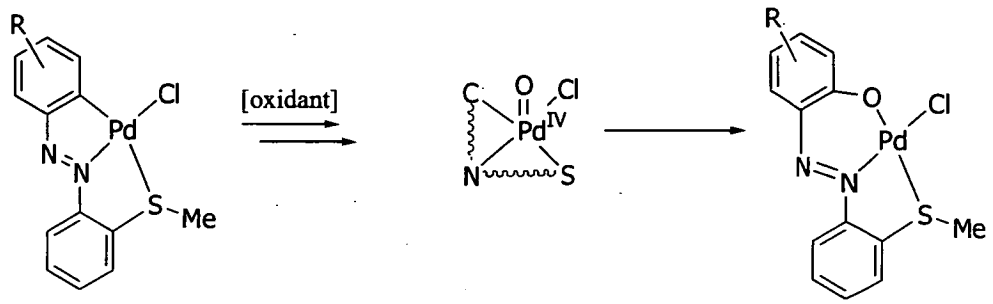
palladium(II) complexes with azo sulfoxide ligands undergo oxygen insertion into a palladium-aryl bond when allowed to react with 3-chloroperbenzoic acid (3-CPBA).[46] It was suggested that the peracid undergoes 'end-on' coordination *via* the oxygen lone pairs followed by heterolytic cleavage of the O-O bond (Scheme 2.16). The terminal proton of the peracid is positioned such that 3-chlorobenzoic acid is ultimately formed as a product.[46] Although coordination of diaroyl peroxide in a similar fashion may be envisaged for the systems under investigation, the absence of the terminal hydrogen (which plays an important role in the cleavage of the peroxo bond) makes it an unlikely mechanism for carbon-oxygen bond formation in the reactions considered in this chapter.

Scheme 2.16: Possible mechanism for oxygen insertion into a palladium-aryl bond with 3-CPBA as oxidant.[46]



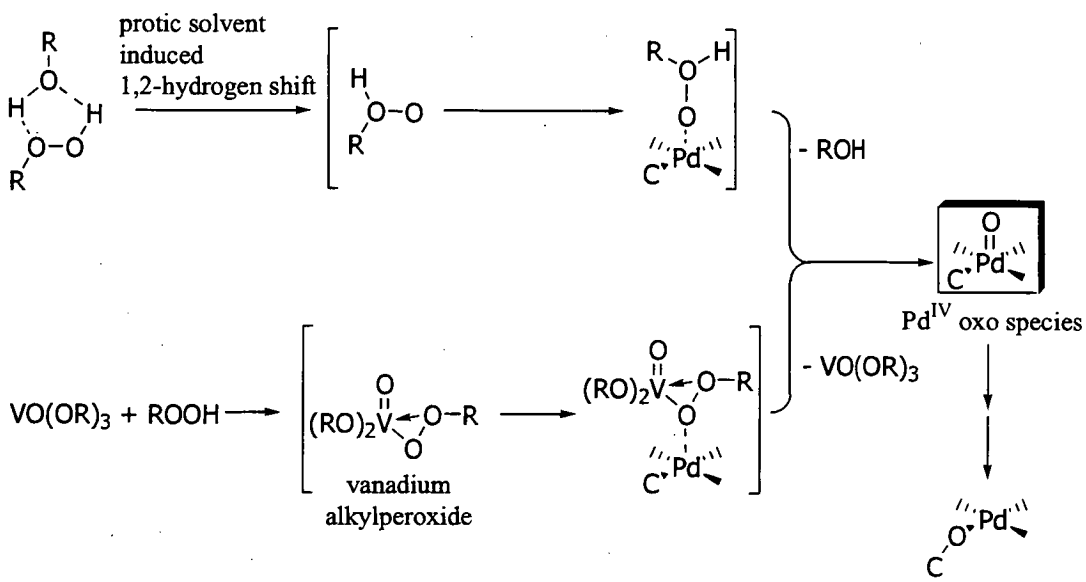
Bandyopadhyay and coworkers have also shown that the reaction of palladium(II) complexes, containing ligands belonging to the class of 2-(sulfinyl)azobenzenes, with *tert*-butylhydroperoxide (Bu^tOOH), $Bu^tOO^{\bullet}$, hydrogen peroxide or 3-CPBA in the presence of an iron(III) porphyrin leads to the insertion of oxygen into a palladium-aryl bond.[3,8,9,36] The oxygenating species in these reactions is predicted to be an oxopalladium(IV) intermediate (Scheme 2.17). It is also postulated that the formation of a palladium(II)-oxidant adduct may precede formation of the oxo species in some cases.

Scheme 2.17: Oxygen insertion into a Pd-aryl bond.

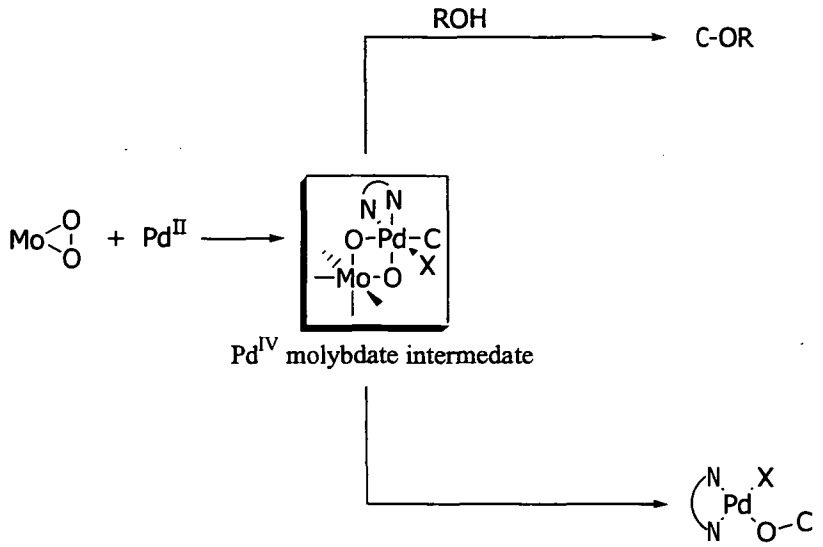


Palladium(IV) oxo species have also been postulated as intermediates in oxygen insertion reactions by van Koten and coworkers.[4,5,7,38,45] The reactions of some cyclopalladated complexes were shown to undergo oxygen insertion on reaction with Bu^tOOH in protic solvents. This reaction was enhanced by the presence of $VO(acac)_2$ or $VO(OBu^t)_3$ as catalyst, with the active catalyst present in the reaction thought to be $V^VO(OOBu^t)(OBu^t)_2$.[4,38,45] Proposed mechanisms for these reactions are shown in Scheme 2.18. Van Koten and coworkers have also observed oxygen insertion and carbon-oxygen bond formation at palladium by the reaction with molybdenum peroxide, $MoO(O_2)_2.HMPT.H_2O$ (HMPT = hexamethylphosphoric triamide).[5] These reactions are assumed to proceed *via* a palladium(IV) molybdate intermediate as shown in Scheme 2.19.

Scheme 2.18: Proposed mechanisms for the insertion of oxygen into a palladium(II)-carbon bond *via* the involvement of a palladium(IV) oxo species, with ROH as solvent.[38]

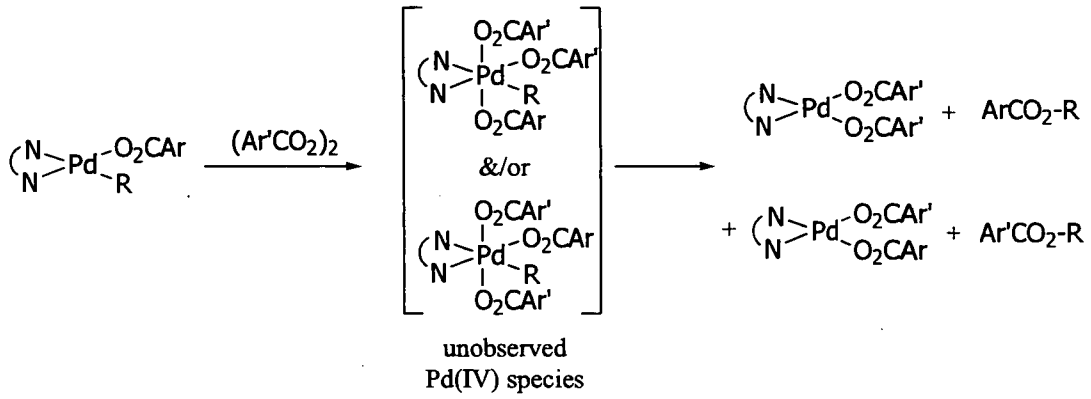


Scheme 2.19: Schematic representation of oxygen insertion and alkoxylation proposed to occur from a palladium(IV) molybdate intermediate.[5]



It is unlikely that a mechanism comparable to any of those described above is occurring in this case. Unlike the situations above, the reactions under consideration are not carried out in protic solvents and no catalysts or inorganic peroxides have been added. A more likely mechanism would be the oxidative addition of the peroxide to form a palladium(IV) intermediate followed by reductive elimination of a carbon-oxygen bond. As mentioned earlier, there is evidence for the oxidative addition of dibenzoyl peroxide to diorganoplatinum(II) complexes (see also Chapter Three).[12,13] Oxidative addition has also been shown to occur at monoorganoplatinum(II) complexes in the reaction of $Pt(O_2CPh)(NCN)$ (NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$) with dibenzoyl peroxide (see Chapter Three). One possible mechanism is shown in Scheme 2.20, involving oxidative addition of $(Ar'CO_2)_2$ to give a six-coordinate intermediate. The lack of identifiable intermediates means that the mechanism suggested in Scheme 2.20 is by no means definitive. It is, however, a reasonable proposal based on the observations made in these studies and related reactions.

Scheme 2.20: Possible mechanism for carbon-oxygen coupling at a monoorganopalladium(II) centre.



2.2.5 Synthesis and Characterisation of Complexes.

All palladium(II) and palladium(IV) complexes were prepared by metathesis reactions involving $PdCl_2(L_2)$, $PdIR(L_2)$ or $PdIMe_2R(L_2)$ and the appropriate silver(I) salt (Schemes 2.21, 2.23 and 2.24 in sections below). This approach has been used in the preparation of a number of known palladium and platinum carboxylates,[20,47-50] but none of the complexes discussed here, with the exception of $Pd(O_2CPh)_2(bpy)$,[16] have been reported previously.

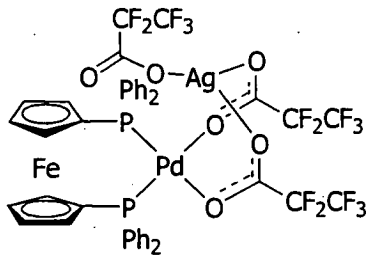
Several other methods of synthesising palladium carboxylate complexes have also been described. The monoorganopalladium(II) complex $Pd(O_2CPh)(C_6F_5)(bpy)$ was prepared from the reaction of $Pd(C_6F_5)(acac\text{-}C^{\gamma})(L_2)$ (acac = acetylacetonato; L_2 = bpy, phen) with benzoic acid in refluxing CH_2Cl_2.[47] Some related bis(carboxylato)palladium(II) complexes have been prepared by the reaction of $Pd(O_2CMe)_2$ with L_2 (phen or bpy) to give $Pd(O_2CMe)_2(L_2)$.[51] Other derivatives of the latter complex were then made by exchange of the acetate using an acid, *e.g.* with CF_3CO_2H to give $Pd(O_2CCF_3)_2(L_2)$.[51]

The synthetic method chosen, *i.e.* the direct reaction of dihalogeno- and monohalogenopalladium complexes with silver(I) salts, has the advantages that it is a

direct route to the desired product using readily accessible reagents, and that the reactions can be carried out easily at low or room temperature in high yields.

Characterisation was carried out by NMR spectroscopy for palladium(II) and palladium(IV) complexes, plus infrared spectroscopy, elemental analysis and, where possible, X-ray crystallography for palladium(II) complexes. On several occasions, significant difficulty was encountered attempting to obtain pure samples suitable for elemental analysis, although in most instances this was overcome by obtaining the complexes in crystalline form. However, for $Pd(O_2CPh)Me(tmeda)$ (**6**) and $Pd(O_2CPh)Tol(bpy)$ (**9**) several attempts at attaining accurate microanalyses failed. Similar difficulties were experienced by Neo *et al.* in attempting to characterise a number palladium(II) phosphine carboxylates.[48] In these cases it was hypothesised that the samples may have been contaminated by trace amounts of $PdCl(O_2CR)(L_2)$ or $Pd(O_2CR)_2(L_2)$-AgO_2CR.[49] An example of the latter type of complex was observed by Neo *et al.* when excess $Ag[O_2CCF_2CF_3]$ was added to a solution of $Pd(O_2CCF_2CF_3)_2(dppf)$, giving crystals of $PdAg(\mu\text{-}O_2CCF_2CF_3)_2(O_2CCF_2CF_3\text{-}O)(dppf)$ (Figure 2.1).[49] Low temperature NMR studies on this complex suggested that the silver was undergoing facile changes between two- and three-coordinate silver(I).[49] Other possibilities could include the persistence of silver halides or other impurities such as finely divided palladium(0).

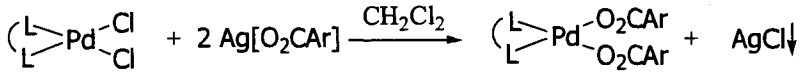
Figure 2.1: Schematic representation of $PdAg(\mu\text{-}O_2CCF_2CF_3)_2(O_2CCF_2CF_3\text{-}O)(dppf)$.[49]



2.2.5.1 Synthesis and Characterisation of $Pd(O_2CAr)_2(L_2)$

Complexes of the form $Pd(O_2CAr)_2(L_2)$ (Ar = Ph, Ar_F; L_2 = bpy, tmeda) were prepared by the reaction of $PdCl_2(L_2)$ with two equivalents of $Ag[O_2CAr]$ in CH_2Cl_2. Reactions, carried out in the absence of light, were complete within 15 minutes, with the precipitation of silver(I) chloride as a second product (Scheme 2.21). Each complex was isolated as a yellow solid and all were stable for several months at ambient temperature. Although $Pd(O_2CPh)_2(bpy)$ (**1**) has been reported previously as a reaction product,[16] no independent synthesis or crystallographic studies were discussed.

Scheme 2.21: Synthesis of $Pd(O_2CAr)_2(L_2)$.

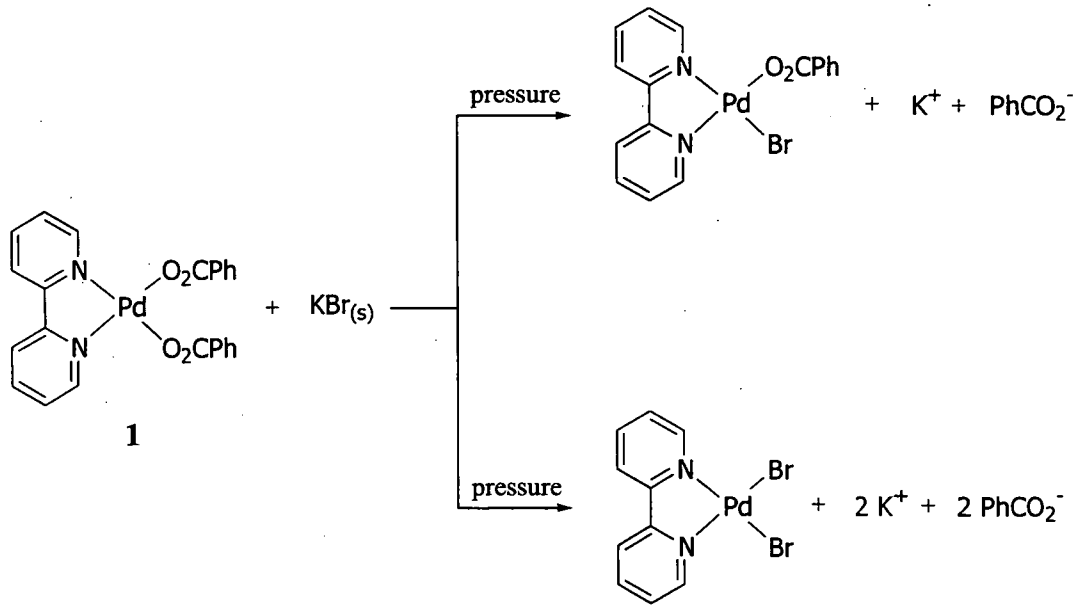


1: L_2 = bpy; Ar = Ph
2: L_2 = tmeda; Ar = Ph
3: L_2 = bpy; Ar = Ar_F
4: L_2 = tmeda; Ar = Ar_F

As expected, characterisation by IR and ^1H NMR revealed a number of similar characteristics between the four complexes (Table 2.2). Infrared spectra were measured in the form of KBr disks. A potential problem with this technique is the possible occurrence of pressure induced changes.[52] Such changes could include the conversion of one or both of the coordinated carboxylate groups into ionic carboxylate, with bromide coordinating to palladium (Scheme 2.22). In order to determine whether this was occurring, IR spectra of complexes **1-4** were compared with those of the free benzoate anions, measured as $K[O_2CPh]$ and $Ag[O_2CAr_F]$ (Table 2.2). Complexes **2-4** showed no indication of free benzoate, and hence no indication of anion exchange. However, when **1** was measured as a KBr disk, more than one set of carboxylate absorptions were present, with signals at 1622, 1596, 1551, 1395 and 1342 cm^{-1}. Absorptions at 1596, 1551 and 1395 cm^{-1} displayed nearly identical wavenumbers, relative intensities and peak shapes to those exhibited by $K[O_2CPh]$, suggesting that the free benzoate anion was present. The second set of

$\nu(CO_2)$ absorptions, at 1622 and 1343 cm^{-1}, implied that only partial anion exchange had occurred. However, it was not clear whether one or both benzoate groups had been replaced. Hence, the latter peaks could feasibly belong to $PdBr(O_2CPh)(bpy)$, unreacted **1** or a combination of the two (Scheme 2.22).

Scheme 2.22: Pressure induced reaction of $Pd(O_2CPh)_2(bpy)$ with KBr.



1

In light of the pressure induced anion exchange experienced by **1** above, spectra for the four complexes were also measured as Nujol mulls between potassium bromide plates. Although anion exchange between Nujol mulls of carboxylate complexes and potassium bromide plates is possible,[52] the short time that the complexes are in contact with the plates reduces the likelihood of this reaction. For **2-4**, there was very little deviation from the values obtained by measuring the samples as KBr disks (Table 2.2). Further to this, the absence of free anionic benzoate signals allowed absorptions for coordinated carboxylate groups in **1** to be confidently assigned (Table 2.2).

Table 2.2: Selected IR (as KBr disk, with Nujol mull measurements shown in parentheses) and ^{1}H NMR (in acetone-d_6 unless otherwise stated; multiplicities are stated, with $^3J_{HH}$ (Hz) is shown in parentheses) data for complexes **1-4**. IR data for K[O_2CPh], Ag[O_2CAr_F] and some related complexes is provided for comparison.

Complex	ν_{max} (cm^{-1})				δ (ppm)		
	$\nu(CO_2)$		$\Delta\nu(CO_2)$	$\nu(CF_3)$	*o*	*m*	*p*
	asym	sym					
$Pd(O_2CPh)_2(bpy)$ (**1**)[a,e]	- (1627 s)	- (1345 vs)	- (282)	-	8.2-8.0 m[c]	7.2 m[c]	
$Pd(O_2CPh)_2(tmeda)$ (**2**)	1616 s (1615 s)	1336 vs (1336 vs)	280 (279)	-	7.91 d[d] (7.6)	7.27 t[d] (7.2)	7.34 t[d] (7.6)
$Pd(O_2CAr_F)_2(bpy)$ (**3**)	1635 s (1635 s)	1357 s (1361 s)	278 (274)	1319 vs (1319 vs)	8.19 d (8.0)	7.69 d (8.0)	-
$Pd(O_2CAr_F)_2(tmeda)$ (**4**)[b]	1622 s (1622 s)	1357 s (1360 s)	265 (262)	1320 vs (1320 vs)	8.04 d (7.9)	7.57 d (8.0)	-
$Pd(O_2CPh)_2(dppf)$[f, 48]	1607 s	1345 vs	262	-	-	-	-
$Pt(O_2CPh)_2(bpy)$[50]	1618	1365	253	-	-	-	-
$Pt(O_2CPh)_2(dppf)$[f, 53]	1632 s	1344 s	288	-	-	-	-
$Pt(O_2CPh)_2(dppm)$[f, 53]	1615 s	1333 s	282	-	-	-	-
$PhCO_2^-$	1595 s	1398 s	197	-	-	-	-
$Ar_FCO_2^-$[e]	1588 s	1386 s	202	1326 vs	-	-	-

Note: For IR – vs = strong signal, s = strong signal, m = medium signal.
For ^{1}H NMR – d = doublet, t = triplet, m = multiplet.

[a] ^{1}H NMR measured in $CDCl_3$.

[b] ^{1}H NMR measured in CD_2Cl_2.

[c] Overlapping resonances.

[d] Complex second order coupling also observed.

[e] Nujol mull results only.

[f] dppf = $Fe(C_5H_4PPh_2)_2$; dppm = $Ph_2PCH_2PPh_2$

Deacon and coworkers have carried out extensive research and provided reviews of the nature of carboxylate coordination.[52] As a result, they have demonstrated that the separation between the asymmetric [$\nu_{asym}(CO_2)$] and symmetric [$\nu_{sym}(CO_2)$] carboxylate stretching frequencies [$\Delta\nu(CO_2)$] can provide an insight into the coordination mode of a carboxylate ligand. Carboxylate ions are able to coordinate to metals as a unidentate ligand, a chelating ligand, a bridging bidentate ligand, a monoatomic bridging ligand or in arrangements involving a combination of these.[52] As a free anion, the two oxygen atoms of the carboxylate are equivalent. Unidentate coordination eliminates this equivalence and causes an increase in $\nu(CO_2)_{asym}$ and

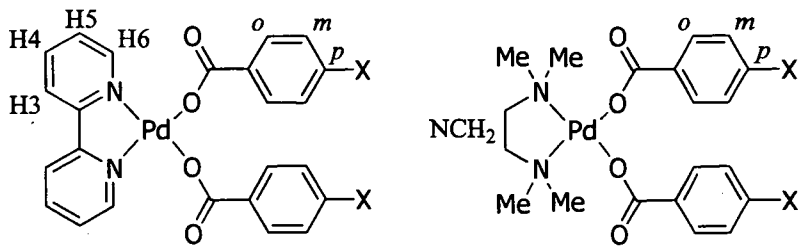
simultaneous decrease in $\nu(CO_2)_{sym}$. Consequently, the value of $\Delta(CO_2)$ is expected to increase relative to the value for the free carboxylate. In contrast, it has been proposed that separations similar to, or significantly less than those for the free ions, indicate chelating or symmetrically bridging carboxylates. This arises from the fact that such bonding modes should not affect the relative C-O bond orders of the carboxylate.[52]

In complexes **1-4**, the asymmetric carboxylate stretching frequency is increased relative to the ionic form, while the symmetric carboxylate stretching frequency is decreased. Hence, the separations between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ are greater than those for the free anion (*i.e.* $\Delta\nu > 197$ cm^{-1} for $PhCO_2^-$ and $\Delta\nu > 202$ cm^{-1} for $Ar_FCO_2^-$) (Table 2.2). As discussed above, this is a good, yet not definitive, indication of unidentate carboxylate coordination and, therefore, a pseudo-ester configuration.[52] These results are comparable with other studies of palladium(II) and platinum(II) benzoates (Table 2.2).[48,50,53]

Owing to their high symmetry, ^1H NMR spectra of these complexes are straightforward. Numbering schemes for complexes **1-4** are shown in Figure 2.2. In all spectra, integration indicated the presence of two benzoate moieties for each bidentate ligand. For complexes **2** and **4**, a sharp singlet was observed for the NCH_2 and NMe protons of the tmeda ligand. The aromatic regions were also uncomplicated for all complexes. Complex **4** displayed a simple pattern of two doublets (*AA'XX'* system), with the lower field signal due to *ortho* protons of the 4-(trifluoromethyl)benzoate group and the higher field doublet attributed to the *meta* protons. The aromatic region of complex **2** showed a doublet, triplet, 'triplet' pattern (from low to high field respectively) corresponding to the *ortho*, *para* and *meta* protons respectively. This represents an *AA'BXX'* system with complex second-order splitting observed for each signal. The spectra for **1** and **3** were slightly more complicated due to the increased number of resonances in the aromatic region and the consequent overlapping of some resonances. Four signals were observed for the bpy ligand, confirming its symmetrical environment, with H6 appearing furthest downfield in each case. As seen for the tmeda analogues, the benzoate groups of **1**

displayed a doublet, triplet, 'triplet' pattern (in a *AA'BXX'* system) with complex second order coupling, while **3** gave rise to two simple doublets with no further coupling.

Figure 2.2: ^{1}H NMR numbering schemes for complexes **1-4**.



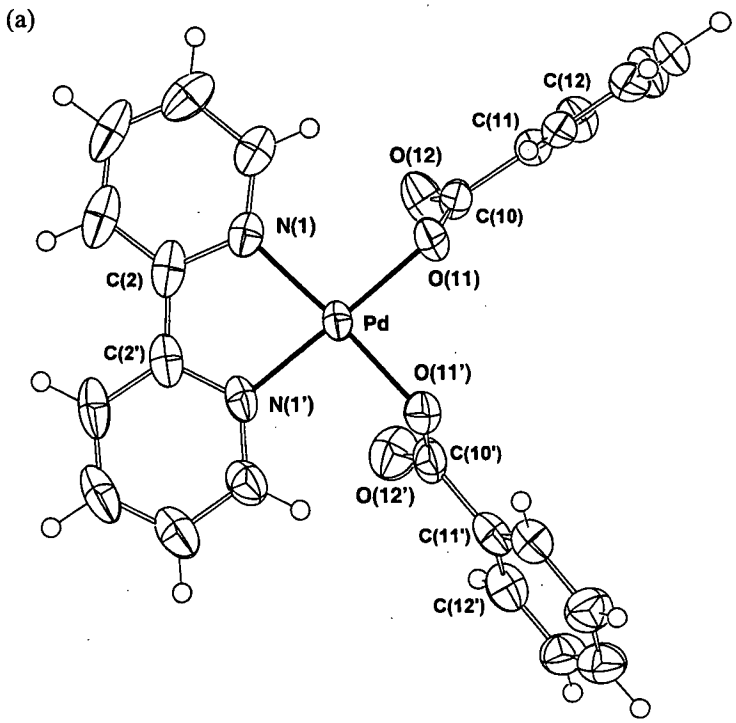
1: X = H
3: X = CF_3

2: X = H
4: X = CF_3

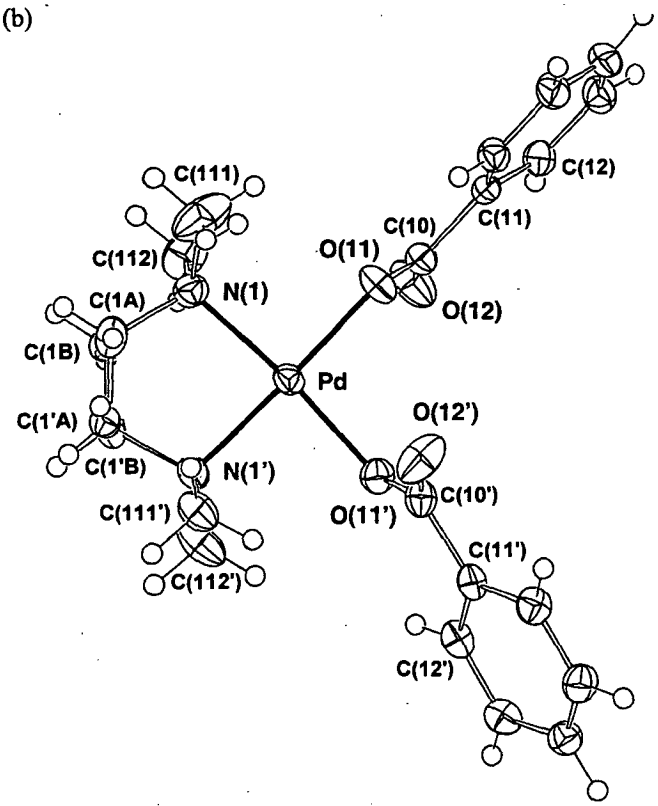
Crystals of **1**, **2** and **4** suitable for X-ray crystallographic studies formed from the reactions of $PdMe_2$(bpy) with $(PhCO_2)_2$, $PdMe_2$(tmeda) with $(PhCO_2)_2$ and $Pd(O_2CAr_F)Me$(tmeda) with $(Ar_FCO_2)_2$ in acetone-d_6, respectively (Figure 2.3). In each case, crystals formed overnight from acetone-d_6 at ambient temperature. The molecular structures of these complexes are shown in Figure 2.3 and selected bond distances and angles are shown in Table 2.3. All complexes are mononuclear and contain approximately square planar geometry around the palladium, formed by the *cis*-bidentate nitrogen donor ligand and two unidentate carboxylate moieties. In each case, the plane formed by CCO_2 in the benzoate group is approximately coplanar with the aromatic ring of the same group, and approximately normal to the N_2O_2 coordination plane. In **1** the uncoordinated oxygen atoms lie on the same side of the N_2O_2 coordination plane, whereas in both complexes containing tmeda as ligand (**2** and **4**) the uncoordinated oxygens occupy opposite sides of the coordination plane. It was also noted that in complex **4** the uncoordinated oxygen is situated on the opposite side of the coordination plane to the axial methyl on the nitrogen adjacent to it. It is feasible that this arrangement is adopted in order to minimise steric interactions between the pendant oxygens and the axially positioned methyl groups of the tmeda ligand. In **4**, one half of the neutral molecule comprises the asymmetric unit of the structure and a crystallographic 2-axis passes through the metal atom and the central bond of the ordered tmeda. The N_2O_2 'plane' deviates significantly from

true planarity, with N(1) lying 0.037(1) Å above and O(11') lying 0.032(1) Å below the mean coordination plane. The other tmeda complex (**2**) has roughly 2-symmetry with a disordered tmeda ligand. By contrast, the bpy complex (**1**) is devoid of crystallographic symmetry and a full molecule comprises the asymmetric unit.

Figure 2.3: Structures of (a) $Pd(O_2CPh)_2(bpy)$ (**1**), (b) $Pd(O_2CPh)_2(tmeda)$ (**2**) and $Pd(O_2CAr_F)_2(tmeda)$ (**4**). Ellipsoids are shown at the 50% probability level.



(b)


C(111)
C(112)
C(1A)
C(1B)
C(1'A)
C(1'B)
C(111')
C(112')
N(1)
N(1')
Pd
O(11)
O(12)
C(10)
C(11)
C(12)
O(12')
O(11')
C(10')
C(11')
C(12')

(c)

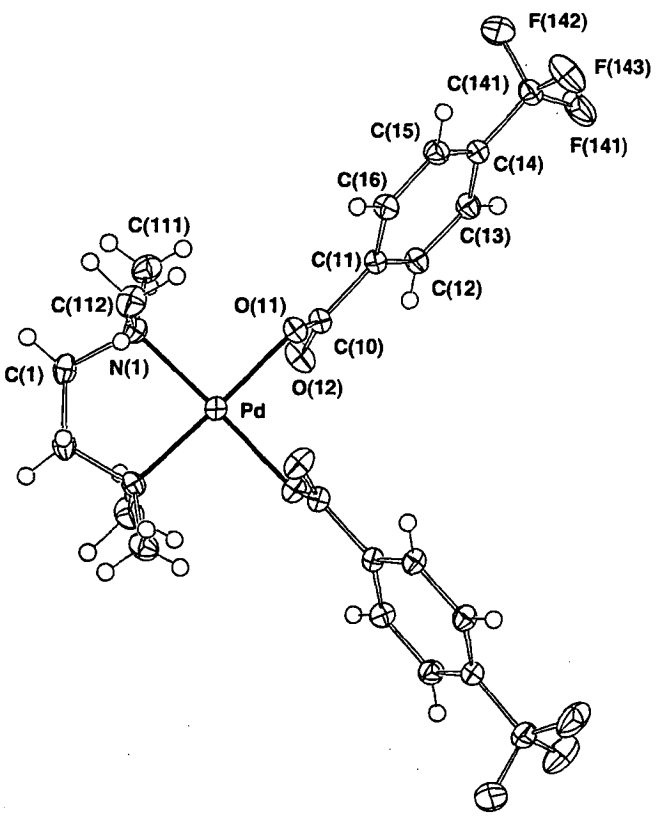

F(142)
F(143)
F(141)
C(141)
C(15)
C(14)
C(16)
C(13)
C(11)
C(12)
C(111)
C(112)
C(1)
N(1)
O(11)
C(10)
O(12)
Pd

Table 2.3: Selected bond distances (Å) and angles (deg.) for **1**, **2** and **4**.

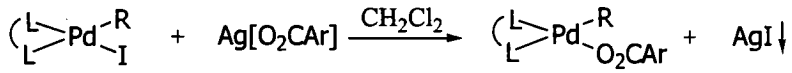
	1	2	4
		Bond Distances (Å)	
Pd-N(1)	2.022(4)	2.049(1)	2.049(1)
Pd-N(1')	2.010(4)	2.052(1)	-
Pd-O(11)	2.006(3)	2.018(1)	2.0442(8)
Pd-O(11')	1.991(4)	2.020(1)	-
C(10)-C(11)	1.525(6)	1.514(2)	1.505(1)
C(10')-C(11')	1.551(8)	1.506(2)	-
C(10)-O(11)	1.272(6)	1.284(2)	1.292(2)
C(10')-O(11')	1.271(7)	1.285(2)	-
C(10)-O(12)	1.213(6)	1.218(2)	1.236(2)
C(10')-O(12')	1.199(7)	1.224(2)	-
		Bond Angles (deg.)	
N(1)-Pd-N(1')	80.72(2)	85.99(6)	86.01(4)
N(1)-Pd-O(11)	96.9(2)	91.65(5)	91.52(4)
N(1)-Pd-O(11')	175.6(2)	172.34(5)	176.82(4)
N(1')-Pd-O(11)	172.8(2)	171.82(5)	-
N(1')-Pd-O(11')	95.0(2)	89.39(5)	-
O(11)-Pd-O(11')	87.3(1)	93.75(5)	91.03(3)
Pd-O(11)-C(10)	120.8(3)	122.2(1)	110.80(8)
Pd-O(11')-C(10')	119.1(3)	120.7(1)	-
		Interplanar dihedral angles (deg.)[a]	
θ	74.4(2)	79.73(7)	79.70(4)
θ'	69.1(2)	71.10(7)	-
ϕ_{Ar}	16.4(2)	4.4(1)	16.81(5)
ϕ'_{Ar}	1.4(3)	13.69(9)	-
ϕ_{bpy}	7.3(2)	-	-

[a] θ, θ' are the angles between the anion CCO_2 planes and the N_2O_2 coordination plane. ϕ_{Ar}, ϕ'_{Ar} are the CCO_2/aromatic ring interplanar dihedral angles of the anions. ϕ_{bpy} is the $C_5N/(C_5N)'$ interplanar dihedral angle of the bpy ligand.

2.2.5.2 Synthesis and Characterisation of $Pd(O_2CAr)R(L_2)$

Complexes of the form $Pd(O_2CAr)R(L_2)$ (Ar = Ph, Ar_F; R = Me, Tol; L_2 = bpy, tmeda) were prepared in a similar manner as described in Section 2.2.5.1, from $PdIR(L_2)$ and one equivalent of $Ag[O_2CAr]$ (Scheme 2.23). Silver(I) iodide precipitated from the reaction mixture.

Scheme 2.23: Synthesis of $Pd(O_2CAr)R(L_2)$.



5: L_2 = bpy; R = Me; Ar = Ph
6: L_2 = tmeda; R = Me; Ar = Ph
7: L_2 = bpy; R = Me; Ar = Ar_F
8: L_2 = tmeda; R = Me; Ar = Ar_F
9: L_2 = bpy; R = Tol; Ar = Ph
10: L_2 = tmeda; R = Tol; Ar = Ph
11: L_2 = bpy; R = Tol; Ar = Ar_F
12: L_2 = tmeda; R = Tol; Ar = Ar_F

As observed for **1-4**, comparison of spectral data revealed a number of similarities and characteristic differences between complexes **5-12** (Table 2.4). When infrared spectra of these complexes were measured using KBr disks, most displayed pressure induced anion exchange similar to that described for **1** in Section 2.2.5.1. Consequently, spectra were measured as Nujol mulls. This presented a problem in that, in some instances, overlap was experienced, with $\nu_{sym}(CO_2)$ appearing as a shoulder on the Nujol absorption at 1376 cm^{-1}. In these cases, the symmetric carboxylate stretching frequency was estimated. Each complex displayed a $\Delta\nu(CO_2)$ greater than that for the free carboxylate anion (Table 2.4). As discussed in detail in Section 2.2.5.1, this implies unidentate carboxylate coordination.

Table 2.4: Selected IR (as Nujol mull) and ^{1}H NMR (in acetone-d_6) data for complexes **5-12**. ^{1}H NMR numbering schemes can be see in Figure 2.4.

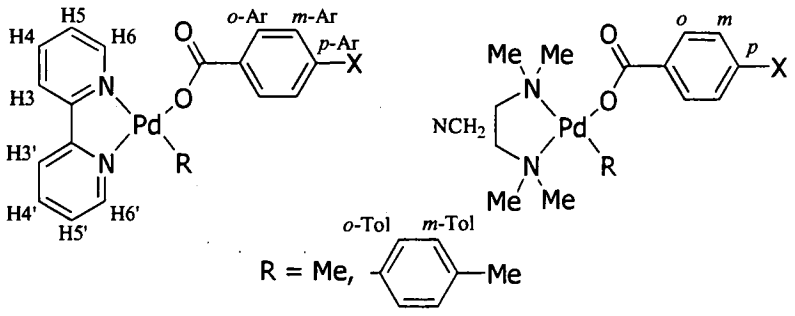
Complex	ν_{max} (cm^{-1})				δ (ppm)		
	$\nu(CO_2)$		$\Delta\nu(CO_2)$	$\nu(CF_3)$	H6 H6'	Pd-Me	Pd-Tol (CH_3)
	asym.	sym.					
$Pd(O_2CPh)Me(bpy)$ (**5**)	1613 s	1353 vs	260	-	8.36 8.60	0.87	-
$Pd(O_2CPh)Me(tmeda)$ (**6**)	1594 s	1350 vs[b]	244	-	-	0.28	-
$Pd(O_2CAr_F)Me(bpy)$ (**7**)[a]	1626 s	1352 m	274	1321 vs	8.43 8.67	0.87	-
$Pd(O_2CAr_F)Me(tmeda)$ (**8**)	1621 s	1360 s[b]	261	1320 vs	-	0.32	-
$Pd(O_2CPh)Tol(bpy)$ (**9**)	1598 s	1347 vs	251	-	8.45 8.26	-	2.20
$Pd(O_2CPh)Tol(tmeda)$ (**10**)	1614 s	1352 vs	262	-	-	-	2.10
$Pd(O_2CAr_F)Tol(bpy)$ (**11**)	1627 s	1360 m[b]	267	1320 vs	8.44 8.25[c]	-	2.21
$Pd(O_2CAr_F)Tol(tmeda)$ (**12**)	1613 s	1360 s[b]	253	1321 vs	-	-	2.11
$PhCO_2^-$[a]	1595 s	1398 s	197	-	-	-	-
$Ar_FCO_2^-$	1588 s	1386 s	202	1326 vs	-	-	-

[a] IR measured as KBr disk.

[b] Estimated value. Overlaps with Nujol peak

[c] Overlapping resonance.

Figure 2.4: ^{1}H NMR numbering schemes for complexes **5-12**.

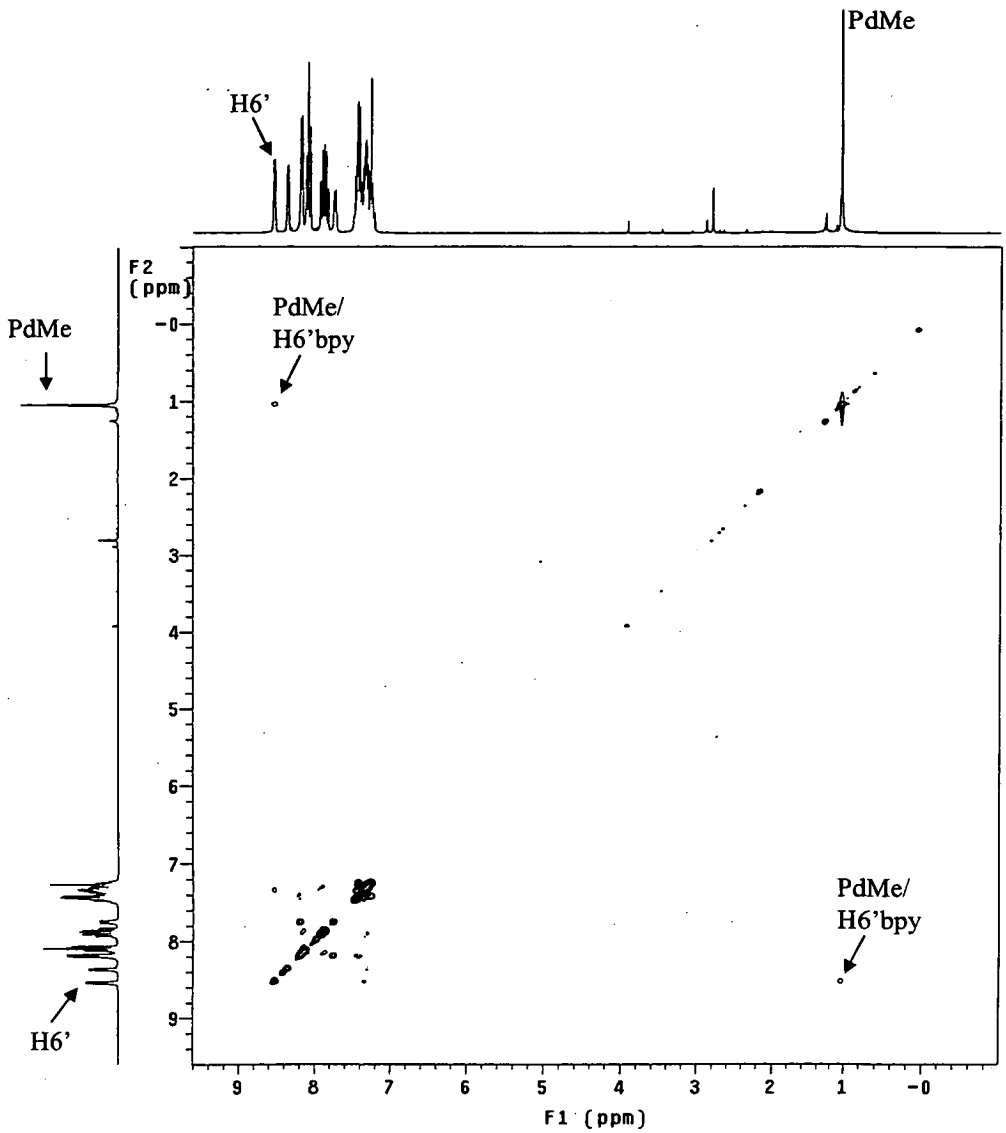


5: R = Me; X = H
6: R = Me; X = H
7: R = Me; X = CF_3
8: R = Me; X = CF_3
9: R = Tol; X = H
10: R = Tol; X = H
11: R = Tol; X = CF_3
12: R = Tol; X = CF_3

Unlike complexes **1-4**, **5-12** are not symmetrical and, as such, have more complex ^{1}H NMR spectra. Numbering schemes for these complexes are shown in Figure 2.4. The greatest challenge came in the assignment of the protons of the 2,2'-bipyridine

ligand for complexes **5**, **7**, **9** and **11**. The H6/6' protons were characterised by their small ^3J coupling, which ranged from 4.4 - 5.6 Hz. In comparing the four complexes, it was noted that each had a doublet arising from H6 or H6' between 8.36 and 8.46 ppm. Furthermore, the two Pd(O_2CAr)Me(bpy) complexes (**5** and **7**) shared similar shifts for H6 or H6' (8.60 and 8.67 ppm, respectively) as did the Pd(O_2CAr)Tol(bpy) complexes (**9** and **11**) with signals at 8.26 and *ca.* 8.25 ppm, respectively. This implies that the protons giving rise to these signals shared similar chemical environments. A NOESY spectrum of complex **5** was used to determine whether the bpy proton adjacent to the methyl group (H6') gave rise to the signal at 8.60 or 8.36 ppm. This showed a clear cross peak between the methyl group and the doublet at 8.60 ppm (Figure 2.5), indicating that this resonance represented H6'. From this, it can be concluded that the proton adjacent to the benzoate moiety (H6) gives rise to the signal at 8.36 ppm. Considering the similarity in shifts observed for **7**, H6 and H6' can be assigned to the resonances appearing at 8.43 and 8.67 ppm, respectively. This logic can also be extended to complexes **9** and **11**. The appearance of resonances at 8.45 and 8.44 ppm, respectively, is clearly related to those observed at similar shifts in the former two complexes. Therefore, these signals can tentatively be assigned to H6 in each complex. Consequently, the doublets appearing at 8.26 and *ca.* 8.25 ppm, respectively, can be assigned to H6' in each case. The upfield positions of H6' in **9** and **11**, compared with those observed for **5** and **7**, is in agreement with observations made by Canty and coworkers that the delocalised π-electrons of the palladium-bonded aryl ring have a shielding effect on the proton in the '6' position of the adjacent bpy ring.[54] This effect is assumed to be caused by the approximately normal orientation of the aryl ring to the coordination plane.[54] From the assignment of H6' in each complex, a combination of coupling constants and gCOSY experiments could be used to assign the other bpy peaks.

Figure 2.5: NOESY spectrum of $Pd(O_2CPh)Me(bpy)$ (**5**) with the PdMe/H6'bpy cross peaks highlighted.



Crystals of $Pd(O_2CPh)Tol(bpy).CH_2Cl_2$ (**9**.CH_2Cl_2) suitable for X-ray crystallography were grown by the slow diffusion of *n*-pentane into a solution of **9** in CH_2Cl_2. The molecular structure of this complex is shown in Figure 2.6 and selected bond distances and angles are shown in Table 2.5. In correspondence with **1**, **2** and **4**, complex **9**.CH_2Cl_2 is mononuclear, containing a near planar, four-coordinate metal atom environment. A *cis*-bidentate nitrogen donor ligand (bpy), a 4-tolyl group and a unidentate benzoate moiety occupy its coordination sites. The complex lacks crystallographic symmetry, and a full molecule comprises the asymmetric unit of the

structure. This is accompanied by a dichloromethane molecule of solvation, disordered in a lattice void.

Figure 2.6: Structure of $Pd(O_2CPh)Tol(bpy)$ (9). Ellipsoids are shown at the 50% probability level. The solvent molecule is omitted for clarity.

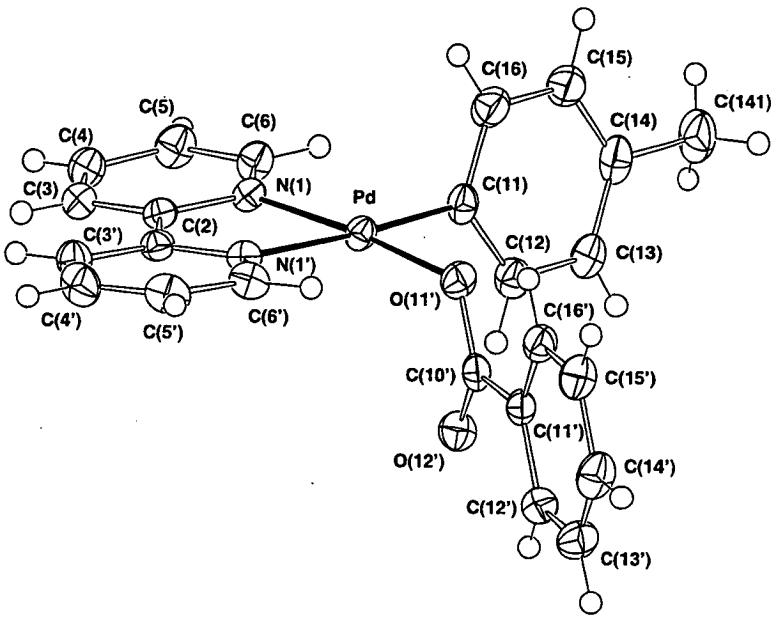


Table 2.5: Selected bond distances (Å) and angles (deg.) for $9.CH_2Cl_2$.

$9.CH_2Cl_2$			
Bond Distances (Å)			
Pd-N(1)	2.027(2)	C(10')-C(11')	1.509(3)
Pd-N(1')	2.111(1)	C(10')-O(11')	1.289(3)
Pd-C(11)	1.983(2)	C(10')-O(12')	1.235(3)
Pd-O(11')	2.035(2)		
Bond Angles (deg.)			
N(1)-Pd-N(1')	79.71(6)	N(1')-Pd-O(11')	93.01(6)
N(1)-Pd-C(11)	96.70(7)	C(11)-Pd-O(11')	93.01(3)
N(1)-Pd-O(11')	172.49(6)	Pd-O(11')-C(11')	117.0(1)
N(1')-Pd-C(11)	175.9(1)		
Interplanar dihedral angles (deg.)[a]			
θ	75.08(7)	ϕ'_{Ar}	2.92(8)
θ'	85.42(6)	ϕ_{bpy}	6.28(7)

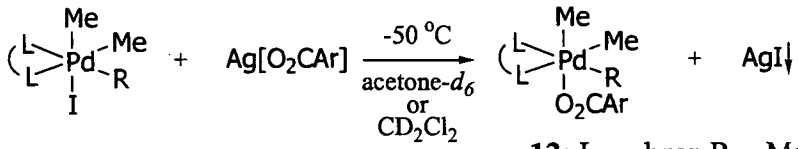
[a] θ is the angle between the N_2CO and Tol coordination plane. θ' is the angle between the anion CCO_2 plane and the N_2O_2 coordination plane. ϕ'_{Ar} is the CCO_2/aromatic ring interplanar dihedral angle of the anions. ϕ_{bpy} is the $C_5N/(C_5N)'$ interplanar dihedral angle of the bpy ligand.

2.2.5.3 In Situ *Synthesis and Characterisation of $Pd(O_2CAr)Me_2R(L_2)$*

The low stability of the palladium(IV) complexes, $Pd(O_2CAr)Me_2R(L_2)$ (Ar = Ph, Ar_F; R = Me, Tol; L_2 = bpy, tmeda), led to unsuccessful attempts at isolation of the pure complexes. Therefore, they were generated and used *in situ* and characterised by ^1H NMR spectroscopy only. The reagents $PdIMe_2R(L_2)$ were freshly prepared, from $PdMeR(L_2)$ and MeI at low temperature for each reaction in order to ensure that no decomposition of the starting material had occurred, as the iodo complex $PdIMe_2R(bpy)$ is known to be unstable above *ca.* –10 °C. These were reacted with $Ag[O_2CAr]$ in the appropriate NMR solvent (acetone-d_6 or CD_2Cl_2) at –50 °C (Scheme 2.24) in an equivalent manner to the reported synthesis of

$Pd(O_2CPh)Me_2(CH_2Ph)(bpy)$.[20] The majority of the silver(I) iodide could be removed by quick filtration through glass fiber filter paper with minimal decomposition.

Scheme 2.24: Synthesis of $Pd(O_2CAr)Me_2R(L_2)$. For simplicity, both isomeric forms of **17** and **18** are not shown.



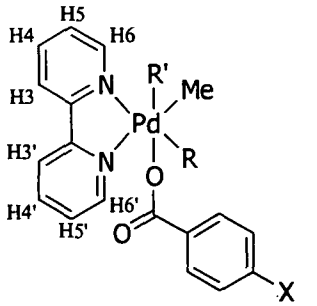
13: L_2 = bpy; R = Me; Ar = Ph
14: L_2 = tmeda; R = Me; Ar = Ph
15: L_2 = bpy; R = Me; Ar = Ar_F
16: L_2 = tmeda; R = Me; Ar = Ar_F
17: L_2 = bpy; R = Tol; Ar = Ph
18: L_2 = bpy; R = Tol; Ar = Ar_F

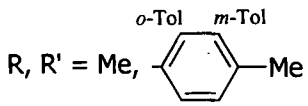
It was important that no decomposition of the reagents, $PdIMe_2R(L_2)$, had occurred as the palladium(II) decomposition product of these complexes are $PdIR(L_2)$, which can also react with silver(I) salts as shown in Scheme 2.23. Consequences of this would include the introduction of additional complexity to NMR spectra and the alteration of observed product distribution in the decomposition of the palladium(IV) complexes. The importance of determining this distribution accurately is discussed in Section 2.2.2.2.

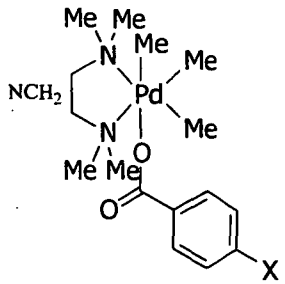
^{1}H NMR characterisation of **13**, **14**, **15** and **16** is straightforward due to the symmetry of the complexes, the presence of only one isomer and the consequently uncomplicated ^{1}H NMR spectra (see Figure 2.7 for numbering schemes for complexes **13-16**). The spectra of these complexes displayed a number of common features. Each showed typical peaks for a symmetrical bidentate ligand. The axial methyl group appeared at high field (between *ca.* 0.6 and 0.9 ppm in acetone-d_6) and integrated as three protons, while the equatorial methyl groups integrated as six protons and appeared further downfield (between *ca.* 1.5 and 1.7 ppm) (Table 2.6). The equatorial methyls of the tmeda complexes appeared

further upfield than the bpy complexes, while the trend was reversed for the axial methyl groups.

Figure 2.7: ^{1}H NMR numbering schemes for complexes **13-16**.







14: X = H
16: X = CF_3

13: R = R' = Me; X = H
15: R = R' = Me; X = CF_3
17a: R = Me; R' = Tol; X = H
17b: R = Tol; R' = Me; X = H
18a: R = Me; R' = Tol; X = CF_3
18b: R = Tol; R' = Me; X = CF_3

Table 2.6: Selected ^{1}H NMR data for complexes **13-16** in acetone-d_6.

Complex	δ (ppm)			
	H6 H6'	**CH_3 (equatorial)**	**CH_3 (axial)**	**CH_3 (Tol)**
13[a]	9.03	1.70	0.62	-
14[b]	-	1.53	0.78	-
15[a]	9.03	1.71	0.69	-
16[b]	-	1.53	0.82	-
17a[a]	9.36	2.09	-	2.08
17b[a]	9.08 8.52	2.00	1.14	2.29
18a[c]	9.34	2.11	-	2.08
18b[c]	9.08 8.52	2.02	1.20	2.29

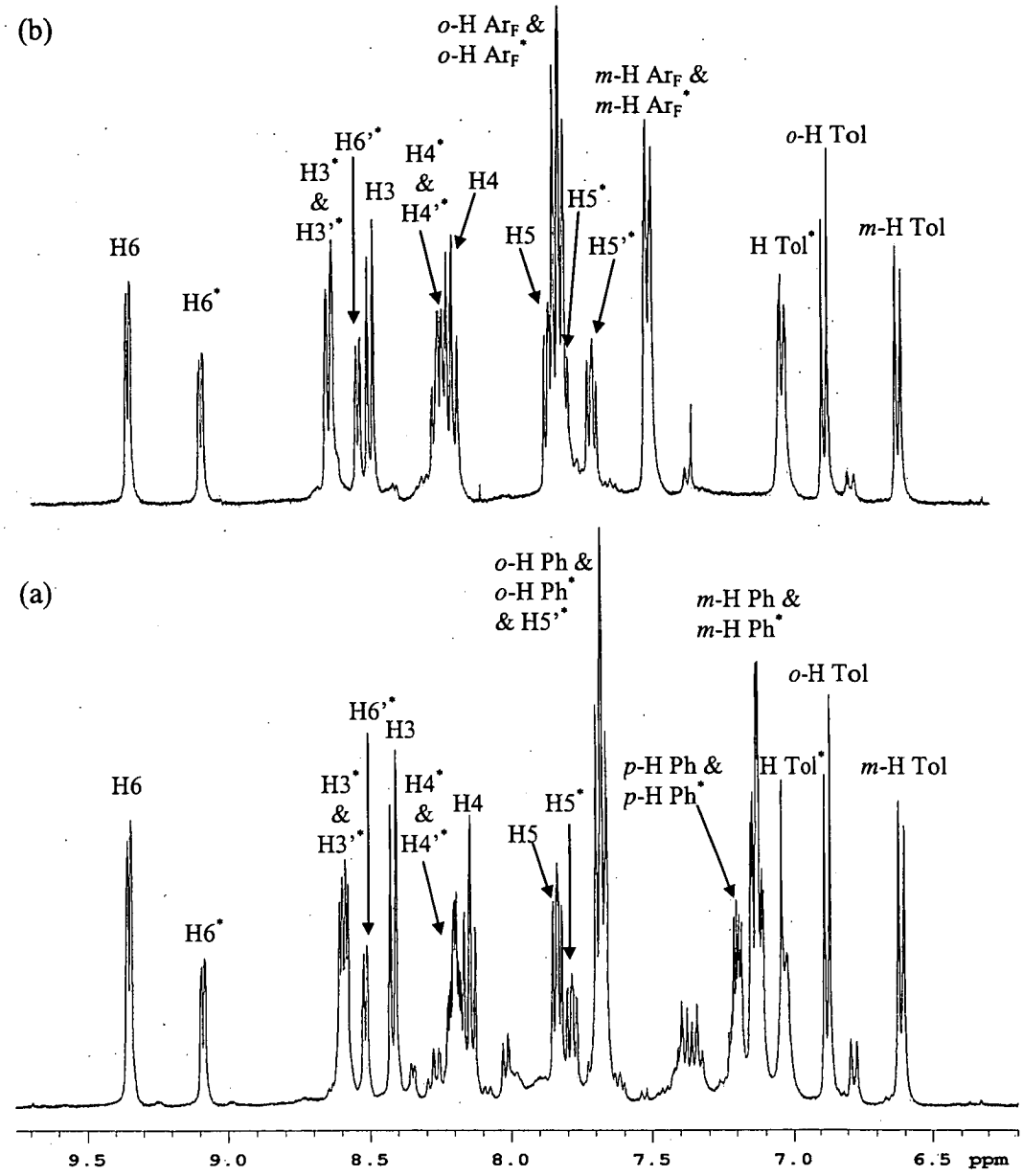
[a] Measured at –30 °C. [b] Measured at –40 °C. [c] Measured at –20 °C.

Characterisation of complexes **17** and **18** proved to be more challenging due to the presence of two isomeric forms which led to increased complexity of the ^{1}H NMR spectra, particularly in the aromatic region (Figure 2.8). Isomers were present in the same ratios as observed in Section 2.2.2.1, *i.e.* 1:1 in acetone-d_6 and 1:2 in CD_2Cl_2. As a result, comparison of spectra recorded in acetone-d_6 and CD_2Cl_2 helped in assigning some resonances. When measured in CD_2Cl_2, isomers were present in inequivalent quantities and the acetone-d_6 solvent resonance (which interfered with some signals at certain temperatures) was no longer present. This led to the identification of a number of resonances in the aliphatic region. Additional comparison of these spectra with those of other complexes reported here, as well as with some related palladium(IV) compounds, $Pd(O_2CPh)Me_2(CH_2Ph)(bpy)$[20] and PdIMePh(bpy),[18,19] also helped to assign some resonances.

Doublets arising from H6/6' were simple to identify as they generally occurred downfield of the other resonances and displayed characteristically small ^3J coupling constants (*ca.* 5 Hz). Using the observation in Section 2.2.5.2 that H6' bpy protons adjacent to 4-tolyl are shifted upfield compared with those adjacent to methyl, H6 and H6' were assigned as shown in Table 2.6. From these assignments, the remaining bpy protons could be identified by their coupling constants and by gCOSY experiments. Protons H3/3' also gave rise to low field doublets but could be distinguished by their larger ^3J coupling constants (*ca.* 8 ppm), while H4/4' and H5/5' appeared with ^4J coupling as triplets of doublets and/or doublets of doublets of doublets.

Resonances arising from the (substituted) benzoate group of each isomer overlapped with the other. Through examination of integrals in CD_2Cl_2, the two sets of doublets furthest upfield in the aromatic region were attributed to the aromatic tolyl protons of complexes with both methyl groups in equatorial positions (*i.e.* **17a** and **18a**). For **17b** and **18b**, a broad doublet attributed to tolyl appeared at *ca.* 7.05 ppm. A second tolyl resonance could not be located in either case.

Figure 2.8: Aromatic regions for ^{1}H NMR of (a) $Pd(O_2CPh)Me_2Tol(bpy)$ (**17**) at –30 °C and (b) $Pd(O_2CAr_F)Me_2Tol(bpy)$ (**18**) at –20 °C. Resonances arising from **17b** and **18b** are marked with an asterisk (*). Both spectra were measured in acetone-d_6.



The stability of these complexes in solution was considerably lower than a number of known triorganopalladium(IV) complexes containing bpy or tmeda (Table 2.7). Stability properties of palladium(IV) complexes can be largely attributed to three main factors: flexibility of the ligand, steric interference and ease of dissociation of the coordinated anion (or solvent). Complexes with rigid chelating ligands are generally more stable than those with flexible, or non-chelating, ligands.

It is probable that the reason for this is that flexible, or monodentate, ligands are able to alter into a configuration that is favourable to decomposition pathways more readily than rigid chelating ligands can. Complexes of tmeda provide a good example of this point. Although tmeda is superior to bpy as a σ-donor, and as such could be expected to form more stable complexes, the flexibility of the ethane backbone of tmeda can have the effect of destabilising complexes.

Table 2.7: Stability of some triorganopalladium(IV) complexes as determined by the temperature of decomposition noted by NMR.

Complex	**Approx. temperature (°C) up to which Pd^{IV} species is stable.**
$Pd(O_2CAr)Me_2Tol(tmeda)$	Not observed
$PdIMe_2Ph(tmeda)$[18]	Not observed
$[PdMe_3(acetone\text{-}d_6)(tmeda)][OTf]$[35]	-60
$[PdMe_2CD_3(acetone\text{-}d_6)(bpy)]I$[32]	-50
$Pd(O_2CAr)Me_3(tmeda)$ (**14**, **16**)	-30
$Pd(O_2CAr)Me_3(bpy)$ (**13**, **15**)	-30
$Pd(O_2CAr)Me_2Tol(bpy)$ (**17**, **18**)	-30
$[PdMe_3(CD_3CN)(tmeda)][OTf]$[35]	-20
$PdIMe_3(tmeda)$[35]	-20
$PdIMe_2Ph(bpy)$[18]	-10
$PdIMe_3(bpy)$[55]	-10

Steric bulk of the ligand can also play a role in complex stability. This concept is, again, well illustrated by the tmeda ligand. Axially positioned methyl groups on tmeda can interfere with other coordinating groups. As a result, complexes with bulky ligands such as tmeda tend to be less stable than analogues with planar ligands such as bpy.[35]

Ease of dissociation is another important factor in this series, as reductive elimination occurs from a five-coordinate intermediate following initial dissociation of a ligand.[17,30,35] Hence, it follows that complexes with more labile ligands (*e.g.* weakly coordinating solvents such as acetone) will undergo reductive elimination

more readily than those with strongly coordinated ligands (*e.g.* iodide or bromide). The apparent higher stability of $[PdMe_3(CD_3CN)(tmeda)][OTf]$ compared with the complexes $Pd(O_2CAr)Me_2R(L_2)$, is likely an anomaly arising from the fact that the decomposition of the former complex was determined using CD_3CN as the solvent,[35] while the latter were measured in non-coordinating solvents (acetone-d_6 or CD_2Cl_2)

Each of these factors is reflected in the relative stabilities of the complexes shown in Table 2.7. In general, tmeda complexes display lower stability than the bpy analogues. Complexes with weakly coordinating solvents such as acetone-d_6 are also seen to decompose at a considerably lower temperature than those with more strongly coordinating solvents such as CD_3CN.

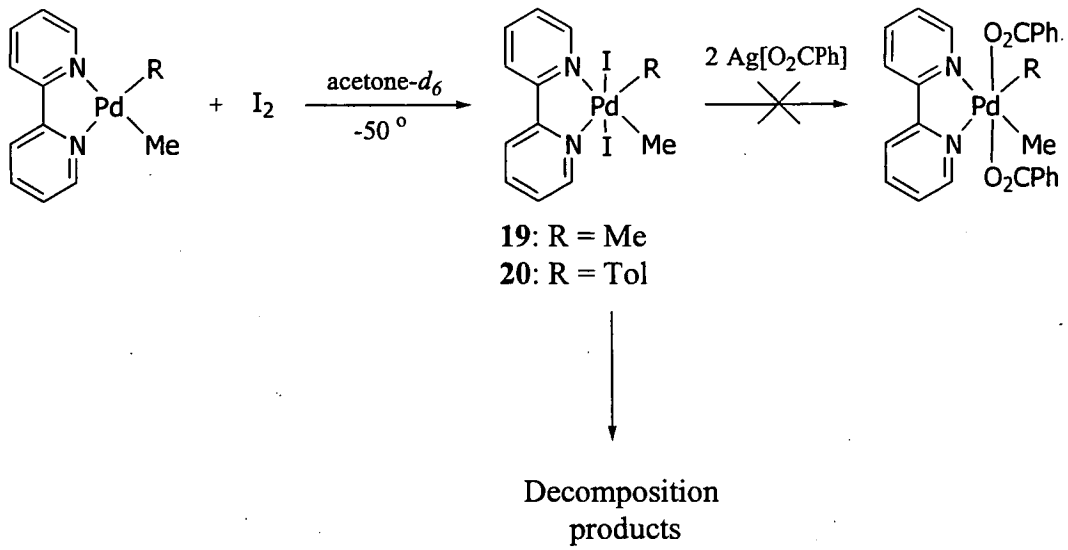
2.2.5.4 Attempted Synthesis of $Pd(O_2CPh)_2MeR(bpy)$

In order to try to determine whether or not direct carbon-oxygen coupling would occur from the unobserved diorganopalladium(IV) intermediates in the absences of other palladium species, attempts were made to prepare $Pd(O_2CPh)_2MeR(bpy)$ (R = Me, Ph). It was hoped that oxidative addition of diiodine to PdMeR(bpy) would form $PdI_2MeR(bpy)$ which could then be used as a reagent in a metathesis reaction with $Ag[O_2CPh]$.

Oxidative addition of diiodine to diorganopalladium(II) complexes containing rigid bidentate ligands has been observed previously by van Asselt *et al.*[56] Diorganopalladium(IV) species of limited stability were obtained, with the *trans* addition product being the sole, or major, product. When diiodine was added to an acetone-d_6 solution of PdMeR(bpy) at low temperature, the *trans* addition products could be identified by ^1H NMR (**19** and **20**, Scheme 2.25). The complexes were relatively stable at low temperature (< *ca.* -30 °C) but decomposed rapidly when warmed to room temperature. Decomposition was not investigated in detail but decomposition products of complex **19** appeared to include iodomethane, $PdI_2(bpy)$ and PdIMe(bpy), while complex **20** appeared to decompose to 4-iodotoluene, iodomethane, $PdI_2(bpy)$ and PdI(Tol)(bpy). Resonances expected for the carbon-

carbon coupling products, ethane and 1,4-xylene, were absent. The presence of $PdI_2(bpy)$ may have been caused by reaction of PdIR(bpy) (R = Me, Tol) with excess diiodine.

Scheme 2.25: Attempted preparation of $Pd(O_2CPh)_2MeR(bpy)$.



In view of previous syntheses reported here, it was expected that the exchange of the iodo ligands with benzoate groups would proceed readily. However, when $Ag[O_2CPh]$ was added to **19** and **20** at low temperature, displacement of the iodo groups did not occur (Scheme 2.25). When the reaction mixtures were allowed to warm to room temperature, decomposition products included methyl benzoate, $Pd(O_2CPh)Tol(bpy)$ and $Pd(O_2CPh)Me(bpy)$. Although these might be expected as decomposition products of the target palladium(IV) complexes, it is likely that they formed by the reaction of $Ag[O_2CPh]$ with the decomposition products of **19** and **20**.

2.3 Conclusions

Diorganopalladium(II) complexes with bidentate nitrogen-donor ligands have been shown to undergo a complicated series of reactions with diaroyl peroxides to form inorganic palladium(II) species and products of carbon-carbon and carbon-oxygen coupling. Diorganopalladium(II) reagents undergo an initial oxidative

addition by diaroyl peroxide to form an undetected diorganopalladium(IV) intermediate. The latter immediately engages in a methyl exchange reaction with the palladium(II) reagent to form a triorganopalladium(IV) and monoorganopalladium(II) complex, both of which are observed spectroscopically [except in the case where the reagent is PdMeTol(tmeda)]. The triorganopalladium(IV) species undergoes reductive elimination by carbon-carbon bond formation *only*, to produce organic compounds and additional monoorganopalladium(II) species. Carbon-oxygen bond formation then occurs by the reaction of monoorganopalladium(II) species with diaroyl peroxide. The exception is $Pd(O_2CAr)Tol(tmeda)$ which reacts to give bitolyl and inorganic palladium.

Palladium(IV) species may be involved in carbon-oxygen bond forming processes but not in the capacity that was expected from initial studies.[16] As discussed above, rather than from the postulated diorganopalladium(IV) intermediate, carbon-oxygen bond formation occurs from the reactions of monoorganopalladium(II) complexes with diaroyl peroxides. Monoorganopalladium(IV) species are suggested as potential intermediates for these reactions, although other mechanisms cannot be excluded, *e.g.* dibenzoyl peroxide is believed to decompose *via* a process involving free radicals,[57-61] so the participation of radicals cannot be fully discounted. These reactions provide a direct model for the oxidation of '$Pd^{II}(O_2CMe)Ar$' to '$Pd^{IV}(O_2CMe)_3Ar$' and the subsequent reductive elimination of an aryl-oxygen bond in the proposed mechanism for the acetoxylation of arenes (Scheme 2.1). However, spectroscopic identification and, hence, conclusive evidence for the involvement of palladium(IV) species remains elusive.

It is feasible that direct carbon-oxygen coupling would be observed from diorganopalladium(IV) species, $Pd(O_2CAr)_2MeR(L_2)$, if they could be isolated free from $PdMeR(L_2)$. However, in the presence of $PdMeR(L_2)$, methyl group exchange overrides any propensity for reductive elimination by carbon-oxygen or carbon-carbon bond formation. Although attempts to prepare examples of $Pd(O_2CAr)_2MeR(L_2)$ species failed, the observation of carbon-iodine bond formation

from related $PdI_2MeR(bpy)$ complexes, and carbon-selenium bond formation from palladium(IV) complexes (Chapter Four) show that decomposition by creation of carbon-heteroatom bonds is possible for diorganopalladium(IV) complexes.

The complexes $Pd(O_2CAr)Tol(tmeda)$ react with $(ArCO_2)_2$ to give 4,4'-bitolyl, rather than by carbon-oxygen coupling as observed for the bpy analogues. The mechanism of this reaction is not understood, and while palladium(IV) intermediates may occur, it is also feasible that free radicals may be involved owing to the expected presence of radicals from the slow decomposition of $(ArCO_2)_2$. Alternatively, the steric bulk of the NMe_2 groups of the tmeda ligand may influence reactions at the metal centre. In the reaction of $Pd(O_2CAr)Tol(tmeda)$ with $(ArCO_2)_2$, the NMe_2 groups may prevent the suitable orientation of the Tol ligand in order to allow oxidative addition of the diaroyl peroxide, consequently blocking the formation of the postulated palladium(IV) intermediate. Similar steric effects are discussed in Chapter Three, in which NMe_2 groups of a NCN-pincer ligand appear to prevent aryl-oxygen coupling from a platinum(IV) complex by hindering the rotation of the axial aryl group and/or by blocking the *ipso* carbon from approaching anions. This may also explain the general lack of success in observing other '$Pd^{IV}Ar$' complexes bearing a tmeda ligand in this and other studies.

2.4 Experimental

2.4.1 General Experimental

2.4.1.1 Instrumentation

NMR spectroscopy was carried out using a Varian Gemini-200 NMR spectrometer at 199.98 MHz or a Varian INOVA-400 NMR spectrometer at 399.69 MHz. Chemical shifts (δ) are reported in ppm relative to TMS and all coupling constants are given in Hz. Peak multiplicity is denoted as singlet (s), doublet (d),

triplet (t), multiplet (m), doublet of doublets (dd), triplet of doublets (td), doublet of doublet of doublets (ddd) or broad (br).

Infrared (IR) spectroscopy was performed using a Bruker IFS 66 FTIR Spectrometer or a Perkin-Elmer Paragon 100 FTIR in the mid IR range (400 – 4000 cm^{-1}). Spectra were measured as KBr disks or Nujol mulls. Elemental analyses were performed by Dr Graham Rowbottom of the Central Science Laboratory, University of Tasmania, using a Carlo Erba EA 1108 Elemental Analyser or a ThermoFinnigan Flash EA 1112 Elemental Analyser. Coupled GC-MS was carried out using a HP 5890 gas chromatograph fitted with a 25 m x 0.52 mm and connected to a 5970B mass selective detector (70 eV ET with He carrier gas).

2.4.1.2 Reagents and Solvents

The reagents $PdCl_2(L_2)$ (L_2 = bpy, tmeda),[35] $PdMe_2(L_2)$,[35] $PdMeTol(L_2)$,[54,62] PdIMe(tmeda),[35] $PdITol(L_2)$[54,62] and $(Ar_FCO_2)_2$[63] were prepared as previously reported, and $Ag[O_2CAr_F]$ was prepared as described for the analogue $Ag[O_2CPh]$.[64] The complex PdIMe(bpy) was prepared as described for PdIMe(tmeda) but starting with $PdMe_2(bpy)$.[35] All other reagents were used as received.

2.4.2 Synthesis of $Pd(O_2CAr)_2(L_2)$

$Pd(O_2CPh)_2(bpy)$ (1). Silver benzoate (0.276 g, 1.20 mmol) was added to a suspension of $PdCl_2(bpy)$ (0.20 g, 0.60 mmol) in dichloromethane (10 mL). The suspension quickly became yellow in colour. It was then stirred for 15 minutes in the absence of light, filtered through a plug of glass fiber filter paper and Celite, and the filtrate evaporated to dryness *in vacuo*. The resulting yellow solid was rinsed with *n*-pentane (3 x 5 mL) and dried *in vacuo*. Yield: 0.23 g (76 %). Crystals suitable for X-ray diffraction were obtained from the reaction of $PdMe_2(bpy)$ with $(PhCO_2)_2$ (*vide infra*). ^{1}H NMR ($CDCl_3$): δ 8.40 (d, 2H, ^3J = 7.6 Hz, H3), 8.30 (dd, 2H, ^3J = 5. 6 Hz, ^4J = 1.0 Hz, H6 bpy), 8.12 (d, 4H, ^3J = 7.2 Hz, ^4J = 1.6 Hz, *o*-H Ph), 8.08 (td, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, H4), 7.41 (t, 2H, ^3J = 7.6 Hz [complex second

order coupling also observed], *p*-H Ph), 7.34 (t, 4H, ^3J = 7.6 Hz [complex second order coupling also observed], *m*-H Ph), 7.26 (ddd [overlaps with solvent peak], 2H, ^3J = 5.6 Hz, ^4J = 1.2 Hz, H5). IR (Nujol mull): ν(CO_2) 1622 s, 1343 s cm^{-1}. Anal. Calcd. C, 57.10; H, 3.59; N, 5.55. Found: C, 57.05; H, 3.53; N, 5.43.

$Pd(O_2CPh)_2$(tmeda) (2). This complex was prepared from $PdCl_2$(tmeda) (0.0224 g, 0.0763 mmol) and silver benzoate (0.0362 g, 0.158 mmol) using a similar procedure to that described for **1**. The product was obtained as a yellow solid. Yield: 0.0342 g (96 %). Crystals suitable for X-ray diffraction were obtained from the reaction of $PdMe_2$(tmeda) with $(PhCO_2)_2$ (*vide infra*). ^{1}H NMR (acetone-d_6): δ 7.91 (d, 4H, ^3J = 7.6 Hz [complex ^4J coupling also observed], *o*-H Ph), 7.34 (t, 2H, ^3J = 7.6 Hz [complex second order coupling also observed], *p*-H Ph), 7.27 (t, 2H, ^3J = 7.2 Hz [complex second order coupling also observed], *m*-H Ph), 3.05 (s, 4H, NCH_2), 2.82 (s, 12H, NCH_3). IR (KBr disk): ν(CO_2) 1616 s, 1576 m, 1336 vs cm^{-1}. Anal. Calcd. C, 51.68; H, 5.64; N, 6.03. Found: C, 51.76; H, 5.61; N, 5.43.

$Pd(O_2CAr_F)_2$(bpy) (3). This complex was prepared from $PdCl_2$(bpy) (0.0504 g, 0.150 mmol) and Ag[O_2CAr_F] (0.0914 g, 0.308 mmol) using a similar procedure to that described for **1**. The product was obtained as a yellow solid. Yield: 0.0900 g (93 %). ^{1}H NMR (acetone-d_6): δ 8.70 (d, 2H, ^3J = 7.6 Hz, H3), 8.39 (td, 2H, ^3J = 7.6 Hz, ^4J = 1.6 Hz, H4), 8.32 (dd, 2H, ^3J = 5.6 Hz, ^4J = 1.2 Hz, H6), 8.19 (d, 4H, ^3J = 8.0 Hz, *o*-H Ar_F), 7.73 (ddd, 2H, ^3J = 5.6 Hz, ^4J = 1.2 Hz, H5), 7.69 (d, 4H, ^3J = 8.0 Hz, *m*-H Ar_F). IR (KBr disk): ν(CO_2) 1635 s, 1566 m, 1350 s cm^{-1}; ν(CF_3) 1319 vs cm^{-1}. Anal. Calcd. C, 48.73; H, 2.52; N, 4.37. Found: C, 48.75; H, 2.52; N, 4.19.

$Pd(O_2CAr_F)_2$(tmeda) (4). This complex was prepared from $PdCl_2$(tmeda) (0.0277 g, 0.0944 mmol) and Ag[O_2CAr_F] (0.0589 g, 0.198 mmol) using a similar procedure to that described for **1**. The product was a obtained as yellow solid. Yield: 0.0215 g (38 %). Crystals suitable for X-ray diffraction were obtained from the reaction of Pd(O_2CAr_F)Me(tmeda) with $(Ar_FCO_2)_2$ (*vide infra*). ^{1}H NMR (CD_2Cl_2): δ 8.04 (d, 4H, ^3J = 7.9 Hz, *o*-H Ar_F), 7.57 (d, 4H, ^3J = 8.0 Hz, *m*-H Ar_F), 2.85 (s, 4H, NCH_2), 2.79 (s, 12H, NCH_3). ^{13}C NMR (CD_2Cl_2): δ 172.1 (*C*=O), 139.1, 130.6,

125.4, 63.2 (NCH_2), 51.9 (NCH_3). IR (KBr disk): $\nu(CO_2)$ 1622 s, 1564 m, 1356 s cm^{-1}; $\nu(CF_3)$ 1320 vs cm^{-1}. Anal. Calcd. C, 43.98; H, 4.03; N, 4.66. Found: C, 43.90; H, 3.98; N, 4.64.

2.4.3 Synthesis of $Pd(O_2CAr)R(L_2)$

$Pd(O_2CPh)Me(bpy)$ (5). Silver benzoate (0.079 g, 0.34 mmol) was added to a suspension of PdIMe(bpy) (0.125 g, 0.31 mmol) in dichloromethane (10 mL). The suspension quickly became yellow in colour. It was then stirred for 15 minutes in the absence of light, filtered through a plug of glass fiber filter paper and Celite, and the filtrate evaporated to dryness *in vacuo*. The resulting yellow solid was rinsed with *n*-pentane (3 x 5 mL) and dried *in vacuo*. Yield: 0.12 g (97 %). ^{1}H NMR (acetone-d_6): δ 8.60 (d, 1H, ^3J = 5.6 Hz, H6), 8.55 (d, 1H, ^3J = 8.4 Hz, H3'), 8.49 (d, 1H, ^3J = 8.0 Hz, H3), 8.36 (d, 1H, ^3J = 4.8 Hz, H6'), 8.21 (td, 1H, ^3J = 8.0 Hz, ^4J = 1.2 Hz, H4), 8.2-8.0 (m, 3H, *o*-H Ph and H4'), 7.65 (ddd, 1H, ^3J = 5.6 Hz, ^4J = 1.6 Hz, H5), 7.56 (ddd, 1H, ^3J = 5.2 Hz, ^4J = 0.8 Hz, H5'), 7.5-7.3 (m, 3H, *m*- and *p*-H Ph), 0.87 (s, 3H, $PdCH_3$). IR (Nujol mull): $\nu(CO_2)$ 1613 s, 1572 m, 1353 vs cm^{-1}. Anal. Calcd. C, 54.22; H, 4.04; N, 7.02. Found: C, 54.01; H, 3.76; N, 6.81.

$Pd(O_2CPh)Me(tmeda)$ (6). This complex was prepared from PdIMe(tmeda) (0.0226 g, 62.0 μmol) and silver benzoate (0.0161 g, 70.3 μmol) using a similar procedure to that described for **5**. The product was obtained as a yellow solid. Yield: 0.0222 g (99 %). ^{1}H NMR (acetone-d_6): δ 7.95 (dd, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, *o*-H Ph), 7.4-7.2 (m, 3H, *m*- and *p*-H Ph), 2.84 (m, 2H, NCH_2), 2.69 (s, 6H, NCH_3), 2.62 (m, 2H, NCH_2), 2.50 (s, 6H, NCH_3), 0.28 (s, 3H, $PdCH_3$). IR (Nujol mull): $\nu(CO_2)$ 1594 s, 1549 m, ~ 1350 vs (overlaps with Nujol peak) cm^{-1}.

$Pd(O_2CAr_F)Me(bpy)$ (7). This complex was prepared from PdIMe(bpy) (0.082 g, 0.20 mmol) and $Ag[O_2CAr_F]$ (0.062 g, 0.21 mmol) using a similar procedure to that described for **5**. The product was obtained as a yellow solid. Yield: 0.081 g (87 %). ^{1}H NMR (acetone-d_6): δ 8.67 (d, 1H, ^3J = 5.6 Hz, H6), 8.57 (d, 1H, ^3J = 8.0 Hz, H3 or H3'), 8.53 (d, 1H, ^3J = 8.0 Hz, H3 or H3'), 8.43 (d, 1H, ^3J = 4.4 Hz, H6'), 8.3-

8.2 (m, 3H, *o*-H Ar_F and H4 or H4'), 8.18 (td, 1H, ^3J = 7.6 Hz, ^4J = 1.6 Hz, H4 or H4'), 7.72 (m, 3H, *m*-H Ar_F and H5 or H5'), 7.64 (dd, 1H, ^3J = 6.4 Hz, ^4J = 1.2 Hz, H5 or H5'), 0.86 (s, 3H, PdCH_3). IR (Nujol mull): ν(CO_2) 1626 s, 1563 m, 1352 s; ν(CF_3) 1321 vs cm^{-1}. Anal. Calcd. C, 48.89; H, 3.24; N, 6.00. Found: C, 48.97; H, 3.29; N, 5.89.

Pd(O_2CAr_F)Me(tmeda) (8). This complex was prepared from PdIMe(tmeda) (0.0392 g, 0.108 mmol) and Ag[O_2CAr_F] (0.0327 g, 0.110 mmol) using a similar procedure to that described for **5**. The product was obtained as a yellow solid. Yield: 0.0453 g (99 %). ^{1}H NMR (acetone-d_6): δ 8.13 (dd, 2H, ^3J = 8.6 Hz, ^4J = 0.86 Hz, *o*-H Ar_F), 7.67 (dd, 2H, ^3J = 8.7 Hz, ^4J = 0.68 Hz, *m*-H Ar_F), 2.85 (m, 2H, NCH_2), 2.72 (s, 6H, NCH_3), 2.67 (m, 2H, NCH_2), 2.52 (s, 6H, NCH_3), 0.32 (s, 3H, PdCH_3). IR (Nujol mull): ν(CO_2) 1621 s, 1574 m, 1360 s; ν(CF_3) 1320 vs cm^{-1}. Anal. Calcd. C, 42.21; H, 5.43; N, 6.56. Found: C, 42.09; H, 5.56; N, 6.45.

Pd(O_2CPh)Tol(bpy) (9). This complex was prepared from PdITol(bpy) (0.0178 g, 0.0440 mmol) and silver benzoate (0.0113 g, 0.0493 mmol) using a similar procedure to that described for **5**. The product was a yellow solid. Yield: 0.0209 g (100 %). Crystals suitable for X-ray diffraction were obtained from the slow diffusion of *n*-pentane into a CH_2Cl_2 solution of **9**. ^{1}H NMR (acetone-d_6): δ 8.58 (m, 2H, H3 and H3'), 8.45 (dd, 1H, ^3J = 5.2 Hz, ^4J = 0.8 Hz, H6'), 8.26 (m, 3H, H6, H4 and H4'), 8.02 (d, 2H, ^3J = 8.0 Hz [complex second order coupling also observed], *o*-H Ph), 7.70 (ddd, 1H, ^3J = 5.2 Hz, ^4J = 0.8 Hz, H5'), 7.59 (ddd, 1H, ^3J = 6.0 Hz, ^4J = 1.2 Hz, H5), 7.41 (d, 2H, ^3J = 8.0 Hz, *o*-H Tol) 7.40-7.28 (m, 3H, *m* and *p*-H Ph and *o*-H Tol), 6.79 (dd, 2H, ^3J = 8.0 Hz, ^4J = 0.6 Hz, *m*-H Tol), 2.20 (s, 3H, CH_3). IR (Nujol mull): ν(CO_2) 1598 s, 1571 m, 1347 vs cm^{-1}.

Pd(O_2CPh)Tol(tmeda) (10). This complex was prepared from PdITol(tmeda) (0.040 g, 0.091 mmol) and silver benzoate (0.021 g, 0.092 mmol) using a similar procedure to that described for **5**. The product was obtained as a yellow solid. Yield: 0.039 g (99 %). ^{1}H NMR (acetone-d_6): δ 7.86 (dd, 2H, ^3J = 8.4 Hz, ^4J = 1.6 Hz, *o*-H Ph), 7.34 (d, 2H, ^3J = 8.0 Hz, *o*-H Tol), 7.3-7.2 (m, 3H, *m*- and *p*-H Ph),

6.64 (dd, 2H, ^3J = 8.0 Hz, ^4J = 0.6 Hz, *m*-H Tol), 2.91 (m, 2H, NCH_2), 2.17 (m, 2H, NCH_2), 2.55 (s, 6H, NCH_3), 2.53 (s, 6H, NCH_3), 2.10 (s, 3H, CH_3). IR (Nujol mull): $\nu(CO_2)$ 1614 s, 1574 m, 1352 vs cm^{-1}. Anal. Calcd. C, 55.24; H, 6.49; N, 6.44. Found: C, 55.36; H, 6.29; N, 6.53.

Pd(O_2CAr_F)Tol(bpy) (11). This complex was prepared from PdITol(bpy) (0.0224 g, 0.0554 mmol) and Ag[O_2CAr_F] (0.0165 g, 0.0555 mmol) using a similar procedure to that described for **5**. The product was obtained as a yellow solid. Yield: 0.0286 g (100 %). ^{1}H NMR (acetone-d_6): δ 8.58 (d, 2H, ^3J = 8.0 Hz, H3 and H3'), 8.44 (d, 1H, ^3J = 4.8 Hz, H6'), 8.25 (m, 3H, H6, H4 and H4'), 8.18 (d, 2H, ^3J = 8.0 Hz, *o*-H Ar_F), 7.71 (m, 3H, H5' and *m*-H Ar_F), 7.58 (t, 1H, ^3J = 5.2 Hz, H5), 7.39 (d, 2H, ^3J = 8.0 Hz, *o*-H Tol), 6.80 (d, 2H, ^3J = 7.8 Hz, *m*-H Tol), 2.21 (s, 3H, CH_3). IR (Nujol mull): $\nu(CO_2)$ 1627 s, 1573 m, ~ 1360 m (overlaps with Nujol peak) cm^{-1}; $\nu(CF_3)$ 1320 vs cm^{-1}. Anal. Calcd. C, 55.31; H, 3.53; N, 5.16. Found: C, 55.03; H, 3.48; N, 5.01.

Preparation of Pd(O_2CAr_F)Tol(tmeda) (12). This complex was prepared from PdITol(tmeda) (0.021 g, 0.048 mmol) and Ag[O_2CAr_F] (0.021 g, 0.070 mmol) using a similar procedure to that described for **5**. The product was obtained as a yellow solid. Yield: 0.022 g (92 %). ^{1}H NMR (acetone-d_6): δ 8.01 (dd, 2H, ^3J = 8.2 Hz, ^4J = 0.8 Hz, *o*-H Ar_F), 7.57 (dd, 2H, ^3J = 8.2 Hz, ^4J = 0.8 Hz, *m*-H Ar_F), 7.32 (d, 2H, ^3J = 8.1 Hz, [complex ^4J coupling also observed], *o*-H Tol), 6.64 (d, 2H, ^3J = 7.6 Hz, [complex ^4J coupling also observed], *m*-H Tol), 2.95 (m, 2H, NCH_2), 2.74 (m, 2H, NCH_2), 2.58 (s, 6H, NCH_3), 2.56 (s, 6H, NCH_3), 2.12 (s, 3H, CH_3). IR (Nujol mull): $\nu(CO_2)$ 1613 s, 1572 m, ~ 1360 s (overlaps with Nujol peak); $\nu(CF_3)$ 1321 vs. Anal. Calcd. C, 50.16; H, 5.41; N, 5.57. Found: C, 50.30; H, 5.33; N, 5.56.

2.4.4 *In Situ* Synthesis of Pd(O_2CAr)$Me_2R(L_2)$

***fac*-Pd(O_2CPh)Me_3(bpy) (13).** Iodomethane (1 mL) was cooled to –35 °C. To this was added $PdMe_2$(bpy) (0.0086 g, 0.0294 mmol) and the solution stirred for 30 min. The volatile components were removed *in vacuo* at low temperature leaving a

pale yellow solid [PdIMe$_3$(bpy)]. The solid was redissolved in acetone-d_6 (0.6 mL) at –70 °C. To this was added silver benzoate (0.0068, 0.0297 mmol) and a reaction was observed immediately. The suspension was stirred for 30 min at –50 °C then quickly filtered through a plug of glass fiber filter paper into a precooled NMR tube. The product was identified by ^{1}H NMR at –50 °C. Only one isomer was observed and this was stable to approximately –30 °C in solution. Attempts to isolate the pure product were unsuccessful. ^{1}H NMR (acetone-d_6, -30 °C): δ 9.01 (d, 2H, ^3J = 4.0 Hz, H6), 8.59 (d, 2H, ^3J = 8.0 Hz, H3), 8.22 (td, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, H4), 7.79 (ddd, 2H, ^3J = 5.2 Hz, ^4J = 1.2 Hz, H5), 7.65 (d, 2H, ^3J = 6.4 Hz, *o*-H Ph), 7.18 (t, 1H, ^3J = 6.8 Hz, *p*-H Ph), 7.11 (t, 2H, ^3J = 7.2 Hz, *m*-H Ph), 1.72 (s, 6H, CH_3), 0.64 (s, 3H, CH_3).

***fac*-Pd(O$_2$CPh)Me$_3$(tmeda) (14).** This complex was prepared from PdMe$_2$(tmeda) (0.0038 g, 0.015 mmol) and silver benzoate (0.0050 g, 0.022 mmol) using a similar procedure to that described for **13**. The product was identified by ^{1}H NMR at –40 °C. Only one isomer was observed and this was stable to approximately –30 °C in solution. Attempts to isolate the pure product were unsuccessful. ^{1}H NMR (acetone-d_6, -40 °C): δ 7.99 (dd, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, *o*-H Ph), 7.35 (m, 3H, *m*- and *p*-H Ph), 3.0 (br, 2H, NCH_2), 2.7 (br, 2H, NCH_2), 2.49 (s, 6H, NCH_3), 2.36 (s, 6H, NCH_3), 1.53 (s, 6H, CH_3), 0.78 (s, 3H, CH_3).

***fac*-Pd(O$_2$CAr$_F$)Me$_3$(bpy) (15).** This complex was prepared from PdMe$_2$(bpy) (0.0072 g, 0.0246 mmol) and Ag[O$_2$CAr$_F$] (0.0095 g, 0.0320 mmol) using a similar procedure to that described for **13**. The product was identified by ^{1}H NMR at –30 °C. Only one isomer was observed and this was stable below approximately –30 °C in solution. Attempts to isolate the pure product were unsuccessful. ^{1}H NMR (acetone-d_6, -30 °C): δ 9.03 (dd, 2H, ^3J = 5.6 Hz, ^4J = 0.8 Hz, H6), 8.40 (d, 2H, ^3J = 8.0 Hz, H3), 8.26 (td, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, H4), 7.84-7.51 (m, 4H, H5 and *o*-H Ar$_F$), 7.50 (d, 2H, ^3J = 8.0 Hz, *m*-H Ar$_F$), 1.71 (s, 6H, CH_3), 0.69 (s, 3H, CH_3).

***fac*-Pd(O$_2$CAr$_F$)Me$_3$(tmeda) (16).** This complex was prepared from PdMe$_2$(tmeda) (0.0124 g, 0.0491 mmol) and Ag[O$_2$CAr$_F$] (0.0160 g, 0.0539 mmol)

using a similar procedure to that described for **13**. The product was identified by ^{1}H NMR at –40 °C. Only one isomer was observed and this was stable to approximately –30 °C in solution. Attempts to isolate the pure product were unsuccessful. ^{1}H NMR (acetone-d_6, -40 °C): δ 8.18 (d, 2H, ^3J = 8.4 Hz, *o*-H Ar_F), 7.72 (d, 2H, ^3J = 8.4 Hz, *m*-H Ar_F), 3.20-2.82 (br, 2H, NCH_2), 2.82-2.60(br, 2H, NCH_2), 2.50 (s, 6H, NCH_3), 2.37 (s, 6H, NCH_3), 1.53 (s, 6H, CH_3), 0.82 (s, 3H, CH_3).

Pd(O_2CPh)Me_2Tol(bpy) (17). This complex was prepared from PdMeTol(bpy) (0.006 g, 0.016 mmol) and Ag[O_2CPh] (0.004 g, 0.017 mmol) using a similar procedure to that described for **13**. The product was identified by ^{1}H NMR at –30 °C. Two isomers were observed and these were stable to approximately –30 °C. ^{1}H NMR (acetone-d_6, -30 °C): **17a**: δ 9.36 (dd, 2H, ^3J = 4.8 Hz, ^4J = 0.8 Hz, H6), 8.42 (d, 2H, ^3J = 8.4 Hz, H3), 8.15 (td, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, H4), 7.84 (ddd, 2H, ^3J = 5.2 Hz, ^4J = 0.8 Hz, H5), 7.68 (m [overlaps with other isomer], *o*-H Ph), 7.19 (m [overlaps with other isomer], *p*-H Ph), 7.14 (m [overlaps with other isomer], *m*-H Ph), 6.87 (d, 2H, ^3J = 8.0 Hz, *o*-H Tol), 6.61 (d, 2H, ^3J = 7.6 Hz, *m*-H Tol), 2.09 (s, 6H, CH_3), 2.08 (s, 3H, CH_3 Tol). **17b**: δ 9.08 (d, 1H, ^3J = 5.6 Hz, H6), 8.60 (m, 2H, H3 and H3'), 8.52 (dd, 1H, ^3J = 5.2 Hz, ^4J = 1.2 Hz, H6'), 8.20 (m, 2H, H4 and H4'), 7.79 (ddd, 1H, ^3J = 5.6 Hz, ^4J = 1.2 Hz, H5), 7.68 (m [overlaps with other isomer], *o*-H Ph, H5'), 7.19 (m [overlaps with other isomer], *p*-H Ph), 7.14 (m [overlaps with other isomer], *m*-H Ph), 7.03 (d (br), 2H, ^3J = 8.0, *m*-H Tol), 2.29 (s, 3H, CH_3 Tol), 2.00 (s, 3H, C$H_{3(eq)}$), 1.14 (s, 3H, C$H_{3(ax)}$).

Pd(O_2CAr_F)Me_2Tol(bpy) (18). This complex was prepared from PdMeTol(bpy) (0.0040 g, 0.0108 mmol) and Ag[O_2CAr_F] (0.0048 g, 0.0162 mmol) using a similar procedure to that described for **13**. The product was identified by ^{1}H NMR at –30 °C. Two isomers were observed and these were stable to approximately –30 °C. ^{1}H NMR (acetone-d_6, -30 °C): **18a**: δ 9.34 (d, 2H, ^3J = 5.2 Hz, H6), 8.49 (d, 2H, ^3J = 8.4 Hz, H3), 8.20 (td, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, H4), 7.86 (ddd, 2H, ^3J = 5.2 Hz, ^4J = 0.8 Hz, H5) 7.83 (m [overlaps with other isomer], *o*-H Ar_F), 7.50 (d [overlaps with other isomer], ^3J = 8.0 Hz, *m*-H Ar_F), 6.88 (d, 2H, ^3J = 8.0 Hz, *o*-H Tol), 6.63 (d, 2H, ^3J = 8.0 Hz, *m*-H Tol), 2.11 (s, 6H, CH_3), 2.08 (s, 3H, CH_3 Tol). **18b**: δ 9.08

(dd, 1H, ^3J = 5.2 Hz, ^4J = 0.8 Hz, H6), 8.64 (d, 2H, ^3J = 8.0 Hz, H3 and H3'), 8.52 (dd, 1H, ^3J = 5.2 Hz, ^3J = 0.8 Hz, H6'), 8.24 (m, 2H, H4 and H4'), 7.83 (m [overlaps with other isomer], *o*-H Ar_F, H5), 7.71 (ddd, 1H, ^3J = 5.6 Hz, ^4J = 1.2 Hz, H5'), 7.50 (d [overlaps with other isomer], ^3J = 8.0 Hz, *m*-H Ar_F), 7.04 (d (br), 2H, ^3J = 7.6 Hz, *m*-H Tol),2.29 (s, 3H, CH_3 Tol), 2.02 (s, 3H, $CH_{3(eq)}$), 1.20 (s, 3H, $CH_{3(ax)}$).

2.4.5 *In Situ* Synthesis of $PdI_2MeR(bpy)$

$PdI_2Me_2(bpy)$ (19). A solution of iodine (0.0054 g, 0.021 mmol) in acetone-d_6 (0.4 mL) was cooled to –50 °C. To this was added a solution of $PdMe_2(bpy)$ (0.0061 g, 0.021 mmol) in acetone-d_6 (0.3 mL) and the mixture stirred for one hour at –70 °C. ^{1}H NMR (acetone-d_6, -40 °C): δ 9.01 (d, 2H, ^3J = 5.6 Hz, H6), 8.77 (d, 2H, ^3J = 8.4 Hz, H3), 8.32 (t, 2H, ^3J = 7.6 Hz, H4), 7.86 (t, 2H, ^3J = 6.8 Hz, H5), 2.75 (s, 6H, CH_3).

$PdI_2MeTol(bpy)$ (20). This complex was prepared from iodine (0.0083 g, 0.033 mmol) and PdMeTol(bpy) (0.0121 g, 0.033 mmol) in the same manner as described for complex **19**. ^{1}H NMR (acetone-d_6, -50 °C): δ 9.12 (d, 1H, ^3J = 4.8 Hz, H6 or H6'), 8.94 (d, 1H, ^3J = 4.4 Hz, H6 or H6'), 8.85 (m, 2H, H3 and H3'), 8.35 (m, 2H, H4 and H4'), 7.99 (d, 2H, ^3J = 8.4 Hz, *o*-H Tol), 7.88 (m, 2H, H5 and H5'), 6.90 (d, 2H, ^3J = 8.4 Hz, *m*-H Tol), 3.19 (s, 3H, CH_3 Tol), 2.30 (s, 3H, CH_3).

2.4.6 ^{1}H NMR Studies of the Reaction of Palladium(II) Complexes with $(ArCO_2)_2$

$PdMeR(L_2)$ (R = Me, Tol; L = bpy, tmeda) with $(ArCO_2)_2$. In a typical experiment, a solution of $PdMeR(L_2)$ in acetone-d_6 or CD_2Cl_2 (0.5 mL) in a NMR tube was cooled to ≤ –50 °C. To this was added a solution of $(ArCO_2)_2$ in acetone-d_6 or CD_2Cl_2 (0.3 mL) in the ratios outlined in Section 2.2. The tube was placed in a NMR probe, precooled to ≤ –50 °C and the solution warmed in 10 °C intervals with monitoring. Products of the reaction were identified by GC-MS and ^{1}H NMR.

$Pd(O_2CAr)R(L_2)$ (R = Me, Tol; L = bpy, tmeda) with $(ArCO_2)_2$. In a typical experiment, a solution of $(ArCO_2)_2$ in acetone-d_6 or CD_2Cl_2 (0.3 mL) was added to a solution of $Pd(O_2CAr)R(L_2)$ in acetone-d_6 or CD_2Cl_2 (0.5 mL) and the reaction allowed to go to completion at ambient temperature (several hours for R = Me and several days for R = Tol). Products of the reaction were identified by GC-MS and ^1H NMR.

2.4.7 X-Ray Data Collection, Structure Determination and Refinement

Structures were solved by Prof Allan H. White and Dr Brian W. Skelton, Chemistry, University of Western Australia. Crystal data and details of the structure determination are presented in Table 2.8. Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans; monochromatic Mo $K\alpha$ radiation, $\lambda = 0.7107_3$ Å; T *ca.* 153 K) yielding $N_{t(otal)}$ reflections, these merging to N unique (R_{int} cited) after 'empirical'/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinements. Anisotropic displacement parameter forms were refined, $(x, y, z, U_{iso})_H$ also. Conventional residuals R, R_w [weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$] on $|F|$ are quoted at convergence. Neutral atom complex scattering factors were employed within the context of the Xtal 3.7 program system.[65]

Table 2.8: Specific crystallographic details for $Pd(O_2CPh)_2(bpy)$ (**1**), $Pd(O_2CPh)_2(tmeda)$ (**2**), $Pd(O_2CAr_F)_2(tmeda)$ (**4**), and $Pd(O_2CPh)Tol(bpy).CH_2Cl_2$ (**9**.CH_2Cl_2).

	1	**2**	**4**	**9**.CH_2Cl_2
formula	$C_{24}H_{18}N_2O_4Pd$	$C_{20}H_{26}N_2O_4Pd$	$C_{22}H_{24}F_6N_2O_4Pd$	$C_{25}H_{22}Cl_2N_2O_4Pd$
fw	504.8	464.9	600.9	559.8
cryst size, mm^3	0.12 x 0.10 x 0.08	0.35 x 0.25 x 0.11	0.42 x 0.25 x 0.06	0.15 x .014 x 0.04
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$C2/c$	$P2_1/n$
a, Å	8.6470(10)	11.7882(8)	23.833(3)	11.8066(5)
b, Å	13.428(2)	14.5363(9)	8.875(1)	16.0809(7)
c, Å	17.477(2)	11.8319(8)	12.068(2)	12.7215(6)
β, deg	96.975(3)	98.072(2)	111.296(3)	104.721(1)
V, $Å^3$	2014	2007	2378	2336
Z	4	4	4	4
ρ_{calcd}, $g.cm^{-3}$	1.66_5	1.53_8	1.67_8	1.58_7
μ_{Mo}, mm^{-1}	0.96	0.95	0.86	1.05
$2\theta_{max}$, deg	60	75	75	65
$T_{min/max}$	0.84	0.87	0.68	0.88
N_t	25727	41400	24162	48574
N	5355	10524	6259	8419
N_0	3985	7757	5759	6404
R_{int}	0.050	0.029	0.031	0.046
R	0.051	0.032	0.026	0.046
R_w	0.060	0.037	0.036	0.052

2.4.7.1 Variations

$Pd(O_2CPh)_2(bpy)$ (1). $(x, y, z, U_{iso})_H$ were constrained at estimates in the refinement.

$Pd(O_2CPh)_2(tmeda)$ (2). Disorder was modeled in the hydrocarbon bridge of the chelate in terms of pairs of methylene sites, occupancies 0.770(5) and complement. $(x, y, z, U_{iso})_H$ were constrained throughout the refinement at estimates.

$Pd(O_2CPh)Tol(bpy).CH_2Cl_2$ (9.CH_2Cl_2). The dichloromethane solvent molecule was modeled in terms of two components with common carbon, occupancies refining

to 0.778(2) and complement. $(x, y, z, U_{iso})_H$ (solvent molecule only) were not refined.

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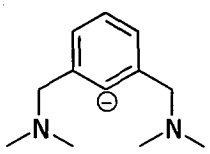
CHAPTER THREE:

Applications of Intramolecular Coordination in Exploring the Mechanism of Carbon-Oxygen Coupling Mediated by Palladium and Platinum Complexes

3.1 Introduction

In investigations where palladium intermediates have proven to be unstable, it is often productive to explore systems that can be used as models for unstable intermediates or that may enhance the possibility for stabilisation. One way in which this can be achieved is through the use of intramolecularly coordinating ligands. This chapter explores the use of a terdentate, NCN-coordinated 'pincer' ligand, $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (Figure 3.1), as a potential means of increasing stability of some palladium systems through intramolecular coordination. The terdentate mode of this ligand leads to the formation of two particularly stable five-membered rings with the metal centre. Furthermore, intramolecular coordination restricts dissociation of ligands, which is often the precursor to decomposition. This is particularly true for complexes with octahedral geometry, which is common for palladium(IV) and platinum(IV) complexes. Platinum systems are also investigated as a more stable model for reactivity similar to that expected for palladium.

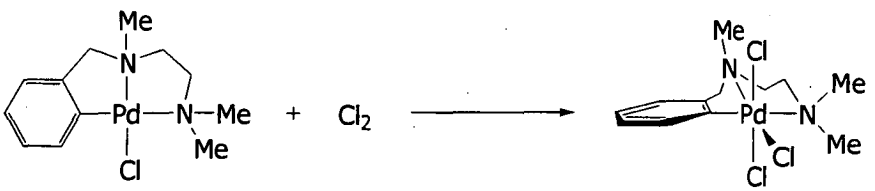
Figure 3.1: The NCN pincer group, $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$.



"NCN"

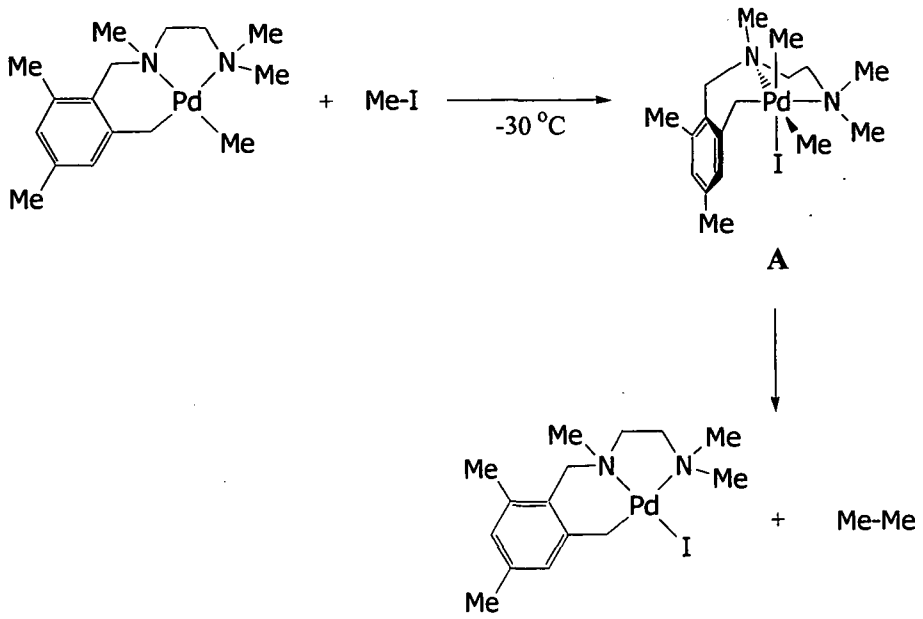
The use of intramolecular coordination as a means of stabilising otherwise unstable intermediates has led to the identification and isolation of a number of unusual complexes.[1-24] One example of this is the use of terdentate, C,N,N'-bound ligands in stabilising palladium(IV) complexes.[22] The reaction of PdCl(CNN') {CNN' = $[C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)\text{-}2]^-$} with Cl_2 led to the identification of a palladium(IV) species, *mer*-$PdCl_3$(CNN'), (Scheme 3.1). The unusually high stability of this complex allowed it to be identified by NMR at room temperature before decomposing slowly over several hours. This stability has been attributed, at least in part, to the strongly electron-donating terdentate ligand.[22]

Scheme 3.1: Reaction of PdCl(CNN') with Cl_2.



A related ligand system, $[C_6H_2(CH_2)(CH_2N(Me)CH_2CH_2NMe_2)Me_2\text{-}1,2,3,5]^-$ (C^*NN'), was used in the investigation of the reaction of PdMe(C^*NN') with iodomethane (Scheme 3.2).[22] No palladium(IV) species were detected at room temperature, but NMR studies at –30 °C detected an intermediate whose structure was thought to be that shown as complex **A**. This structure shows a number of similarities with $PdBrMe_2(CH_2Ph)$(tmeda).[25] Complex **A** decomposes cleanly to give ethane and PdI(C^*NN').

Scheme 3.2: Reaction of PdMe(C^NN') with iodomethane in acetone-d_6.



The NCN ligand shown in Figure 3.1 has been used to particularly good effect by van Koten and coworkers in 'trapping' reaction intermediates.[10-20,26] The arenium class of complexes provides a good example of this.[10-16] It was found that when iodomethane was reacted with $[Pt(OH_2)(NCN)][BF_4]$, the expected five-coordinate oxidative addition product was not observed. Rather, the methyl group had become bonded to the carbon atom of the aryl ring that was originally bonded to the platinum centre (Scheme 3.3).[10,11] This structure is thought to be the result of a 1,2-methyl shift from the platinum to the metal bonded aryl carbon, and is considered to represent a frozen intermediate in the reductive elimination of a carbon-carbon bond. Subsequent extension to include the reactions of other cationic and neutral Pt^{II}(NCN) complexes with different oxidants (organic halides, methyl triflate, trimethylsilyl chloride and trimethylsilyl triflate) led to the identification and isolation of a variety of arenium complexes (Figure 3.2).[10-16,23]

Scheme 3.3: Formation of an arenium complex, $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}2,6)]^+$, from the reaction of $Pt(OH_2)(C_6H_3(CH_2NMe_2)_2\text{-}2,6)]^+$ and MeI.[10,11]

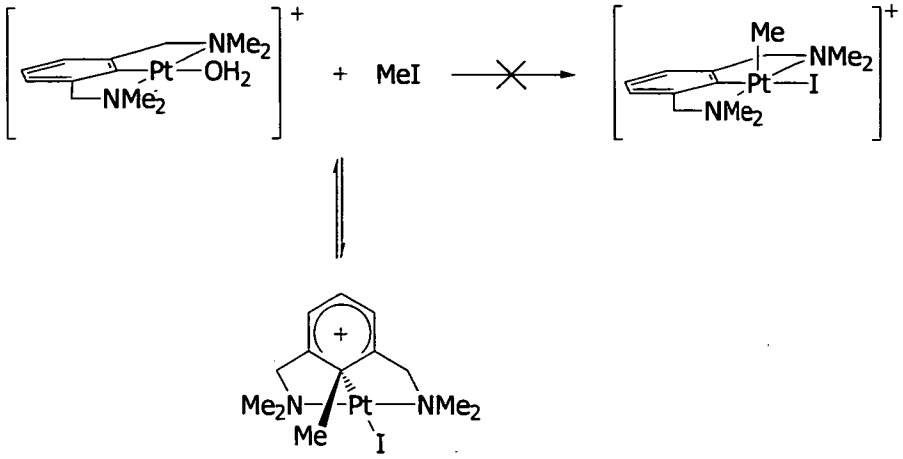
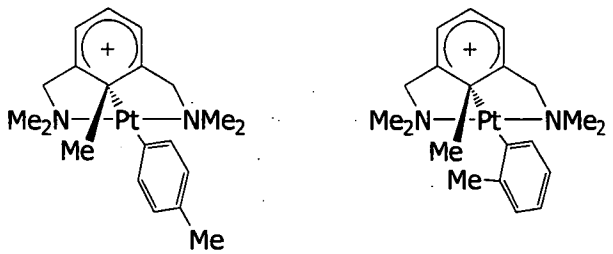
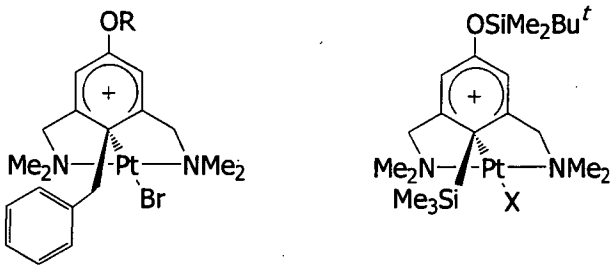


Figure 3.2: Some examples of identified arenium species.[12,15]





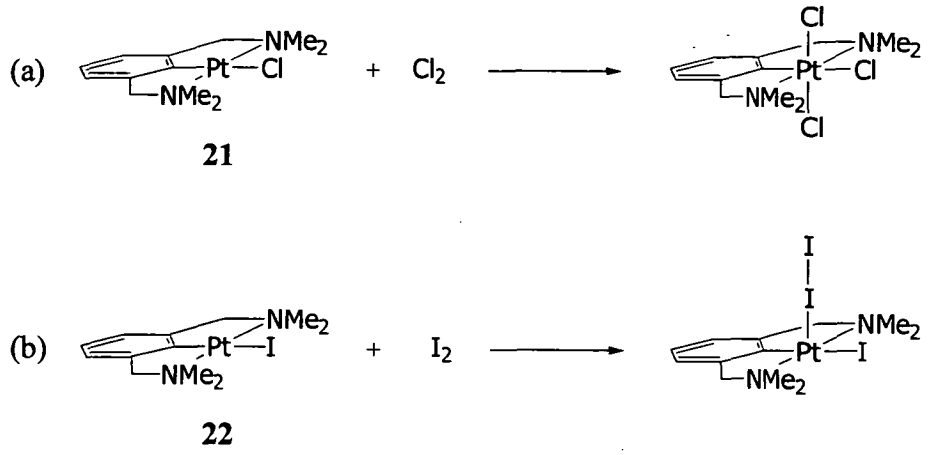
R = H, Me

X = I, Cl

The stabilising ability of the NCN ligand has also led to the isolation of complexes that model the initial stages of oxidative addition.[17-20] When PtCl(NCN) was allowed to react with Cl_2, the oxidative addition product $PtCl_3(NCN)$ was obtained (Scheme 3.4a).[27] However, when the analogous reaction of PtI(NCN) with I_2 was carried out, the product was not the expected octahedral $PtI_3(NCN)$ but rather

a square pyramidal complex incorporating a η^1-bonded neutral iodine molecule in a near linear arrangement, as seen in Scheme 3.4b.[17]

Scheme 3.4: Reaction of (a) PtCl(NCN) with Cl_2[27] and (b) PtI(NCN) with I_2.[17]



In light of the successes in obtaining stable metal(IV) complexes using pincer ligands as outlined above, the reactions of dibenzoyl peroxide, $(PhCO_2)_2$, and iodomethane with $Pd(O_2CPh)(NCN)$ were investigated. This study was subsequently extended to include reactions with PtX(NCN) [X = O_2CPh, 4-tolyl (Tol)] in order to search for stable M(IV) complexes that could act as models for various intermediates in the acetoxylation of arenes (Scheme 2.1), and in the reactions of $PdMeR(L_2)$ (R = Me, Tol; L_2 = tmeda, bpy) with $(ArCO_2)_2$ (Ar = Ph, Ar_F) discussed in Chapter Two.

3.2 Results and Discussion

3.2.1 Reaction of M(O_2CPh)(NCN) (M = Pd, Pt) and PtTol(NCN) with ($PhCO_2$)$_2$

3.2.1.1 Reaction of M(O_2CPh)(NCN) with ($PhCO_2$)$_2$

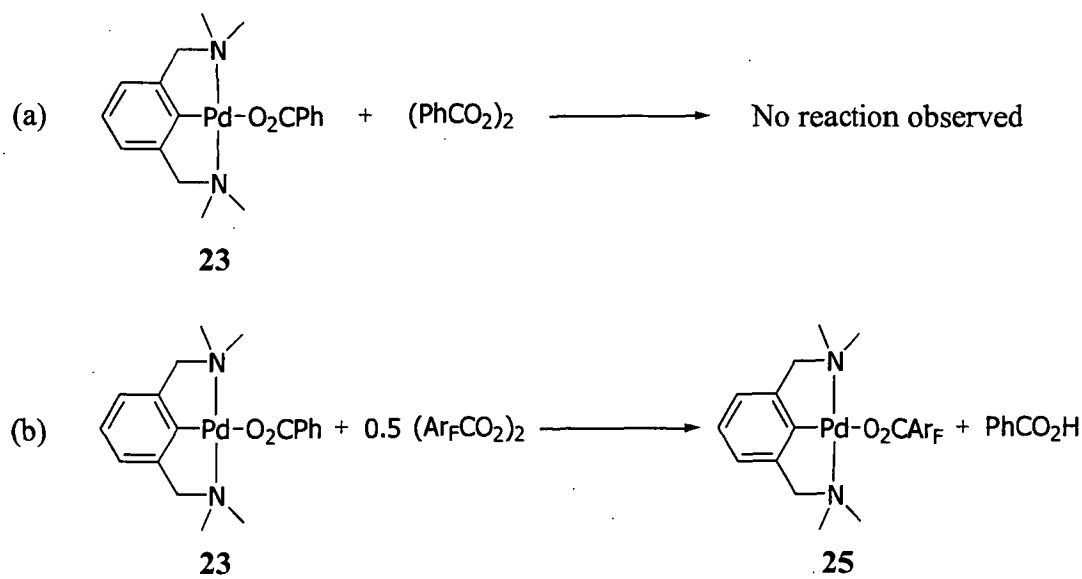
The complexes M(O_2CPh)(NCN) [M = Pd (**23**), Pt (**24**)] were chosen for initial studies in order that anticipated reactions with ($PhCO_2$)$_2$ would approximate the simple carboxylate donor set proposed for the acetoxylation of arenes, *i.e.* '$M^{IV}(O_2CPh)_3(NCN)$' compared with '$M^{IV}(O_2CMe)_3(C)$' (Scheme 2.1, Chapter Two).[28,29] It was also hoped that these reactions would provide an insight into the mechanism involved in carbon-oxygen bond formation from the reactions of monoorganopalladium(II) benzoates with diaroyl peroxides (Section 2.2). Details of the synthesis and characterisation of **23** and **24** are given in Section 3.2.3.1.

When the palladium complex Pd(O_2CPh)(NCN) (**23**) was allowed to react with ($PhCO_2$)$_2$ at ambient temperature over several days in acetone-d_6, no reaction was observed and no palladium(IV) species were detected by ^{1}H NMR (Scheme 3.5a). A gradual decomposition of dibenzoyl peroxide was noted along with the concurrent formation of benzoic acid. The decomposition of dibenzoyl peroxide is complex, but benzoic acid is commonly observed as a decomposition product.[30-34] It is thought to take place *via* an initial unimolecular fission to give free benzoate radicals followed by a chain reaction that can include reaction with the solvent. Decarboxylation of the benzoate radical is slow (half life of about one hour at 90 °C), which allows formation of products derived from the benzoate radical.[34] The absence of aroyl peroxide decomposition in the reactions described in Chapter Two may be due to the faster rates (and, hence, shorter reaction times) of these reactions.

When **23** was mixed with (Ar_FCO_2)$_2$, a reaction occurred to give Pd(O_2CAr_F)(NCN) (**25**) and $PhCO_2H$. Although still quite slow, the reaction was significantly faster than that described above. Significant reaction was seen after one

hour at room temperature and the reaction went to completion within two hours at 60 °C. This may indicate that the complex **23** is reacting with $(Ar_FCO_2)_2$ and not with the decomposition product Ar_FCO_2H. Full consumption of reagents was observed when the reaction was carried out in a 2:1 ratio of complex to peroxide, and products were formed in approximately equal amounts. No palladium(IV) intermediates or products of carbon-oxygen coupling were observed (Scheme 3.5b). Identification of the product **25** was carried out by its independent synthesis from PdCl(NCN) and silver(I) 4-(trifluoromethyl)benzoate, as described in Section 3.2.3.1. Complexes **23** and **25** were found to have nearly identical ^{1}H NMR spectra in the aliphatic and higher field aromatic regions. Therefore, the reaction was monitored by the disappearance of the $(Ar_FCO_2)_2$ and $Pd(O_2CPh)$ resonances and appearance of $PhCO_2H$ and $Pd(O_2CAr_F)$ resonances in the downfield aromatic region. The formation of benzoic acid may arise from the involvement of radical intermediates as described above. However, other mechanisms, such as the involvement of water, cannot be excluded.

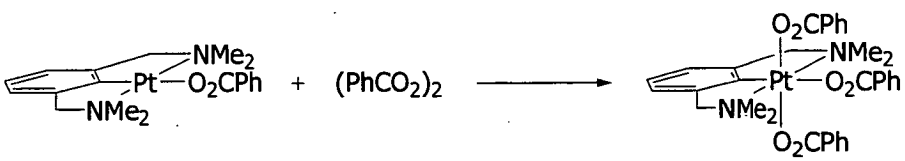
Scheme 3.5: Reaction of $Pd(O_2CPh)(NCN)$ (**23**) with (a) $(PhCO_2)_2$ and (b) $(Ar_FCO_2)_2$ in acetone-d_6.



When a similar reaction was carried out with the platinum analogue (**24**) and $(PhCO_2)_2$, a slow reaction occurred at room temperature. The emerging product showed signs of symmetry with one singlet appearing for the NCH_2 and one for the

NMe protons. Resonances due to ligand CH_2 protons were moved downfield by 0.3 ppm compared with **24**, and $^3J_{Pt\text{-}H}$ coupling was reduced from 46 to 28 Hz. The NMe signal did not shift significantly (upfield by 0.02 ppm) but $^3J_{Pt\text{-}H}$ coupling decreased markedly from 36 to 25 Hz. Two sets of benzoate resonances appeared in the aromatic region, one with integrals double that of the other. This indicated the presence of three benzoate groups, two of which shared equivalent chemical environments. All of these changes were consistent with the formation of *mer*-$Pt^{IV}(O_2CPh)_3(NCN)$ (**27**) (Scheme 3.6). No further reaction of this complex was observed. Yellow crystals precipitated from the reaction after several days and their identity was confirmed as **27** by X-ray crystallography. For details of the preparative study and characterisation of **27**, see Section 3.2.3.2.

Scheme 3.6: Reaction of $Pt(O_2CPh)(NCN)$ (**24**) with $(PhCO_2)_2$.



24 **27**

This reaction provides confirmation that oxidative addition can occur at a d^8 monoorganometal(II) centre, '$MOCN_2$', as is postulated in the reaction of $Pd(O_2CAr)R(L_2)$ with $(ArCO_2)_2$ (Section 2.2.4). It also acts as a model for the oxidative addition to '$Pd^{II}(O_2CMe)Ar$' in the acetoxylation of arenes (Scheme 2.1).[28,29] Consequently, complex **27** can be considered a model for the proposed '$Pd^{IV}(O_2CMe)_3Ar$' intermediate in the acetoxylation of arenes, which is thought to undergo reductive elimination *via* carbon-oxygen bond formation (Scheme 2.1).[28,29] In contrast, **27** is a stable complex and no reductive elimination has been observed. This is likely to be due, at least in part, to the stability of the ligand aryl group imparted by intramolecular coordination, and the presumed difficulties in achieving carbon-oxygen coupling while the NCN group remains chelated.

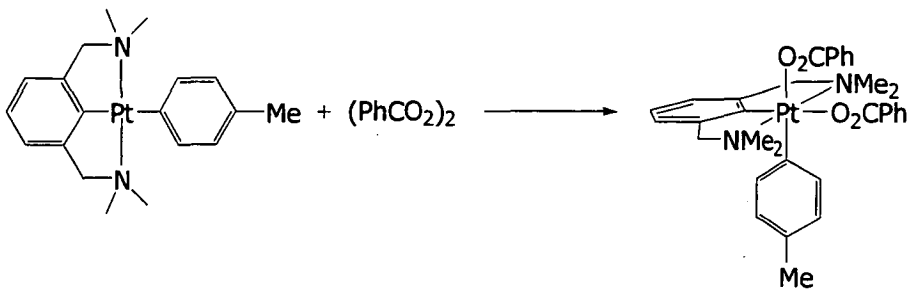
In an attempt to determine whether oxidative addition was taking place *via cis*- or *trans*-addition, complex **24** was allowed to react with $(Ar_FCO_2)_2$ in a ^1H NMR study.

Although complicated, the spectrum did reveal that the species formed were probably platinum(IV) species. This was indicated by the characteristic downfield shift observed for resonances in the aromatic regions along with the CH_2 resonance. Furthermore, no platinum(II) species, **24** or $Pt(O_2CAr_F)(NCN)$ (**26**) could be identified. The high complexity of the spectrum indicated a scrambling of the aroate groups. Therefore, it was not possible to determine whether initial addition had been *cis*- or *trans*-oriented.

3.2.1.2 Reaction of PtTol(NCN) with $(PhCO_2)_2$

Previous unsuccessful attempts at the isolation or identification of PdTol(NCN)[35] meant that the investigation of the reaction of MTol(NCN) with dibenzoyl peroxide was restricted to the platinum(II) analogue, PtTol(NCN) (**30**). The reaction occurred slowly to give a major product that, unlike **27** above, had two resonances for the CH_2 and NMe protons of the ligand. Furthermore, ^2J coupling was observed for CH_2 indicating the inequivalence of these protons and suggesting that the groups positioned above and below the plane of the ligand were not the same. This was supported by the presence of resonances in the aromatic region arising from two inequivalent benzoate groups and a 4-tolyl group. Each of the aromatic protons of the 4-tolyl moiety gave rise to separate resonances, two of which had $^3J_{Pt\text{-}H}$ coupling. As seen for **27** above, $^3J_{Pt\text{-}H}$ coupling decreased for CH_2 and NMe. These factors suggested the formation of the *cis*-oxidative addition product, *cis*-$Pt(O_2CPh)_2Tol(NCN)$ (**28**) (Scheme 3.7).

Scheme 3.7: Reaction of PtTol(NCN) with $(PhCO_2)_2$.



30 **28**

The formation of **28** was generally accompanied by the appearance of other species identified by GC-MS and ^{1}H NMR as Pt(O_2CPh)(NCN) (**24**), toluene and benzoic acid. If left in solution for extended periods the amount of these products increased and eventually (greater than one week), they were the sole species present. While the mechanism responsible for the production of these products is unclear, the involvement of benzoate radicals is a distinct possibility. As discussed in Section 3.2.1.1, the decomposition of dibenzoyl peroxide proceeds *via* the formation of benzoate radicals which can undergo reaction with other species or solvent. An alternative explanation could be that water, even in trace amounts, is involved in the decomposition of **28**. However, the mechanism by which this would occur is not clear.

The difficulty in obtaining **28** in a pure form from the reaction described above, meant that an independent synthesis was sought in order to confirm the identity of the complex. Isolation of a complex with identical spectroscopic properties as **28** was successful from the metathesis reaction between *cis*-PtI_2Tol(NCN) and Ag[O_2CPh] (Section 3.2.3.2). Crystals suitable for structural studies were also obtained (Section 3.2.3.2).

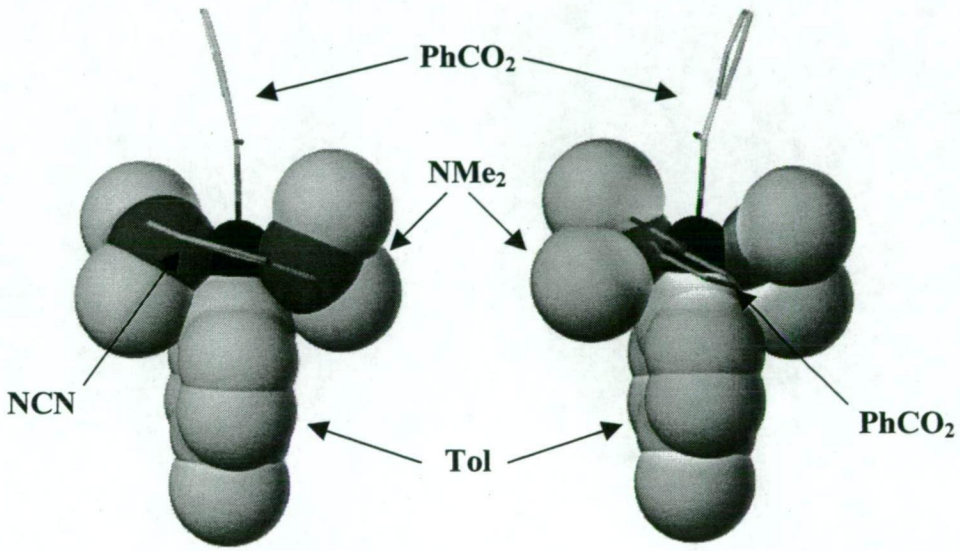
3.2.1.3 Stability of Pt(O_2CPh)$_2$Tol(NCN)

To better study the stability of **28** and to observe its decomposition in the absence of dibenzoyl peroxide, the complex was prepared *via* an independent synthesis (described in Section 3.2.3.2). Samples were subjected to different conditions and their behaviour monitored by ^{1}H NMR spectroscopy. Complex **28** was stable after several hours at 50 °C in dry acetone-d_6. Its stability was then tested at higher temperatures by heating in dry toluene-d_8 to 90 °C. No signs of decomposition were observed, even after eight hours at this temperature.

The high stability exhibited by this complex suggests that C(sp^2)-O bond formation may be elusive for platinum(IV) species. However, it is also possible that the lack of decomposition of **28** is attributed to the arrangement of ligands around the

metal. Examination of a partial space-filling diagram of the complex reveals that the orientation of the two coordinated NMe_2 groups restricts the rotation of the 4-tolyl group (Figure 3.3). This may prevent the 4-tolyl moiety from moving into an orientation that is favourable for intramolecular carbon-oxygen coupling, or may hinder the approach of a dissociated benzoate anion, thus blocking these decomposition pathways.

Figure 3.3: Partial space-filling diagrams of $Pt(O_2CPh)_2Tol(NCN)$ (**28**) showing the restriction of the 4-tolyl moiety. Platinum, 4-tolyl and NMe_2 groups are shown as space-filling spheres, while the rest of the molecule is shown as wireframe. Hydrogen atoms are omitted for clarity.



Decomposition of **28** was observed eventually (after several days in solution). The resulting ^1H NMR spectrum revealed a complex mixture of products, which appear to include toluene, benzoic acid and $Pt(O_2CPh)(NCN)$. As no dibenzoyl peroxide was present in this solution, it is unlikely that a radical mechanism is involved in this decomposition. The involvement of trace amounts of water in the decomposition is considered a possibility.

3.2.2 Reaction of M(O_2CPh)(NCN) (M = Pt, Pd) with Organic Halides

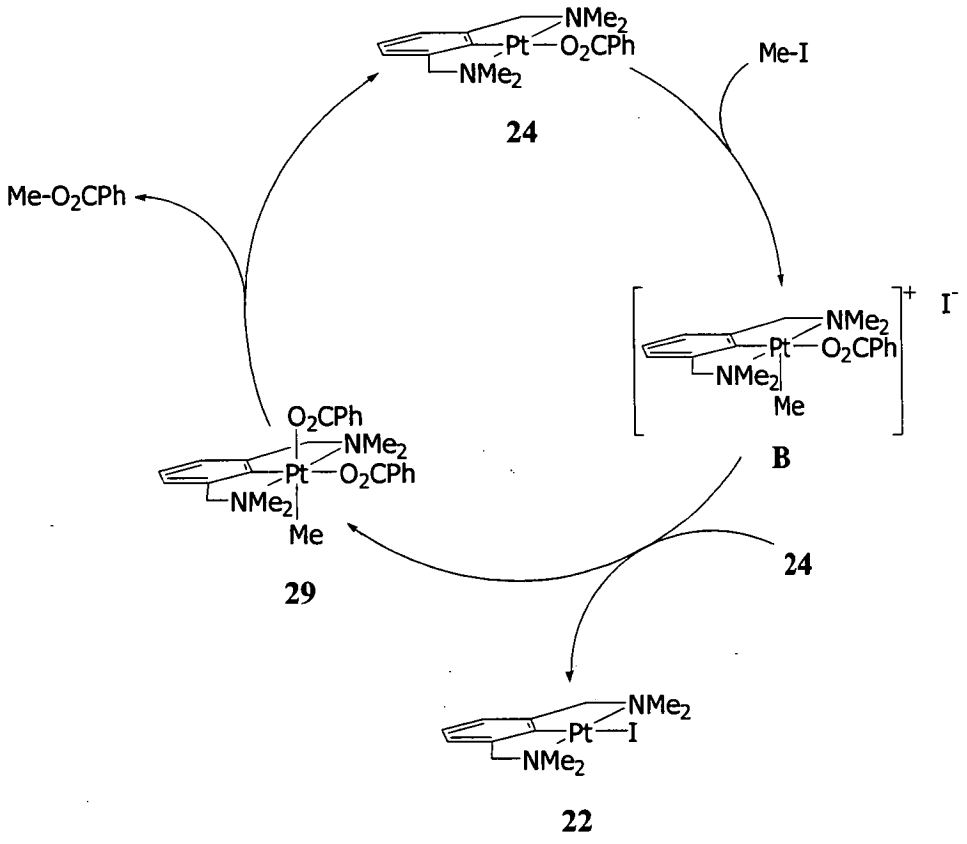
3.2.2.1 Reaction of M(O_2CPh)(NCN) with Iodomethane

Metal(II) reagents analogous to PtTol(NCN) (**30**) but containing a M-alkyl group are not known. Therefore, in an attempt to investigate reactions involving complexes incorporating an unrestrained M-aryl bond, an alternative synthetic strategy involving the oxidative addition of organic halides to M(O_2CPh)(NCN) was explored. The reaction of **30** was not investigated as its reaction with iodomethane has already been shown to give the arenium species [PtTol($MeC_6H_3(CH_2NMe_2)_2$-2,6]I (Figure 3.2).[12]

Iodomethane was added to Pt(O_2CPh)(NCN) (**24**) in order to attempt the synthesis of a Pt^{IV}Me analogue of Pt(O_2CPh)$_2$Tol(NCN) (**28**) and examine its decomposition. This reaction was compared with that of the palladium substrate, Pd(O_2CPh)(NCN) (**23**). The reaction of **24** with an excess of iodomethane proceeded slowly and cleanly at room temperature to give PtI(NCN) and Me-O_2CPh in a 1:1 ratio, along with unreacted iodomethane. Inspection of this reaction using ^{1}H NMR revealed the involvement of an intermediate whose appearance coincided with that of PtI(NCN). At room temperature, the intermediate was only visible at low levels but when the reaction was carried out at 0 °C, it was present in a larger amount. Its spectrum showed a number of similarities to that of Pt(O_2CPh)$_2$Tol(NCN) (**28**) (Section 3.2.1.2). The CH_2 and NMe protons each displayed two resonances and the CH_2 resonance displayed ^2J coupling indicating that groups above and below the plane of the ligand were not equivalent. Two sets of benzoate signals were present in the aromatic region and a singlet due to a Pt^{IV}Me group appeared at 1.66 ppm. Somewhat surprisingly, this suggested that the intermediate was not the product of the oxidative addition of iodomethane, Pt(O_2CPh)IMe(NCN), but rather *cis*-Pt(O_2CPh)$_2$Me(NCN) (**29**) (for full details of characterisation see Section 3.2.3.2).

It is proposed that the intermediate *cis*-Pt(O_2CPh)$_2$Me(NCN) (**29**) undergoes reductive elimination to form Me-O_2CPh and reform Pt(O_2CPh)(NCN) (**24**), which can then react again with the remaining iodomethane. A cyclic process continues until all of the platinum is in the form PtI(NCN) (Scheme 3.8), suggesting the reaction of **24** with iodomethane occurs in a 2:1 ratio. When the reaction was carried out with a 2:1 ratio of **24**:MeI, the expected products, PtI(NCN), Me-O_2CPh and **24** (reformed during the reaction), were formed slowly in 1:1:1 ratio, with full consumption of MeI (eq 3.1). There was no evidence for the involvement of arenium species in these reactions.

Scheme 3.8: Reaction of Pt(O_2CPh)(NCN) with iodomethane.

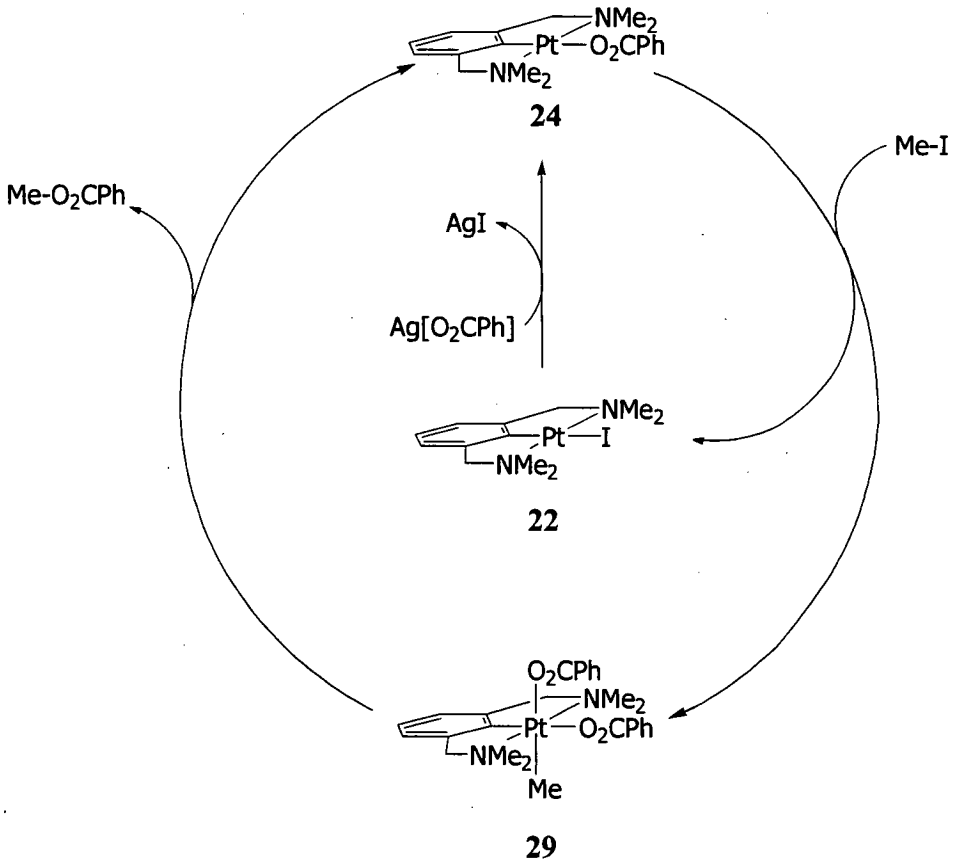


$$2\ \underset{\mathbf{24}}{Pt(O_2CPh)(NCN)} + MeI \rightarrow \underset{\mathbf{22}}{PtI(NCN)} + Me\text{-}O_2CPh + \underset{\mathbf{24}}{Pt(O_2CPh)(NCN)} \quad (3.1)$$

The knowledge that **24** can be formed by reaction of PtI(NCN) with Ag[O_2CPh] (Section 3.2.3.1) suggested that Scheme 3.8 could have potential as a catalytic cycle

by ensuring that all the platinum(II) in the system was available for further reaction with iodomethane (Scheme 3.9). This potential was explored. Theoretically, the cycle would only be limited by the amount of iodomethane and silver(I) salt added. When the reaction was carried out with **24** in the presence of ten equivalents each of iodomethane and Ag[O_2CPh], Me-O_2CPh was clearly the dominating product with a small amount of **29** visible as the sole platinum species. However, an experiment run in parallel in the absence of the platinum complex also yielded Me-O_2CPh in a comparable amount. Therefore, no further investigation was carried out into the catalytic potential of this reaction.

Scheme 3.9: Potential catalytic cycle involving the reaction of Pt(O_2CPh)(NCN) (**24**) with iodomethane and silver benzoate.



The mechanism by which **29** forms is not obvious. It has been established that a wide range of organoplatinum(II) complexes undergo oxidative addition of iodomethane *via* an S_N2-type mechanism. For some systems, NMR spectroscopy

indicates the presence of cationic platinum(IV) intermediates such as *fac*-$[Pt^{IV}Me_3(bpy)(solvent)]^+$ and, consequently, iodide ion prior to the formation of *fac*-$Pt^{IV}IMe_3(bpy)$.[36] These observations, along with the finding that **24** reacts with sodium iodide to form PtI(NCN), has led to the proposal of a possible mechanism as shown in Scheme 3.10. It involves the initial formation of a cationic species, **B**, and free iodide ion (eq 3.2). Iodide can then undergo anion exchange with **24** (eq 3.3) liberating ionic benzoate, which can coordinate to intermediate **B** to form **29** (eq 3.4). As mentioned in Section 2.2.4, there is a precedent for a five-coordinate organoplatinum(IV) species, $PtMe_3(L)$ (L^- = $[\{(2\text{-}^iPr_2C_6H_3)NC(CH_3)\}_2CH]^-$).[37] However, coordination of a solvent molecule, or presence of the benzoate group in a bidentate coordination mode, cannot be discounted for intermediate **B**.

Scheme 3.10: Possible mechanism for the formation of $Pt(O_2CPh)_2Me(NCN)$.

$$\underset{\mathbf{24}}{Pt^{II}(O_2CPh)(NCN)} + MeI \rightarrow \underset{\mathbf{B}}{[Pt^{IV}(O_2CPh)Me(NCN)]^+} + I^- \quad (3.2)$$

$$\underset{\mathbf{24}}{Pt^{II}(O_2CPh)(NCN)} + I^- \rightarrow \underset{\mathbf{22}}{Pt^{II}I(NCN)} + PhCO_2^- \quad (3.3)$$

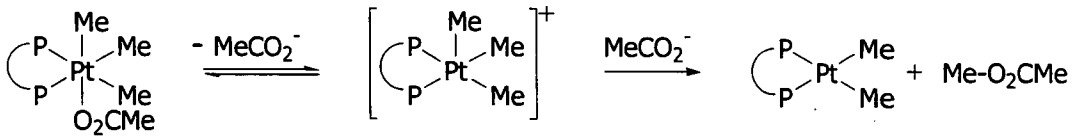
$$\underset{\mathbf{B}}{[Pt^{IV}(O_2CPh)Me(NCN)]^+} + PhCO_2^- \rightarrow \underset{\mathbf{29}}{cis\text{-}Pt^{IV}(O_2CPh)_2Me(NCN)} \quad (3.4)$$

When similar reactions were carried out using the palladium(II) analogue, **23**, and an excess of iodomethane, the observed products were PdI(NCN) and Me-O_2CPh in equal amounts. The reaction of two equivalents of **23** with one of iodomethane led to the formation of PdI(NCN), Me-O_2CPh and $Pd(O_2CPh)(NCN)$ in 1:1:1 ratio. No palladium(IV) intermediate(s) could be detected spectroscopically in either of these reactions. However, the similarity in the observed products and the stoichiometry of these reactions with those of the platinum analogues does suggest that a common mechanism is a strong possibility.

3.2.2.2 Decomposition of $Pt(O_2CPh)_2Me(NCN)$

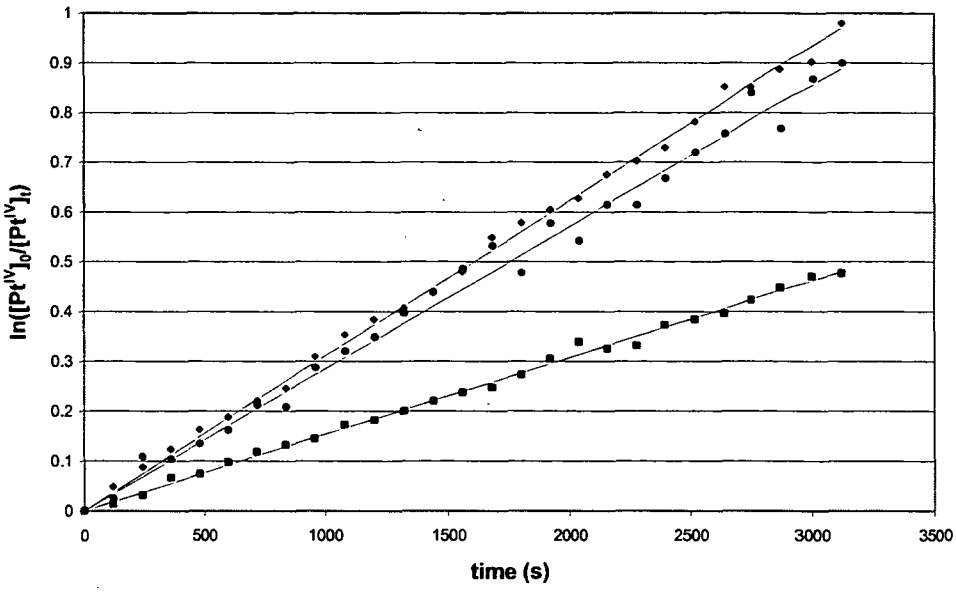
The decomposition of $Pt(O_2CPh)_2Me(NCN)$ (**29**) occurs *via* the reductive elimination of $Me\text{-}O_2CPh$, providing a platinum(IV) model for the carbon-oxygen bond forming step in the catalysis shown in Scheme 2.1. The mechanism involved in this reductive elimination is likely to be similar to that proposed for the decomposition of *fac*-$Pt^{IV}(O_2CMe)Me_3(dppe)$ [dppe = 1,2-bis(diphenylphosphino)ethane].[38] Kinetic studies on the latter complex found that carbon-oxygen coupling reactions were independent of acetate concentration while being accelerated by more polar solvents and acids and by the presence of more electron withdrawing carboxylates. These data support a mechanism in which initial acetate dissociation is followed by nucleophilic attack at the methyl group to form $Me\text{-}O_2CMe$ (Scheme 3.11).[38,39]

Scheme 3.11: Mechanism for the formation of carbon-oxygen bonds from $Pt(O_2CMe)Me_3(dppe)$.[38,39]



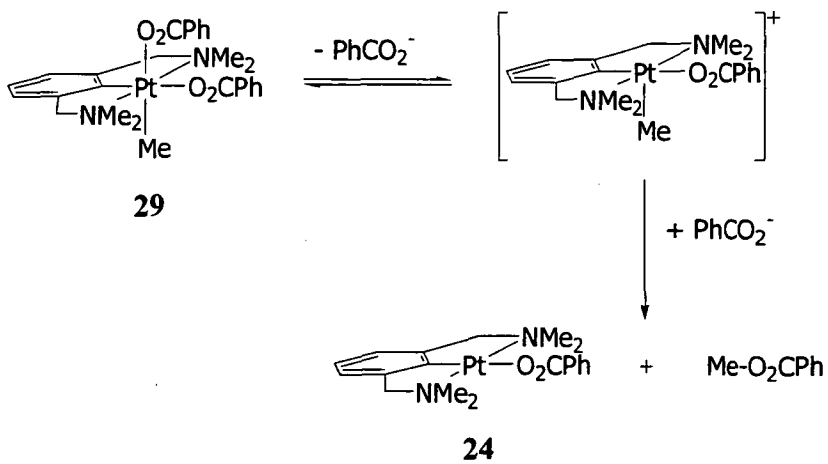
Analogous kinetic studies carried out on the decomposition of **29** support the notion that reductive elimination occurs *via* a similar mechanism. Reductive elimination from **29** followed first order kinetics to give $Pt(O_2CPh)(NCN)$ (**25**) and $Me\text{-}O_2CPh$ as the only products. Kinetic studies have shown that, at 50 °C, decomposition in acetone-d_6 ($k_{obs} = 3.11 \times 10^{-4}\ s^{-1}$) occurs at approximately twice the rate as seen in less polar toluene-d_8 ($k_{obs} = 1.54 \times 10^{-4}\ s^{-1}$) (Figure 3.4). This solvent dependence indicates that a polar or ionic transition structure is probably involved. It was also found that, as observed above, the external concentration of benzoate ions had little effect on the rate. When carried out in the presence of 3 mM tetrabutylammonium benzoate, $[N(Bu^n)_4][O_2CPh]$, in acetone-d_6, the observed rate constant (k_{obs}) was $2.85 \times 10^{-4}\ s^{-1}$. This is comparable with the rate observed in the absence of excess benzoate (Figure 3.4).

Figure 3.4: First order kinetic plots of the decomposition of $Pt(O_2CPh)_2Me(NCN)$ in acetone-d_6 (◆), toluene-d_8 (■) and in 3 mM $[N(Bu^n)_4][O_2CPh]$ in acetone-d_6 (●).



It is therefore feasible to propose a mechanism in which benzoate dissociation leads to the formation of a five-coordinate cationic intermediate, $[Pt(O_2CPh)Me(NCN)]^+$ (Scheme 3.12). This would be followed by nucleophilic attack of the benzoate on the methyl group, eliminating $Me\text{-}O_2CPh$ and **24**.

Scheme 3.12: Proposed mechanism for reductive elimination from $Pt(O_2CPh)_2Me(NCN)$ (**29**).



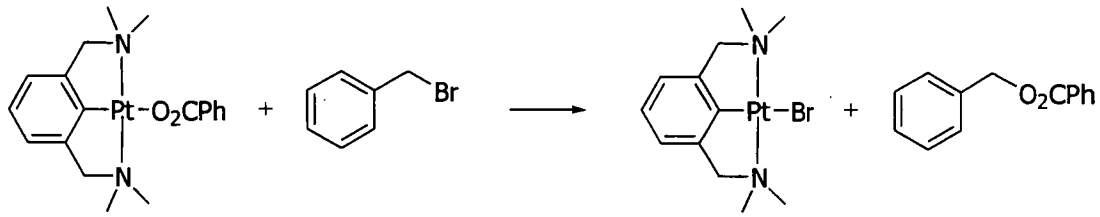
29

24

3.2.2.3 Reaction of $Pt(O_2CPh)(NCN)$ with Benzyl Bromide

In order to determine whether a comparable process would be observed for the reaction of **24** with bulkier organic halides, similar experiments were carried out using benzyl bromide (BzBr) as oxidant. The reaction of **24** and excess BzBr was monitored by ^1H NMR. It proceeded very slowly at room temperature to form PtBr(NCN) and Bz-O_2CPh in equal amounts (Scheme 3.13). The same products were observed when large excesses of BzBr and Ag[O_2CPh] were added. No platinum(IV) intermediates were detected in either case. It is likely that this reaction proceeds in a similar fashion to the analogous reaction with iodomethane, but other routes cannot be discounted.

Scheme 3.13: The reaction of $Pt(O_2CPh)(NCN)$ (**24**) with benzyl bromide.



24

3.2.3 Synthesis and Characterisation of Complexes

All new palladium(II) and platinum(II) complexes, in addition to $Pt^{IV}(O_2CPh)_2Tol(NCN)$ (**28**), were prepared in a similar way as described in Section 2.2.5 by metathesis reactions between known complexes, $M^{II}Cl(NCN)$ and $Pt^{IV}I_2Tol(NCN)$, and silver(I) salts. This method has been used previously in the preparation of related complexes.[5,35] The remaining two platinum(IV) complexes, **27** and **29**, were prepared by different approaches.

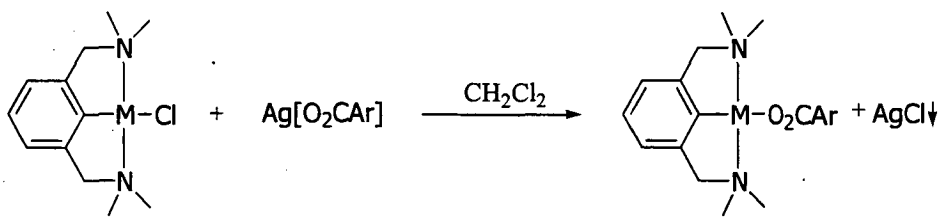
Identification of the complexes was achieved primarily through ^1H NMR spectroscopy. In addition, elemental analyses, crystal structures and mass spectral

data were obtained for most complexes. Metal(II) complexes were also characterised by ^{13}C NMR.

3.2.3.1 Synthesis and Characterisation of $M(O_2CAr)(NCN)$

Complexes **23**, **24**, **25** and **26** were prepared by an analogous method to that described by van Koten and coworkers for the preparation of $M(O_2CR)(NCN)$ (M = Pt, Pd; R = Me, CF_3).[5,35] Complexes $M(O_2CAr)(NCN)$ (M = Pd, Pt; Ar = Ph, Ar_F) were obtained by the reaction of MCl(NCN) with $Ag[O_2CAr]$ in CH_2Cl_2. Reactions were complete when stirred for one hour (palladium complexes) or overnight (platinum complexes) in the absence of light, with silver(I) chloride precipitating as the other product (Scheme 3.14).

Scheme 3.14: Preparation of $M(O_2CAr)(NCN)$.

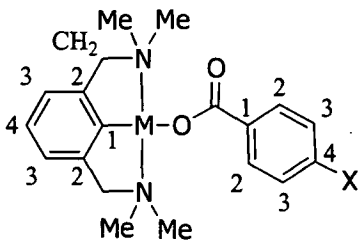


23: M = Pd; Ar = Ph
24: M = Pt; Ar = Ph
25: M = Pd; Ar = Ar_F
26: M = Pt; Ar = Ar_F

The numbering scheme for NMR spectroscopic studies of these complexes is shown in Figure 3.5. Each of the complexes has uncomplicated ^1H NMR spectra showing integration as expected for the proposed formulae. The CH_2 and NMe protons give rise to singlets and, when M = Pt, typical $^3J_{Pt\text{-}H}$ coupling is observed. As can be seen in Table 3.1, resonances arising from the ligand remain nearly constant between all four complexes. A typical spectrum of the aromatic region is shown in Figure 3.6. This reflects the similar configuration expected for the palladium(II) and platinum(II) complexes, and suggests that substitution at the 4-position of the benzoate group is sufficiently removed from the ligand so as not to

have an effect on it. Comparison with related complexes reveal similar resonances for the NCN ligand (Table 3.1). Signals arising from the benzoate group vary slightly depending on the metal and on the nature of the group occupying the 4-position of the aryl ring. Not surprisingly, resonances for the aryl group substituted with the electron withdrawing CF_3 group are downfield of those for the unsubstituted benzoate.

Figure 3.5: Numbering scheme for ^1H and ^{13}C NMR studies of $M(O_2CAr)(NCN)$.



X = H, CF_3

Table 3.1: ^1H NMR data for complexes **23-25** and **26**. Spectra are measured in acetone-d_6 unless otherwise stated. Where appropriate, $^3J_{Pt-H}$ coupling (Hz) is given in parentheses. Related compounds are included for comparison.

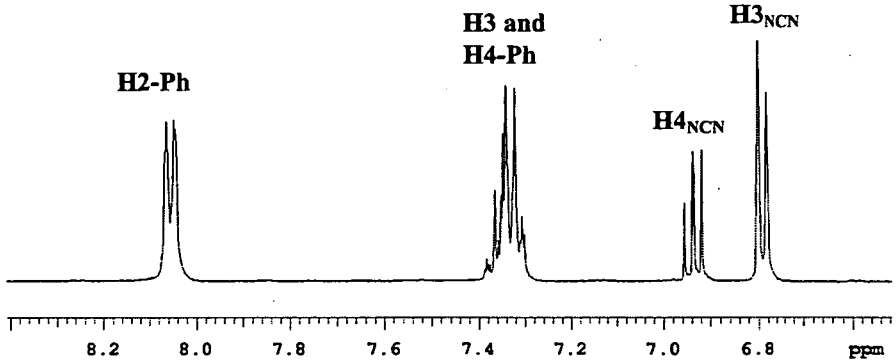
Complex	δ (ppm)						
	Ar			NCN			
	H2	H3	H4	H3	H4	CH_2	NMe
$Pd(O_2CPh)(NCN)$ (**23**)	8.04	7.37-7.30 m [b]		6.79	6.94	4.06	2.88
$Pt(O_2CPh)(NCN)$ (**24**)	8.12	7.44-7.35 m [b]		6.82	6.96	4.15 (46)	3.06 (36)
$Pd(O_2CAr_F)(NCN)$ (**25**)	8.22	7.68	-	6.80	6.95	4.06	2.88
$Pt(O_2CAr_F)(NCN)$ (**26**)	8.27	7.71	-	6.79	6.93	4.09 (48)	3.04 (37)
$Pt(O_2CMe)(NCN).H_2O$ [a, 35]	-	-	-	6.80[c]		4.00 (50)	3.03 (38)
$Pd(O_2CMe)(NCN).H_2O$[35]	-	-	-	6.83[c]		4.00	2.82
$Pt(O_2CCF_3)(NCN)$ [a, 35]	-	-	-	6.83[c]		4.02 (48)	3.01 (38)
$Pd(O_2CCF_3)(NCN)$ [a, 35]	-	-	-	6.85[b]		4.05	2.83

[a] Measured in $CDCl_3$

[b] m = multiplet

[c] Only one resonance reported.

Figure 3.6: Aromatic region of the ^{1}H NMR spectrum of Pd(O_2CPh)(NCN)(**23**).



As noted for ^{1}H NMR studies, ^{13}C NMR spectra of these complexes showed many similarities (Table 3.2). The resonance appearing furthest downfield, between 169.9-172.3 ppm in each case, was that of the carbonyl carbon, which is in the typical range for a benzoate group.[40] There was little variation between resonances for $C2_{NCN}$ (145.0-146.5 ppm), $C3_{NCN}$ (119.8-120.4 ppm) and $C4_{NCN}$ (123.7-125.2 ppm) of the NCN ligand. Carbon $C1_{NCN}$ showed some differences depending on the metal to which it was bound. The platinum complexes, **24** and **26**, give rise to signals at 140.5 and 141.7 ppm, respectively, while the palladium complex **25** has a resonance at 155.4 ppm. The $C1_{NCN}$ signal for **23** was not observed. The carbon atoms of the CH_2 and NMe groups also show a slight dependence on the metal. The CH_2 and NMe signals for both of the palladium complexes appear at 74.7 and 52.2 ppm, respectively. For **24** and **26**, signals for these groups are at 77.3 and 53.4 ppm, and 77.4 and 53.8 ppm, respectively. As seen in ^{1}H NMR studies, the substitution of the benzoate group had no effect on the chemical shifts observed for the NCN ligand. Furthermore, the similarity between the spectra again implies that the complexes have very similar configurations in solution. Resonances observed for the NCN ligand agreed closely with shifts of related compounds (Table 3.2).

Table 3.2: Selected ^{13}C NMR data for complexes **23-25** and **26**. Spectra are measured in acetone-d_6 unless otherwise stated. Related compounds are included for comparison.

Complex	δ (ppm)						
	C=O	NCN					
		C1	C2	C3	C4	CH_2	NMe
$Pd(O_2CPh)(NCN)$ (**23**)	171.7	[a]	146.5	120.4	125.0	74.7	52.2
$Pt(O_2CPh)(NCN)$ (**24**)	172.3	140.5	145.6	120.0	124.4	77.3	53.8
$Pd(O_2CAr_F)(NCN)$ (**25**)	169.9	155.4	146.4	120.4	125.2 or 125.0	74.7	52.2
$Pt(O_2CAr_F)(NCN)$ (**26**)	170.1	141.7	145.0	119.8	123.7	77.4	53.4
$Pt(O_2CMe)(NCN)$ [b, 5]	183.2	[a]	143.7	119.1	122.9	76.9	53.3
$Pt(O_2CPr^i)(NCN)$ [b, 5]	[a]	[a]	143.6	118.9	122.8	76.9	53.1
$Pd(OPh)(NCN)$ [b, 41]	-	155.7	145.1	119.5 or 118.9	124.1	74.4	52.3
$Pt(OPh)(NCN)$ [b, 41]	-	143.2	144.0	119.1	122.9	77.7	54.0

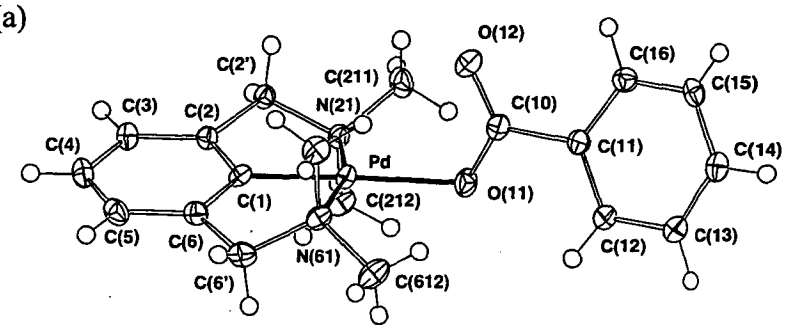
[a] No signal observed/reported.

[b] Measured in $CDCl_3$.

Crystals of $Pd(O_2CPh)(NCN)$ (**23**) and $Pt(O_2CPh)(NCN)$ (**24**) suitable for X-ray crystallographic studies were grown by slow diffusion of *n*-pentane into a CH_2Cl_2 solution of the complex at room temperature. Resulting crystal structures of these complexes are shown in Figure 3.7, with selected bond distances and angles in Table 3.3. Complexes **23** and **24** are isostructural (identical space group and similar cell dimensions) and have approximate square planar geometry, where the maximum deviation from the 'CN_2O' mean planes in 0.009(1) Å for **23**. The M-C and M-O distances do not differ significantly, but the Pd-N distances are *ca.* 0.02 Å longer than their Pt-N counterparts. This observation is consistent with other observed trends in which Pd-N, P, O, S and Cl distances are similar to, or longer than, isostructural platinum analogues.[42-49] Both **23** and **24** are devoid of crystallographic symmetry. The pincer group has a *mer*-terdentate arrangement around the metal centre with chelate arms of the same chirality, so that the M(NCN) array has approximate 2-symmetry with the M-C bond lying on the '2-axis'. Each of the nitrogen atoms has one methyl group that is almost coplanar with the M(NCN) plane in an 'equatorial' position. The other methyls have an 'axial' position such that the two axial methyls occupy opposite sides of the M(NCN) plane. Within each benzoate group, the carboxylate is approximately coplanar with its aromatic ring.

Figure 3.7: Structures of (a) $Pd(O_2CPh)(NCN)$ (**23**) and (b) $Pt(O_2CPh)(NCN)$ (**24**). Ellipsoids are shown at the 50% probability level.

(a)



(b)

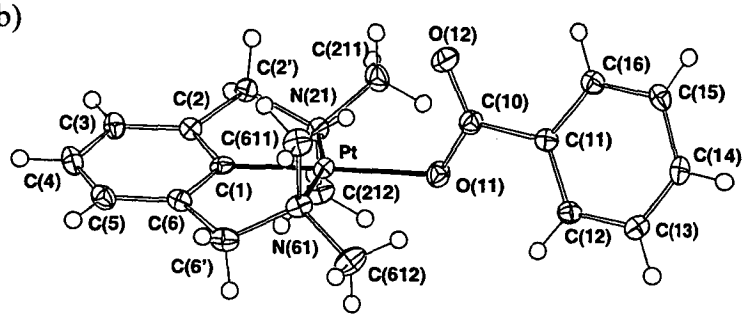


Table 3.3: Selected bond distances (Å) and angles (deg.) for **23** and **24**.

	23	**24**
	Bond Distances (Å)	
M-C(1)	1.895(2)	1.906(2)
M-N(21)	2.099(2)	2.080(2)
M-N(61)	2.102(2)	2.080(2)
M-O(11)	2.140(1)	2.143(2)
C(10)-O(11)	1.279(2)	1.275(3)
C(10)-O(12)	1.240(2)	1.238(3)
	Bond Angles (deg.)	
C(1)-M-N(21)	81.68(7)	82.15(10)
C(1)-M-N(61)	81.32(7)	82.22(10)
N(21)-M-N(61)	163.00(6)	164.37(9)
O(11)-M-C(1)	177.44(7)	177.64(10)
O(11)-M-N(21)	100.67(6)	100.11(8)
O(11)-M-N(61)	96.33(6)	95.51(9)
M-C(1)-C(2)	119.2(1)	119.0(2)
M-C(1)-C(6)	119.6(1)	118.8(2)
M-O(11)-C(10)	117.0(1)	119.2(1)

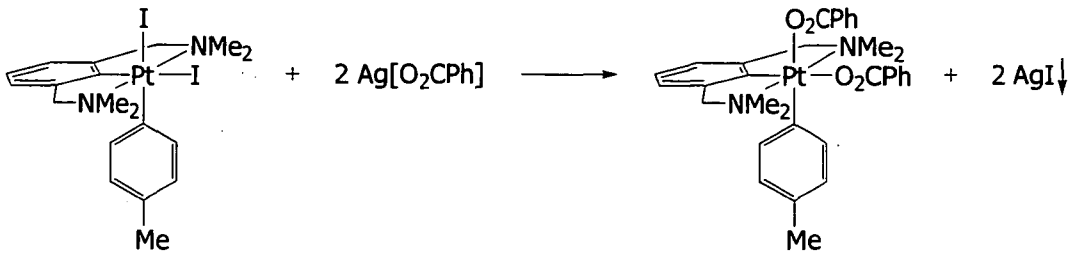
3.2.3.2 Synthesis and Characterisation of Platinum(IV) Complexes

The platinum(IV) complexes, $Pt(O_2CPh)_3(NCN)$ (**27**), $Pt(O_2CPh)_2Tol(NCN)$ (**28**) and $Pt(O_2CPh)_2Me(NCN)$ (**29**), were prepared in order to confirm their identities in the reactions described in preceding sections, and to observe their behaviour in the absence of reagents such as dibenzoyl peroxide. Complex **27** was isolated in 68 % yield by the reaction of **24** with one equivalent of dibenzoyl peroxide in acetone at 50 °C. The reaction proceeded in the same manner as described in the NMR studies discussed in Section 3.2.1.1 (Scheme 3.6).

The preparation of pure **28** was not as straightforward as expected in light of the success of other metathesis reactions. The complex was obtained by the overnight

reaction of the known species $PtI_2Tol(NCN)$ with two equivalents of $Ag[O_2CPh]$ in acetone in the absence of light (Scheme 3.15). ^1H NMR of the isolated white solid did show the presence of the desired product, but it was accompanied by unidentified impurities. In order to obtain a pure sample, crystals were grown from an acetone solution at room temperature. This gave the desired product but only in a low yield.

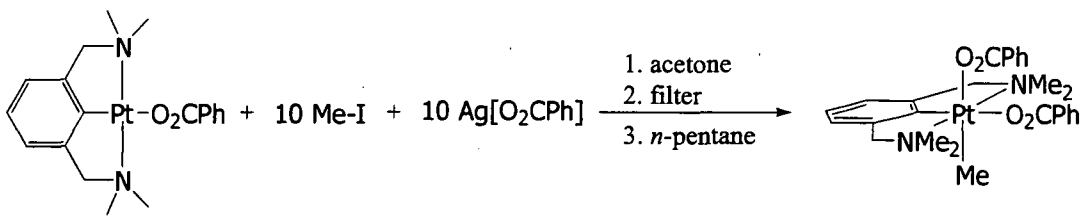
Scheme 3.15: Preparation of $Pt(O_2CPh)_2Tol(NCN)$ (**28**).



28

The technique used to prepare $Pt(O_2CPh)_2Me(NCN)$ (**29**) stemmed from the observation that when **24** was allowed to react with a large excess of iodomethane and $Ag[O_2CPh]$, all of the platinum in the reaction was present as **29**. Therefore, a suspension of **24** and ten equivalents each of silver benzoate and iodomethane in acetone was stirred overnight in the absence of light. The suspension was filtered and the desired product precipitated with *n*-pentane in 71 % yield (Scheme 3.16).

Scheme 3.16: Preparation of $Pt(O_2CPh)_2Me(NCN)$ (**29**).

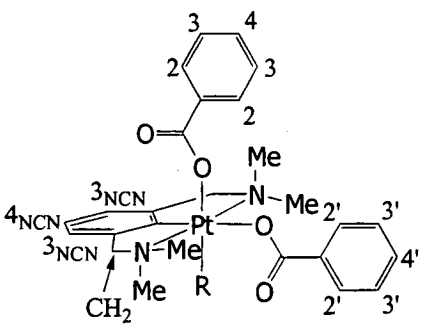


24 **29**

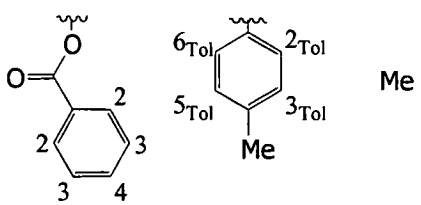
Although ^1H NMR studies revealed some similarities between all three of the platinum(IV) complexes, **28** and **29** are clearly more closely related to each other than either is to $Pt(O_2CPh)_3(NCN)$ (**27**). Numbering schemes for **27**, **28** and **29** are shown in Figure 3.8. The $H3_{NCN}$ and $H4_{NCN}$ resonances of the ligand vary only

slightly between the three complexes (Table 3.4). Proton $H3_{NCN}$ appears as a doublet in the range 7.04-6.99 ppm, while $H4_{NCN}$ gives rise to a doublet of doublets between 7.10 and 7.25 ppm. The most notable differences between the spectra are due to the different nature of the CH_2 and NMe groups. For complexes **28** and **29**, two signals are observed for each of the latter groups. The CH_2 protons give rise to two doublets with large coupling constants (14-15 Hz) indicating the occurrence of ^2J coupling. Each of these doublets also shows platinum satellites with $^3J_{Pt\text{-}H}$ = 33-38 Hz. The NMe protons give rise to two singlets with platinum satellites ($^3J_{Pt\text{-}H}$ = 25-39 Hz). Splitting of the CH_2 and NMe signals indicates the presence of inequivalent groups above and below the Pt(NCN) coordination plane. By contrast, **27** has identical groups in both axial positions and, consequently, only one singlet is seen for the CH_2 and NMe groups. The latter resonances have platinum satellites with $J_{Pt\text{-}H}$ = 28 and 25 Hz respectively.

Figure 3.8: Numbering scheme for ^{1}H NMR studies of complexes **27**, **28** and **29**.



R =



27 **28** **29**

Table 3.4: Selected ^{1}H NMR data for complexes **27**, **28** and **29**. Spectra are measured in acetone-d_6 unless otherwise stated and $^3J_{Pt\text{-}H}$ (Hz) coupling is shown in parentheses. Related compounds are included for comparison.

Complex	δ (ppm)				
	NCN				R
	H3	H4	CH_2	NMe	
$Pt(O_2CPh)_3(NCN)$ (**27**)	7.04	7.13	4.45 (28)	3.05 (25)	-
$Pt(O_2CPh)_2Tol(NCN)$ (**28**)	7.05	~ 7.25[a]	4.30 (38) 4.15 (33)	3.11 (25) 2.60 (39)	8.21 (29), 6.92, 6.67, 6.11 (40), 2.26
$Pt(O_2CPh)_2Me(NCN)$ (**29**)	6.99	7.10	4.47 (36) 4.33 (34)	3.11 (26) 2.94 (36)	1.65 (70)
$PtI_2Tol(NCN)$ [b, 26]	6.98	7.19	4.58 (30) 4.09(31)	3.77 (30) 2.39 (43)	8.94 (37), 6.83, 6.55, 6.01 (38), 2.33

[a] Overlapping resonance

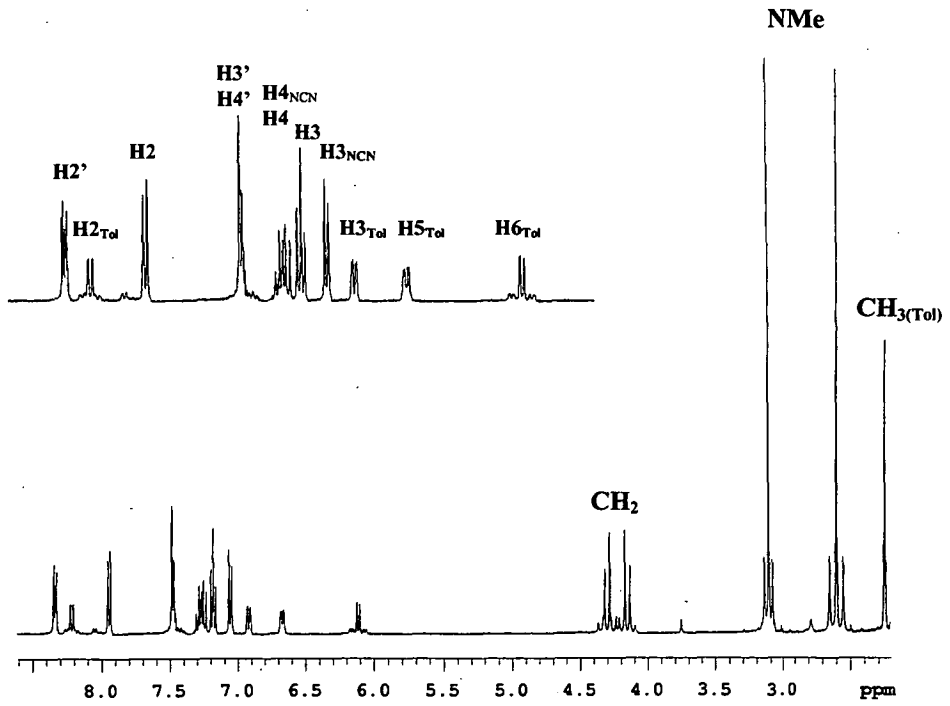
[b] Measured in $CDCl_3$

Another similarity between the three complexes is the presence of inequivalent benzoate groups in each. In the case where three benzoate groups were present (**27**) it was possible to distinguish between the one that was *trans* to the NCN aryl group ('equatorial') and those above and below the plane ('axial'). Since the latter groups are equivalent, they give rise to only one set of resonances with integrals double that of the 'equatorial' benzoate. Therefore, by comparing integrals, the signals for the group in the 'equatorial' position was found to appear downfield of those occupying 'axial' positions. Benzoate resonances appeared in equivalent positions in complexes **28** and **29**. As such, the set of signals occurring furthest downfield in each could be assigned to the benzoate *trans* to the NCN aryl group.

The $Pt^{IV}Me$ group of complex **29** gives rise to a singlet at 1.66 ppm. This resonance is accompanied by platinum satellites with $^2J_{Pt\text{-}H}$ coupling of 70 Hz, which is typical of a $Pt^{IV}Me$ group *trans* to a carboxylate moiety.[38] As mentioned in Section 3.2.1.2, the 4-tolyl group of complex **28** gives rise to four well-resolved resonances in the aromatic region, two of which have platinum satellites. A similar observation was noted by van Koten *et al.* in ^{1}H NMR studies of $PtI_2Tol(NCN)$,[26] and it was suggested that this pattern reflects a fixed orientation of the 4-tolyl group perpendicular to the plane of the ligand and to the N-Pt-N axis.[26] Comparisons with this complex led to the tentative assignment of the tolyl protons. The resonances

displaying $^3J_{Pt-H}$ coupling are due to $H2_{Tol}$ and $H6_{Tol}$, while those without arise from $H3_{Tol}$ and $H5_{Tol}$. Of the two signals with platinum satellites, the most upfield signal is likely to be $H6_{Tol}$ (δ 6.11 ppm, $^3J_{Pt-H}$ = 40 Hz), compared with δ 6.01 ppm for $PtI_2Tol(NCN)$ in $CDCl_3$.[26] This is due to shielding effects expected from being positioned under the aryl group of the ligand (*i.e.* influence of π-electrons). Consequently, the low field signal with platinum satellites would be $H2_{Tol}$ (δ 8.21 ppm, $^3J_{Pt-H}$ = 29 Hz), compared with δ 8.94 ppm for $PtI_2Tol(NCN)$ in $CDCl_3$.[26] Additional comparison suggests that of the remaining signals, the downfield one (6.92 ppm) is caused by $H3_{Tol}$, while the other (6.67 ppm) originates from $H5_{Tol}$. The ^{1}H NMR spectrum of **28** is shown in Figure 3.9.

Figure 3.9: ^{1}H NMR spectrum of $Pt(O_2CPh)_2Tol(NCN)$ (**28**).

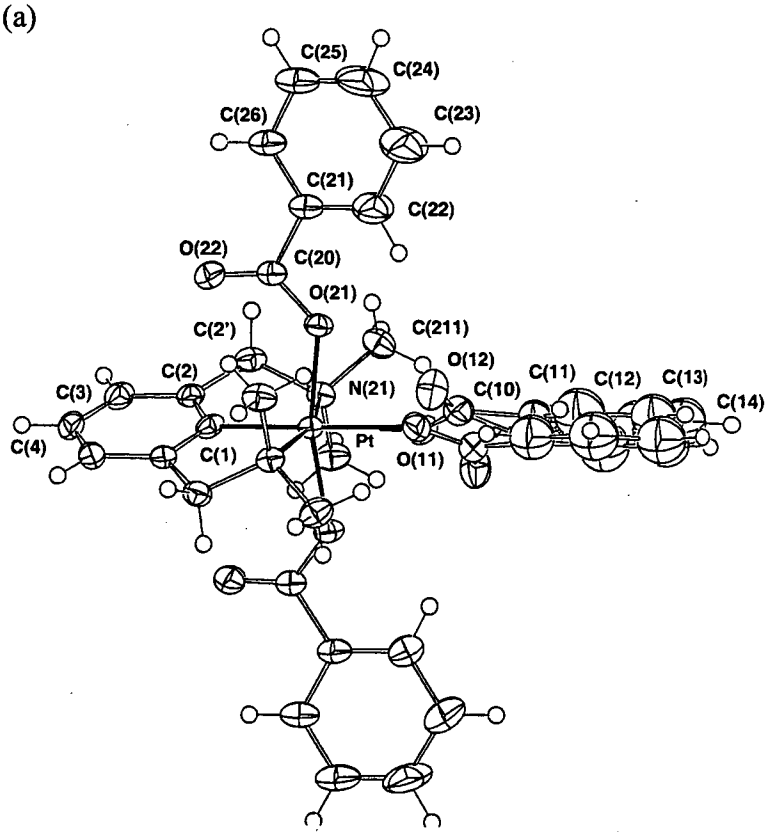


Crystals of each complex suitable for X-ray crystallographic studies were grown by the slow diffusion of *n*-pentane into an acetone solution of the complex. The complexes were obtained as the solvated species, **27**.½Me_2CO, **28**.Me_2CO and **29**.$Me_2CO.H_2O$. Structures of these species and selected bond distances and angles

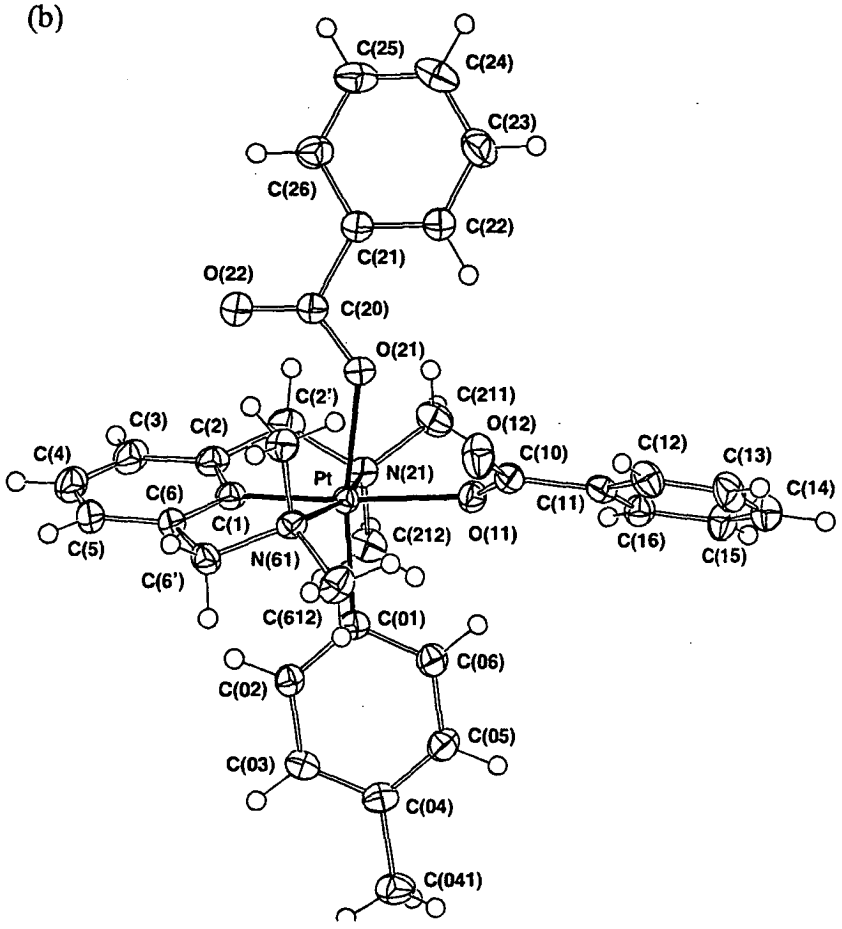
can be found in Figure 3.10 and Table 3.5 respectively. The structural features of these complexes bear several similarities to the $M(O_2CPh)(NCN)$ complexes discussed in Section 3.2.3.1. Molecules **28** and **29** are devoid of any crystallographic symmetry, but when **27** was modeled in space group *C*2/*c*, it was found to lie on a crystallographic 2-axis. In **27**, **28** and **29**, the NCN ligand occupies a *mer*-terdentate arrangement around the metal. The M(NCN) array has approximate 2-symmetry for **28** and **29** and exact 2-symmetry for **27**, with the M-C bond lying on the 2-axis. The phenyl of the equatorial benzoate ligand in **27** is disordered over two sites, each with a population of 0.50. As noted for the M(II) complexes, the axial methyl groups on the nitrogen atoms are located on opposite sides of the M(NCN) plane, and the carboxylate group of each unidentate benzoate is roughly coplanar with its aromatic ring.

Figure 3.10: Structures of complexes (a) $[Pt(O_2CPh)_3(NCN)].½Me_2CO$ (**27**.$½Me_2CO$) (b) $[Pt(O_2CPh)_2Tol(NCN)].Me_2CO$ (**28**.Me_2CO) and (c) $[Pt(O_2CPh)_2Me(NCN)].Me_2CO.H_2O$ (**29**.$Me_2CO.H_2O$). Ellipsoids are shown at the 50% probability level. Solvent molecules are omitted for clarity.

(a)



(b)


C(25)
C(24)
C(23)
C(26)
C(22)
C(21)
O(22)
C(20)
O(21)
C(2')
C(211)
C(3)
C(2)
O(12)
C(4)
C(10)
C(12)
C(13)
Pt
N(21)
C(6)
C(11)
C(14)
C(1)
C(212)
O(11)
C(5)
C(16)
C(15)
N(61)
C(6')
C(612)
C(01)
C(06)
C(02)
C(05)
C(03)
C(04)
C(041)

(c)

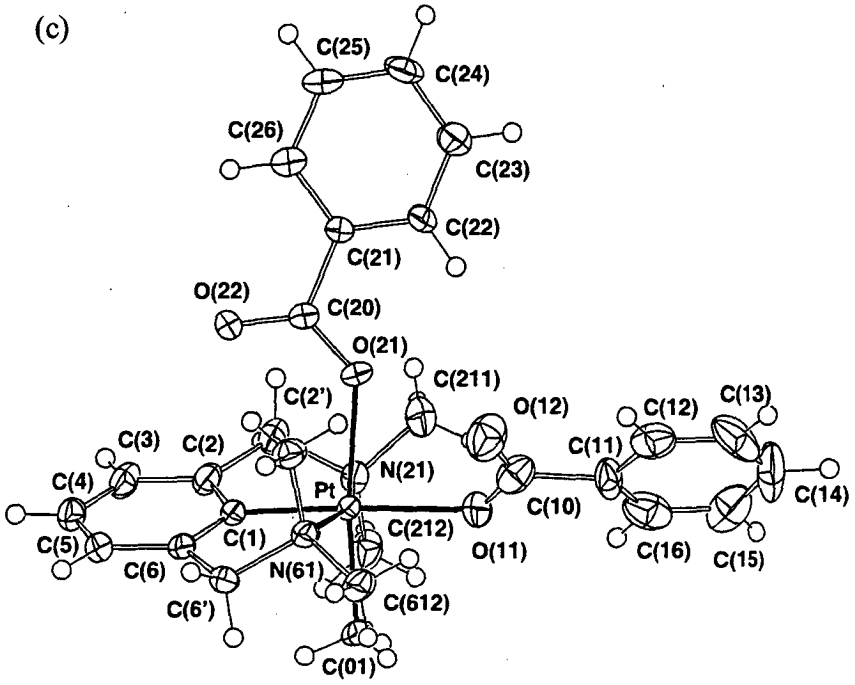

C(25)
C(24)
C(26)
C(23)
C(22)
C(21)
O(22)
C(20)
O(21)
C(211)
C(2')
O(12)
C(12)
C(13)
C(3)
C(2)
C(11)
N(21)
C(4)
Pt
C(10)
C(14)
C(5)
C(1)
C(212)
O(11)
C(16)
C(15)
C(6)
N(61)
C(6')
C(612)
C(01)

Table 3.5: Selected bond distances (Å) and angles (°) for **27.**½Me_2CO, **28.**Me_2CO and **29.**$Me_2CO.H_2O$.

	27.½Me_2CO	**28.**Me_2CO	**29.**$Me_2CO.H_2O$
	Bond Distances (Å)		
Pt-C(1)	1.951(1)	1.949(4)	1.935(5)
Pt-N(21)	2.116(3)	2.135(3)	2.137(6)
Pt-N(61)	2.116(3)	2.134(3)	2.120(5)
Pt-O(11)	2.145(6)	2.144(3)	2.144(5)
Pt-O(21)	2.004(4)	2.121(3)	2.169(4)
Pt-C(01)	-	2.036(4)	2.045(6)
C(10)-O(11)	1.31(1)	1.288(5)	1.225(9)
C(10)-O(12)	1.24(1)	1.232(4)	1.245(9)
C(20)-O(21)	1.320(5)	1.280(5)	1.276(6)
C(20)-O(22)	1.192(5)	1.235(4)	1.236(7)
	Bond Angles (deg.)		
C(1)-Pt-N(21)	82.13(9)	82.1(1)	81.9(2)
C(1)-Pt-N(61)	82.13(9)	81.1(1)	81.0(2)
N(21)-Pt-N(61)	164.3(1)	163.2(1)	162.8(2)
O(11)-Pt-C(1)	173.3(2)	173.9(1)	173.1(2)
O(11)-Pt-N(21)	104.0(3), 91.8(3)	92.4(1)	92.5(2)
O(11)-Pt-N(61)	-	104.4(1)	104.7(2)
O(21)-Pt-N(21)	87.3(1)	85.5(1)	84.1(2)
O(21)-Pt-N(61)	94.8(1)	95.6(1)	95.5(2)
O(21)-Pt-O(11)	80.4(4), 84.9(4)	80.5(1)	86.2(2)
O(21)-Pt-C(1)	97.38(8)	96.4(1)	97.2(2)
O(21)-Pt-O(21')	165.2(1)	-	-
O(21)-Pt-C(01)	-	169.9(1)	172.2(2)
C(01)-Pt-N(21)	-	91.9(1)	93.6(2)
C(01)-Pt-N(61)	-	89.8(1)	88.8(2)
C(01)-Pt-C(1)	-	92.9(2)	89.9(2)
O(21')-Pt-N(21)	94.8	-	-
O(21')-Pt-N(61)	-	-	-
Pt-C(1)-C(2)	117.6(2)	117.4(2)	117.5(4)
Pt-C(1)-C(6)	117.6(2)	119.0(3)	118.8(4)
Pt-O(11)-C(10)	158(1)	129.2(2)	125.7(5)
Pt-O(21)-C(20)	133.3(3)	135.2(3)	132.6(4)
Pt-C(01)-C(02)	-	126.5(3)	-
Pt-C(01)-C(06)	-	117.0(3)	-

In keeping with the increase in coordination number, metal ligand distances are increased compared with M(II) complexes. In each complex, the axial benzoate group(s) sits almost parallel with the 'vertical' plane running through C(1), O(21) and O(11). The pendant oxygen lies above (and below, in the case of **27**) the metal-bound carbon of the ligand. In **28** and **29**, the organic group (Tol for **28** and Me for **29**) is situated *cis* to the terdentate NCN ligand. The plane of the tolyl group of **28** makes a dihedral angle of 10.8(1)° with the 'vertical' plane.

Excluding complex **27**, which is affected by disorder, the Pt-O distances within each molecule are similar, regardless of their location in the coordination sphere. However, it should be noted that there is a significant difference between the 'axial' Pt-O distances in **28** and **29**. This is possibly a consequence of the differing *trans*-effect of methyl compared with 4-tolyl. The very short 'axial' Pt-O distance seen for **27** (2.004(4) Å) may reflect the change in *trans* influence on replacing a carbon donor with an oxygen. The angles formed by the *trans* groups with the metal centre (*i.e.* O-Pt-O for **27** and O-Pt-C for **28** and **29**) were considerably less than 180° and bowed away from the NCN ligand. This is presumably in response to the diminished angle imposed by the N-Pt-N array.

3.3 Conclusions

The use of the intramolecularly coordinating NCN ligand, $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$, allowed the successful isolation of a series of platinum(IV) complexes that provided models for some palladium(IV) species suspected as intermediates in carbon-oxygen bond forming processes. Attempts to observe analogous palladium(IV) complexes were unsuccessful.

The monoorganoplatinum(IV) complex $Pt(O_2CPh)_3(NCN)$ (**27**) provides a model for the proposed monoorganopalladium(IV) intermediate in the acetoxylation of arenes, '$Pd^{IV}(O_2CMe)_3Ar$' (Scheme 2.1, Chapter Two), and for the suspected intermediates in the reactions between $Pd(O_2CAr)Tol(bpy)$ and $(ArCO_2)_2$ (Chapter Two). All consist of a metal(IV) centre surrounded by one aryl group and three

carboxylate groups [or perhaps more in the case of the catalysis reaction, depending on the coordination mode of the carboxylate group in satisfying the presumed need for octahedral geometry at palladium(IV)]. It is prepared by the oxidation of a monoorganometal(II) species as is expected to occur in the catalytic reaction. No decomposition of **27** was observed, probably due to the intramolecular stabilisation of the platinum-bound aryl group.

Diorganoplatinum(IV) complexes *cis*-$Pt(O_2CPh)_2Me(NCN)$ (**29**) and *cis*-$Pt(O_2CPh)_2Tol(NCN)$ (**28**) were observed in the reactions of $Pt(O_2CPh)(NCN)$ (**24**) with iodomethane and PtTol(NCN) with dibenzoyl peroxide, respectively, and subsequently isolated by independent syntheses. Concerted *cis*-addition of $(PhCO_2)_2$ would be consistent with the observed products, and with the conclusions of Rashidi *et al.* (Scheme 2.13, Section 2.2.4.1).[50]

Kinetic studies on the decomposition of **29** are consistent with carbon-oxygen bond formation *via* initial dissociation of a benzoate group followed by interaction of this benzoate group with the methyl group of the cationic intermediate. This mechanism is analogous to that reported for carbon-oxygen bond formation from $PtMe_3(O_2CR)(L_2)$ (R = Me, CF_3; L_2 = bidentate phosphine).[38,39] By contrast, **28** was highly stable in solution. This may be caused by restricted movement of the 4-tolyl group imposed by bulky NMe_2 groups of the NCN ligand, preventing intramolecular carbon-oxygen bond formation, and/or the absence of suitable conditions at the *ipso*-carbon for attack by a benzoate ion.

As discussed in Chapter Two, similar reasons might be responsible for the lack of aryl-oxygen coupling in the reaction between $Pd(O_2CPh)Tol(tmeda)$ and $(PhCO_2)_2$. Although the NMe_2 groups occupy *cis* positions in the tmeda complex, compared with *trans* positions in the NCN complex, they would still be expected to create significant crowding around the metal. If addition of the peroxide occurs *via* concerted *cis* addition as suggested above, migration of the 4-tolyl group to an axial position would be required. The steric bulk of the NMe_2 groups may make this position unfavourable, hence blocking the formation the palladium(IV) intermediate,

'$Pd^{IV}(O_2CPh)_3Tol(tmeda)$'. In contrast, the reaction of $Pd(O_2CPh)Tol(bpy)$ with $(PhCO_2)_2$ does result in formation of Tol-O_2CPh, where the proposed intermediate, '$Pd^{IV}(O_2CPh)_3Tol(bpy)$', would not suffer from steric congestion.

Although these platinum(IV) compounds are useful models for predicting the reaction behaviour of related palladium species, care must be taken in drawing conclusions about palladium chemistry from platinum models. For example, the proposed involvement of free radials in the decomposition of dibenzoyl peroxide (Section 3.2.1.1) indicates that free radical mechanisms cannot be entirely discounted.

3.4 Experimental

3.4.1 General Experimental

3.4.1.1 Instrumentation

Elemental analysis, GC-MS and ^1H NMR spectroscopy were carried out as described in Section 2.3.1.1. ^{13}C NMR spectroscopy was performed on a Varian INOVA-400 NMR operating at 100.50 MHz. Mass spectra were performed by Dr Noel Davies or Mr Marshall Hughes of the Central Science Laboratory, University of Tasmania. Spectra were recorded on a Kratos Concept ISQ mass spectrometer using the LSIMS technique in a 3-nitrobenzoyl (mnba) matrix and an *m/z* scanning range of 50-1500 with an 8 kV probe.

3.4.1.2 Reagents and Solvents

All reactions and manipulations of air and moisture sensitive compounds were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were purified and dried in the normal manner.[51] The reagents MX(NCN) (M= Pd,

Pt; Cl, I)[11] and 4-tolyllithium was prepared as described. Other reagents were used as received.

3.4.2 Synthesis of PtTol(NCN) and M(O_2CAr)(NCN)

PtTol(NCN) (30). In a variation on the preparation described by Terheijden *et al,*[35] a sample of excess freshly prepared 4-tolyllithium (0.25 g, 2.5 mmol) was dissolved in dry diethyl ether (3 mL). This was filtered under inert atmosphere into a cooled (-78 °C) suspension of PtCl(NCN) (0.25 g, 0.59 mmol) in dry diethyl ether (10 mL). The suspension was stirred at low temperature for *ca.* 20 minutes, then at room temperature for two hours. The solvent was removed *in vacuo* and the residue taken up in CH_2Cl_2. The suspension was filtered through Celite, the volume of filtrate reduced and *n*-pentane added to precipitate the off-white product. The solid was rinsed several times with diethyl ether and dried *in vacuo*. Yield: 0.18 g (62 %). Characterisation was as reported by Terheijden *et al.*[35]

Pd(O_2CPh)(NCN) (23). To a sample of silver benzoate (0.09 g, 0.39 mmol) was added a solution of PdCl(NCN) (0.12 g, 0.36 mmol) in acetone (5 mL). The suspension was stirred for one hour in the absence of light then filtered through Celite. The filtrate was concentrated *in vacuo* and *n*-pentane added to precipitate the product. The resulting white solid was isolated, rinsed with *n*-pentane (3 x 2 mL) and dried *in vacuo*. Yield: 0.15 g (98 %). Crystals suitable for X-ray diffraction were obtained by the diffusion of *n*-pentane into a CH_2Cl_2 solution of **23**. ^{1}H NMR (acetone-d_6): δ 8.06 (m, 2H, H2 Ph), 7.4-7.3 (m, 3H, H3 and H4 Ph), 6.94 (dd, 1H, ^3J = 7.8 Hz and ^3J = 6.6 Hz, $H4_{NCN}$), 6.79 (d, 2H, ^3J = 7.5 Hz, $H3_{NCN}$), 4.05 (s, 4H, NCH_2), 2.89 (s, 12H, NCH_3). ^{13}C NMR (acetone-d_6): δ 171.70 (*C*=O), 146.47 ($C2_{NCN}$), 130.33, 128.15, 124.94 ($C4_{NCN}$), 120.35 ($C3_{NCN}$), 74.70 (NCH_2), 52.18 (NCH_3). LSIMS (in mnba): *m/z* 418.1 ($[M]^+$, 3.5 %), 297.1 ($[M\text{-}PhCO_2]^+$, 100 %). Anal. Calcd: C, 54.49; H, 5.78; N, 6.69. Found: C, 54.72; H, 5.65; N, 6.82.

Pt(O_2CPh)(NCN) (24). This compound was prepared from PtCl(NCN) (0.16, 0.38 mmol) and silver benzoate (0.09 g, 0.39 mmol) using a similar procedure to that

described for **23**, but with stirring continued overnight. Yield: 0.18 g (95 %). Crystals suitable for X-ray diffraction were obtained by the diffusion of pentane into a CH_2Cl_2 solution of **24**. ^{1}H NMR (acetone-d_6): δ 8.10 (m, 2H, H2 Ph), 7.4-7.3 (m, 3H, H3 and H4 Ph), 6.92 (dd, 1H, ^3J = 8.5 Hz and ^3J = 6.3 Hz, $H4_{NCN}$), 6.79 (d, 2H, ^3J = 7.7 Hz, $H3_{NCN}$), 4.08 (s, 4H, $^3J_{Pt\text{-}H}$ = 49 Hz, NCH_2), 3.05 (s, 12H, $^3J_{Pt\text{-}H}$ = 38 Hz, NCH_3). ^{13}C NMR (acetone-d_6): δ 172.34 (*C*=O), 145.61 ($C2_{NCN}$), 140.47 ($C1_{NCN}$), 139.43, 130.87, 130.39, 128.39, 124.43 ($C4_{NCN}$), 119.96 ($C3_{NCN}$), 77.29 (NCH_2), 53.80 (NCH_3). LSIMS (in mnba): *m/z* 507.1 ([M]$^+$, 7 %), 385.1 ([M-$PhCO_2$-H]$^+$, 100 %). Anal. Calcd: C, 44.96; H, 4.77; N, 5.52. Found: C, 44.86; H, 4.60; N, 5.77.

Pd(O_2CAr_F)(NCN) (25). This compound was prepared from PdCl(NCN) (0.008 g, 0.24 mmol) and silver 4-(trifluoromethyl)benzoate (0.010 g, 0.33 mmol) using a similar procedure to that described for **23**. Yield: 0.011 g (96 %). ^{1}H NMR (acetone-d_6): δ 8.22 (d, 2H, ^3J = 8.0 Hz, H2 Ar_F), 7.68 (d, 2H, ^3J = 8.0 Hz, H3 Ar_F), 6.95 (dd, 1H, ^3J = 8.0 Hz and ^3J = 7.2 Hz, $H4_{NCN}$), 6.80 (d, 2H, ^3J = 7.6 Hz, $H3_{NCN}$), 4.06 (s, 4H, NCH_2), 2.88 (s, 12H, NCH_3). ^{13}C NMR (acetone-d_6): δ 169.85 (*C*=O), 155.45 ($C1_{NCN}$), 146.43 ($C2_{NCN}$), 130.78, 125.24/125.00 ($C4_{NCN}$), 120.40 ($C3_{NCN}$), 74.67 (NCH_2), 52.15 (NCH_3). LSIMS (in mnba): *m/z* 486.1 ([M]$^+$, 1 %), 297.1 ([M-Ar_FCO_2]$^+$, 100 %).

Pt(O_2CAr_F)(NCN) (26). This compound was prepared from PtCl(NCN) (0.127 g, 0.30 mmol) and silver 4-(trifluoromethyl)benzoate (0.091 g, 0.31 mmol) using a similar procedure to that described for **24**. Yield: 0.17 g (98 %). ^{1}H NMR (acetone-d_6): δ 8.28 (d, 2H, ^3J = 8.5 Hz, H2 Ar_F), 7.72 (d, 2H, ^3J = 8.5 Hz, H3 Ar_F), 6.93 (dd, 1H, ^3J = 8.4 Hz and ^3J = 6.3 Hz, $H4_{NCN}$), 6.80 (d, 2H, ^3J = 7.7 Hz, $H3_{NCN}$), 4.10 (s, 4H, $^3J_{Pt\text{-}H}$ = 49 Hz, NCH_2), 3.05 (s, 12H, $^3J_{Pt\text{-}H}$ = 38 Hz, NCH_3). ^{13}C NMR (acetone-d_6): δ 170.11 (*C*=O), 145.00 ($C2_{NCN}$), 143.76, 141.74 ($C1_{NCN}$), 130.83, 125.35, 123.75 ($C4_{NCN}$), 119.77 ($C3_{NCN}$), 77.38 (NCH_2), 53.54 (NCH_3). LSIMS (in mnba): *m/z* 575.2 ([M]$^+$, 3 %), 385.1 ([M-Ar_FCO_2]$^+$, 100 %). Anal. Calcd: C, 41.74; H, 4.03; N, 4.87. Found: C, 41.62; H, 4.08; N, 4.68.

3.4.3 Synthesis of Platinum(IV) Complexes

***mer*-Pt(O_2CPh)$_3$(NCN) (27).** A solution of Pt(O_2CPh)(NCN) (0.0406 g, 0.0800 mmol) and dibenzoyl peroxide (0.0194 g, 0.0801 mmol) in acetone (5 mL) was heated to 50 °C and stirred for 90 minutes. The volume was reduced and *n*-pentane added to precipitate the product. The yellow solid was rinsed with *n*-pentane and dried *in vacuo*. Yield: 0.0407 g (68 %). ^{1}H NMR (acetone-d_6): δ 8.39 (m, 2H, H2' Ph_{eq}), 7.90 (d, 4H, ^3J = 7.2 Hz, [complex second order coupling also observed], H2 Ph_{ax}), 7.5-7.4 (m, 5H, H3' and H4' Ph_{eq} and H4 Ph_{ax}), 7.31 (t, 4H, ^3J = 7.2 Hz, [complex second order coupling also observed], H3 Ph_{ax}), 7.13 (dd, 1H, ^3J = 8.4 Hz and ^3J = 6.3 Hz, $H4_{NCN}$), 7.04 (d, 2H, ^3J = 7.8 Hz, $H3_{NCN}$), 4.45 (s, 4H, $^3J_{Pt\text{-}H}$ = 28 Hz, NCH_2), 3.05 (s, 12H, $^3J_{Pt\text{-}H}$ = 25 Hz, NCH_3). LSIMS (in mnba): *m/z* 749.4 ([M]$^+$, <1 %), 628.3 ([M-PhCO$_2$]$^+$, 100 %), ([M-2PhCO$_2$]$^+$, 18 %), 385.2 ([M-H-3PhCO$_2$]$^+$, 50 %). Anal. Calcd for **27**.H_2O: C, 51.61; H, 4.73; N, 3.65. Found: C, 51.81; H, 4.56; N, 3.51.

***cis*-Pt(O_2CPh)$_2$Tol(NCN) (28).** To a solution of crude *cis*-PtI$_2$Tol(NCN) [prepared as described by van Koten *et al.*[26] from PtTol(NCN) (0.012 g, 0.025 mmol) and iodine (0.006 g, 0.024 mmol)] in CH_2Cl_2 (3 mL) was added silver benzoate (0.014 g, 0.061 mmol). The suspension was stirred overnight in the absence of light, filtered through Celite and evaporated to dryness leaving a white impure solid. The solid was dissolved in a minimum of acetone and kept at room temperature. A colourless crystalline solid formed within 24 hours in low yield. Crystals suitable for X-ray diffraction were obtained by slow diffusion of *n*-pentane into an acetone solution of **28** at room temperature. ^{1}H NMR (acetone-d_6): δ 8.34 (m, 2H, H2' Ph_{eq}), 8.21 (dd, 1H, ^3J = 8.4 Hz, ^4J = 2.2 Hz, $^3J_{Pt\text{-}H}$ = 29 Hz, $H2_{Tol}$), 7.94 (d, 2H, ^3J = 8.0 Hz, [complex second order coupling also observed], H2 Ph_{ax}), 7.5-7.4 (m, 3H, H3' and H4' Ph_{eq}), 7.32-7.26 (m, 2H, H4 Ph_{ax} and $H4_{NCN}$), 7.18 (t, 2H, ^3J = 7.2 Hz, [complex second order coupling also observed], H3 Ph_{ax}), 7.05 (d, 2H, ^3J = 7.6 Hz, $H3_{NCN}$), 6.92 (dd, 1H, ^3J = 8.4 Hz, ^4J = 2.3 Hz, $H3_{Tol}$), 6.67 (dd, 1H, ^3J = 8.0 Hz, ^4J = 2.0 Hz, $H5_{Tol}$), 6.11 (dd, 1H, ^3J = 8.2 Hz, ^4J = 2.2 Hz, $^3J_{Pt\text{-}H}$ = 40 Hz, $H6_{Tol}$), 4.30 (d, 2H, ^2J = 14.6 Hz, $^3J_{Pt\text{-}H}$ = 38 Hz, NCH_2), 4.15 (d, 2H, ^2J = 14.6 Hz, $^3J_{Pt\text{-}H}$ = 33 Hz,

NCH_2), 3.11 (s, 6H, $^3J_{Pt-H}$ = 25 Hz, NCH_3), 2.60 (s, 6H, $^3J_{Pt-H}$ = 39 Hz, NCH_3), 2.26 (s, 3H, CH_3). Anal. Calcd: C, 55.07; H, 5.04; N, 3.89. Found: C, 54.85; H, 4.78; N, 3.82.

***cis*-Pt(O_2CPh)$_2$Me(NCN) (29).** To a suspension of Pt(O_2CPh)(NCN) (0.010 g, 0.020 mmol) and silver benzoate (0.045 g, 0.20 mmol) in acetone (3 mL) was added iodomethane (12 μL, 0.19 mmol). The suspension was stirred at room temperature overnight in the absence of light then filtered through Celite. The filtrate was concentrated *in vacuo* and pentane added to precipitate the product. The resulting white precipitate was isolated, rinsed with *n*-pentane (3 x 1 mL) and dried *in vacuo*. Yield: 0.009 g (71 %). Crystals suitable for X-ray diffraction were obtained by the diffusion of *n*-pentane into an acetone solution of **29** at -20 °C. ^{1}H NMR (acetone-d_6): δ 8.27 (m, 2H, H2' Ph_{eq}), 7.99 (d, 2H, ^3J = 8.0 Hz, [complex second order coupling also observed], H2 Ph_{ax}), 7.42 (m, 3H, H3' and H4' Ph_{eq}), 7.33 (t,1H, ^3J = 7.2 Hz, [complex second order coupling also observed], H4 Ph_{ax}), 7.27 (t, 2H, ^3J = 7.2 Hz, H3 Ph_{ax}), 7.10 (dd, 1H, J = 8.4 Hz and J = 6.8 Hz, $H4_{NCN}$), 6.99 (d, 2H, ^3J = 7.6 Hz, $H3_{NCN}$), 4.47 (d, 2H, ^2J = 14.4 Hz, $^3J_{Pt-H}$ = 36 Hz, NCH_2), 4.34 (d, 2H, ^2J = 14.4 Hz, $^3J_{Pt-H}$ = 34 Hz, NCH_2), 3.10 (s, 6H, $^3J_{Pt-H}$ = 26 Hz, NCH_3), 2.94 (s, 6H, $^3J_{Pt-H}$ = 36 Hz, NCH_3), 1.62 (s, 3H, $^2J_{Pt-H}$ = 70 Hz, CH_3). LSIMS (in mnba): *m/z* 642.2 ([M-H]$^+$, <1 %), 522.2 ([M-$PhCO_2$]$^+$, 75 %), 385.1 ([M-H-2$PhCO_2$-Me]$^+$, 100 %). Anal. Calcd: C, 50.38; H, 5.01; N, 4.35. Found: C, 50.18; H, 4.98; N, 4.27.

3.4.4 ^{1}H NMR Studies of the Reactions of Palladium(II) and Platinum(II) Complexes

M(O_2CPh)(NCN) (M = Pd, Pt) with ($ArCO_2$)$_2$ (Ar = Ph, Ar_F). In a typical experiment, a solution of ($ArCO_2$)$_2$ in acetone-d_6 (0.3 mL) was added to a solution of M(O_2CAr)(NCN) in acetone-d_6 (0.4 mL). A ^{1}H NMR spectrum was measured immediately after mixing and the reaction monitored until all reagents were consumed. Products of the reaction were identified by ^{1}H NMR.

PtTol(NCN) with $(PhCO_2)_2$. A solution of $Pt(O_2CPh)(NCN)$ and $(PhCO_2)_2$ in dry CD_2Cl_2 was monitored by ^1H NMR. Even under dry conditions, it was difficult to avoid the production of $Pt(O_2CPh)(NCN)$ (**24**), toluene and benzoic acid. Products of the reaction were identified by GC-MS and ^1H NMR.

$M(O_2CPh)(NCN)$ (M = Pd, Pt) with RX (RX = MeI, BzBr). In a typical experiment, an excess of RX was added to a solution of $M(O_2CAr)(NCN)$ in acetone-d_6 (0.7 mL) at room temperature. A ^1H NMR spectrum was measured immediately after mixing and the reaction monitored until all $M(O_2CAr)(NCN)$ was consumed. Products of the reaction were identified by GC-MS and ^1H NMR. This reaction was also carried out at different temperatures and using a 2:1 ratio of reactants.

3.4.5 ^1H NMR Studies of Platinum(IV) Complexes

$Pt(O_2CPh)_2Tol(NCN)$ (28). A solution of **28** in dry acetone-d_6 (0.7 mL) was heated to 50 °C. The sample was monitored by ^1H NMR at *ca.* two hour intervals for several hours. It was then kept at room temperature and monitored daily. This reaction was also carried out in dry toluene-d_8 at 90 °C.

Kinetic studies of the decomposition of $Pt(O_2CPh)_2Me(NCN)$ (29). A solution of **29** (0.0032 g, 0.0050 mmol) in acetone-d_6 (800 μL) was placed in a NMR probe preheated to 50 °C. The sample was monitored for one hour with one spectrum collected every two minutes. Products were identified by ^1H NMR and GC-MS analysis. This experiment was also carried out in toluene-d_8 and a 3 mM solution of tetrabutylammonium benzoate in acetone-d_6.

3.4.6 X-Ray Data Collection, Structure Determination and Refinement

Structures were solved by Prof Allan H. White and Dr Brian W. Skelton, Chemistry, University of Western Australia, as described in Section 2.3.7. Crystal data and details of the structure determination are presented in Table 3.6.

Table 3.6: Specific crystallographic details for $Pd(O_2CPh)(NCN)$ (**23**), $Pt(O_2CPh)(NCN)$ (**24**), $Pt(O_2CPh)_3(NCN).½Me_2CO$ (**27**.$½Me_2CO$), $Pt(O_2CPh)_2Tol(NCN).Me_2CO$ (**28**.Me_2CO) and $Pt(O_2CPh)_2Me(NCN).Me_2CO.H_2O$ (**29**.$Me_2CO.H_2O$).

	23	**24**	**27**.$½Me_2CO$	**28**.Me_2CO	**29**.$Me_2CO.H_2O$
formula	$C_{19}H_{24}N_2O_2Pd$	$C_{19}H_{24}N_2O_2Pt$	$C_{34.5}H_{37}N_2O_{6.5}Pt$	$C_{36}H_{42}N_2O_5Pt$	$C_{30}H_{40}N_2O_6Pt$
fw	418.8	507.5	778.8	777.8	717.7
cryst size, mm^3	0.32x0.23x0.14	0.24x0.22x0.09	0.20x0.14x0.07	0.28x0.22x0.18	0.35x0.09x0.06
cryst system	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	*P*-1	*P*-1	*C*2/*c*	*P*-1	$P2_1/n$
a, Å	8.9377(5)	8.9088(8)	13.0359(8)	11.8427(8)	9.3107(7)
b, Å	9.980696)	10.0224(8)	30.474(2)	12.6435(8)	11.6368(9)
c, Å	11.1160(6)	11.1315(9)	8.9499(6)	12.8944(8)	27.094(2)
α, deg	110.956(1)	110.808(2)	-	100.580(2)	-
β, deg	102.367(1)	102.223(2)	120.484(2)	114.772(1)	95.497(2)
γ, deg.	98.624(1)	98.923(2)	-	104.139(1)	-
V, $Å^3$	$876._2$	$878._7$	1767	1608	1461
Z	2	2	4	2	4
ρ_{calcd}, $g.cm^{-3}$	1.58_7	1.91_8	1.46_3	1.60_6	1.63_1
μ_{Mo}, mm^{-1}	1.07	8.0	4.0	4.4	4.9
$2\theta_{max}$, deg	75	75	75	75	65
$T_{min/max}$	0.70, 0.90	0.33, 0.67	0.50, 0.79	0.47, 0.75	0.57, 0.80
N_t	18083	18095	36780	33458	46630
N	9000	9008	8038	16522	10619
N_0	7730	8216	6547	12566	8242
R_{int}	0.025	0.034	0.060	0.044	0.046
R	0.032	0.025	0.038	0.040	0.049
R_w	0.036	0.031	0.052	0.044	0.072

3.4.6.1 Variations

$Pd(O_2CPh)(NCN)$ (23): $(x, y, z, U_{iso})_H$ were refined.

$Pt(O_2CPh)_3(NCN).½Me_2CO$ ($27.½Me_2CO$): As modeled in space group *C*2/*c*, the benzoate group *trans* to the NCN ligand is disordered about the axis over two sets of sites of equal occupancy. The difference between the two components of the coordinated oxygen is 0.50(1) Å. Attempted refinement in a lower symmetry space group was unsuccessful.

$Pt(O_2CPh)_2Me(NCN).Me_2CO.H_2$) ($29.Me_2CO.H_2O$): Hydrogen atoms were not located in association with the putative water molecule oxygen atom. A substantial difference map residue (9 e $Å^{-3}$) was located 0.7 Å from the metal atom, suggesting, for example, possible cocrystallisation of a minor related impurity.

3.5 References

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CHAPTER FOUR:
Carbon-Selenium Bond Formation at Palladium Centres as a Model For Carbon-Oxygen Bond Formation

4.1 Introduction

Coupling reactions between carbon and oxygen at palladium centres can potentially be modeled by reactions involving other chalcogens such as sulfur and selenium. Several studies have been carried out on the oxidative addition of diorganyl dichalcogenides [$(RE)_2$] to platinum and palladium complexes, which are related to reactions of diaroyl peroxides discussed in Chapter Two.[1-9] While the majority of these investigations have been concerned with additions to palladium(0), platinum(0) and platinum(II) complexes, a small body of work has also considered addition to palladium(II) complexes, resulting in the isolation of some stable diorganopalladium(IV) complexes.[9]

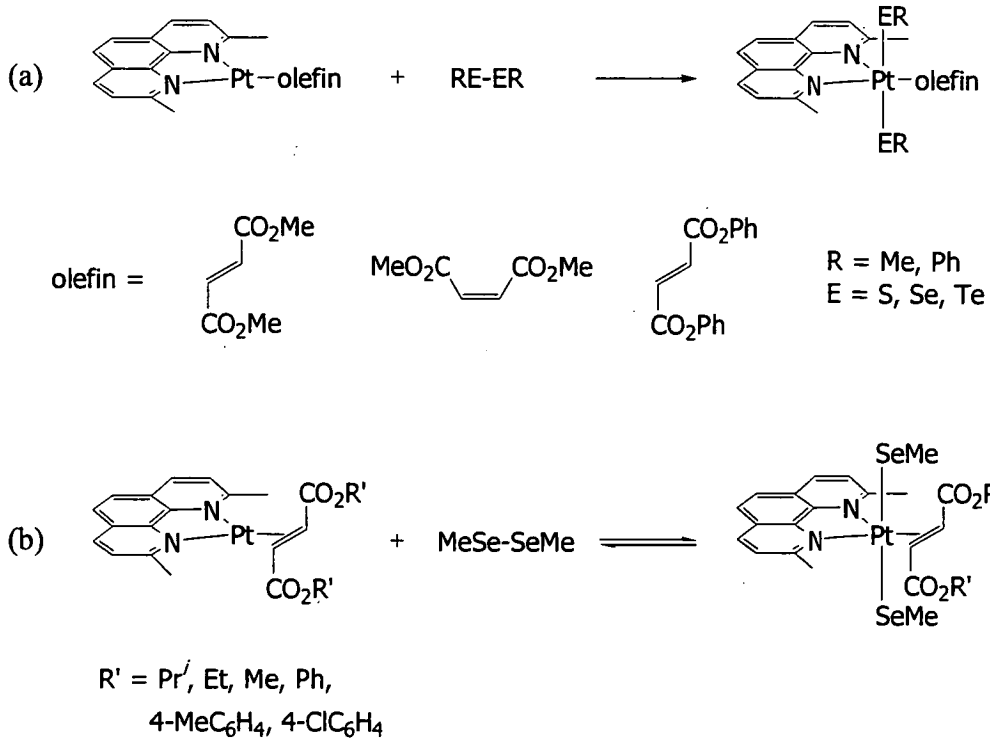
While sulfur may be expected to be a better electronic model for oxygen than selenium, previous studies have shown that palladium(IV) complexes incorporating sulfur-metal bonds tend to be less stable than selenium analogues.[9] Therefore, diorganyl diselenides were chosen over diorganyl disulfides in an attempt to observe and isolate palladium(IV) species.

The reaction of $(RSe)_2$ with platinum(0) complexes leads to cleavage of the Se-Se bond and the formation of a platinum(II) product. Reaction between $Pt(PPh_3)_4$ and $(PhSe)_2$ resulted in the displacement of two of the PPh_3 ligands and formation of *cis*-$Pt(SePh)_2(PPh_3)_2$, which then underwent isomerisation to *trans*-$Pt(SePh)_2(PPh_3)_2$.[5] By contrast, when the same reaction was carried out using $Pd(PPh_3)_4$ as reagent, dinuclear complexes with two bridging selenolate ligands were

formed, *cis*- and *trans*-$[Pd_2(SePh)_4(PPh_3)_2]$.[3,5,10] Analogous results were found for the oxidative addition of $(ThTe)_2$ and $(ThSe)_2$ (Th = C_4H_3S) to $Pd(PPh_3)_4$.[4,7] The reaction of $Pt(PPh_3)_4$ with $(ThSe)_2$ gave a mixture of *cis*- and *trans*-$Pt(SeTh)_2(PPh_3)_2$.[4]

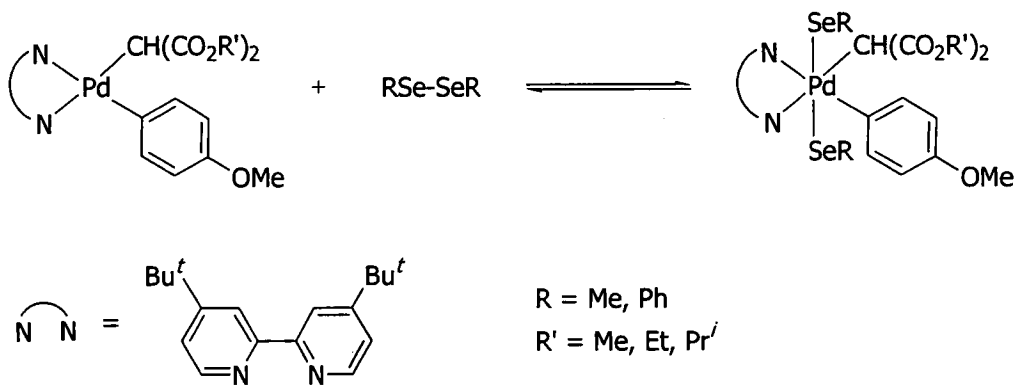
The reaction of platinum(0) complexes of the form Pt(olefin)(dmphen) (olefin = dimethylmaleate, dimethylfumarate, diphenylfumarate; dmphen = 2,9-dimethyl-1,10-phenanthroline) with $(RE)_2$ (R = Me, Ph; E = S, Se) and $(PhTe)_2$ also resulted in the oxidative addition of the dichalcogenide, yielding platinum(II) complexes of the form *trans*-$Pt(ER)_2$(olefin)(dmphen) (Scheme 4.1a).[1,2] In the case where the oxidant was dimethyl diselenide and the olefin was a fumaric ester [diethylfumarate, diisopropylfumarate, diphenylfumarate, di(4-methylphenyl)fumarate, di(4-chlorophenyl)fumarate], equilibria involving detectable concentrations of all species were established (Scheme 4.1b).[1] These complexes display trigonal bipyramidal geometry.

Scheme 4.1: Reaction of $(RE)_2$ with platinum(0) complexes Pt(olefin)(dmphen).



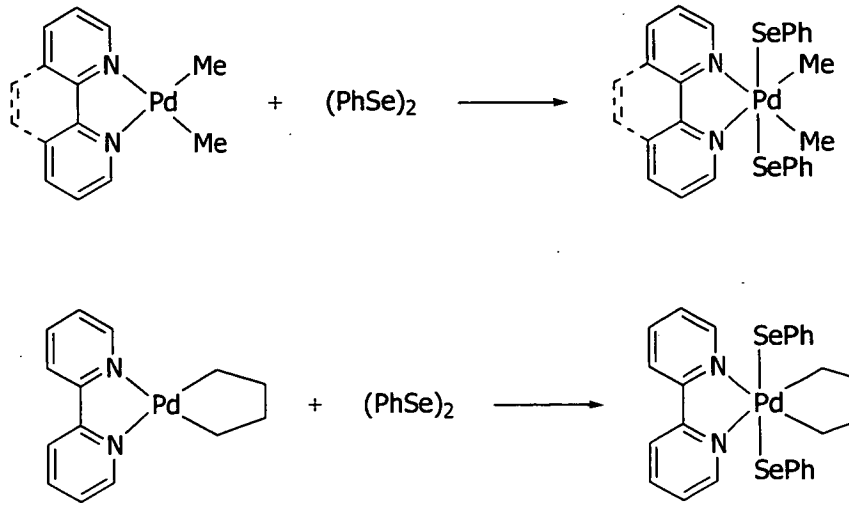
Investigations into oxidative addition reactions of $(RSe)_2$ to platinum(II) and palladium(II) complexes are limited.[8,9,11] The most straightforward of those reported have involved the quantitative addition of $(PhSe)_2$ to $PtMe_2(L_2)$ (L_2 = bpy, phen) to give the *trans*-addition product, $Pt(SePh)_2Me_2(L_2)$.[9,11] In a slightly more complicated scenario, reversible cleavage of the selenium-selenium bond in $(RSe)_2$ (R = Me, Ph) was observed during its reaction with platinum(II) complexes of the form $Pt[CH(CO_2R')_2](Anis)(Bu^tbpy)$ (R' = Me, Et, Pr^i), as shown in Scheme 4.2.[8]

Scheme 4.2: Reversible oxidative addition of $(RSe)_2$ to Pt(II) complexes, $Pt[CH(CO_2R')_2](Anis)(Bu^tbpy)$.[8]



Reports of oxidative addition of diorganyl diselenides to palladium(II) complexes to give diorganopalladium(IV) complexes are rare.[9,12] Canty and coworkers found that the reaction between $(PhSe)_2$ and palladium(II) complexes $PdMe_2(L_2)$ (L_2 = bpy, phen) and $Pd(CH_2CH_2CH_2CH_2)(bpy)$ led to the formation of moderately stable palladium(IV) complexes, as shown in Scheme 4.3.[9] The complexes $Pd(SePh)_2Me_2(L_2)$ underwent decomposition *via* both carbon-carbon and carbon-selenium bond formation.[9] Similar reactions were carried out using diphenyl disulfide as oxidant, and while $Pd(SPh)_2Me_2(bpy)$ was detected transiently, these palladium(IV) species did not display the same level of stability as the selenium analogues, and were not able to be isolated.[9,12]

Scheme 4.3: The reaction of $(PhSe)_2$ with Pd(II) complexes, $PdMe_2(L_2)$ (L_2 = bpy, phen) and $\overline{Pd(CH_2CH_2CH_2CH_2)}(bpy)$.[9]



Motivated by the latter studies, reactions of bis(4-chlorophenyl) diselenide [$(ClC_6H_4Se)_2$] with PdMeR(tmeda) [R = Me, 4-tolyl (Tol)] and PdMeAr(bpy) [Ar = 4-anisyl (Anis), Tol] were investigated as potential models for the reactions of PdMeR(tmeda) (R = Me, Tol) and PdMeTol(bpy) with diaroyl peroxides discussed in Chapter Two. Reactions with PdMeR(dmpe) (R = Me, Tol; dmpe = 1,2-bis(dimethylphosphino)ethane) were also studied as bidentate phosphine analogues of PdMeR(tmeda).

4.2 Results and Discussion

4.2.1 ^{1}H NMR Studies of the Reaction of PdMeAr(bpy) (Ar = Anis, Tol) with $(ClC_6H_4Se)_2$

4.2.1.1 The reaction of PdMe(Anis)(bpy) with $(ClC_6H_4Se)_2$

PdMe(Anis)(bpy) was chosen as an aryl-containing analogue of $PdMe_2(bpy)$ in an attempt to observe aryl-selenium coupling from a palladium(IV) species. The choice of *para*-substituted aryl groups in both reagents led to a simplified aromatic region in

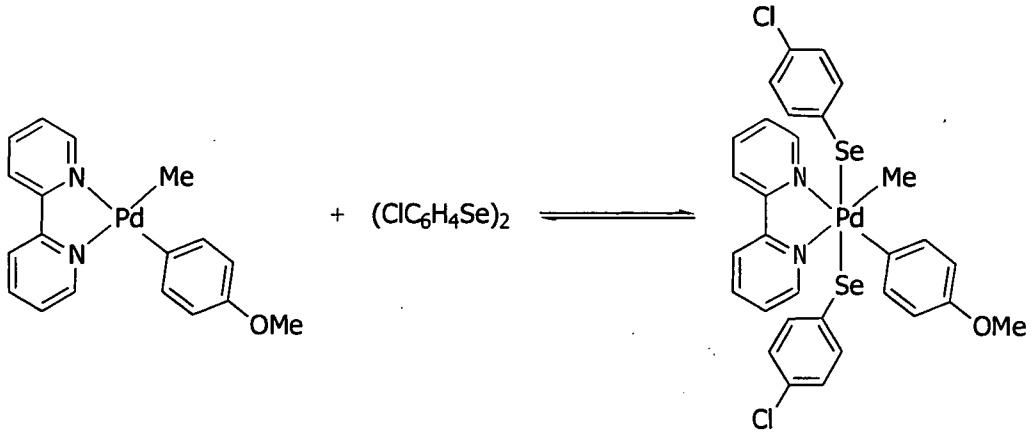
^{1}H NMR spectroscopy, and provided well resolved aliphatic signals to follow in addition to the PdMe group.

The reaction of PdMe(Anis)(bpy) with $(ClC_6H_4Se)_2$ was studied by ^{1}H NMR spectroscopy in CD_2Cl_2 at several temperatures. When the reagents were mixed in equal amounts at room temperature, the reaction proceeded slowly (overnight) to form a complex mixture of products along with an insoluble orange solid.

When the same reaction was carried out at temperatures below *ca.* –25 °C, a slow reaction was observed to form an intermediate palladium(IV) species. The reaction did not proceed to full consumption of the reagents, with the palladium(IV) species always present along with the palladium(II) and diselenide reagents. The formation of the palladium(IV) species was indicated by the appearance of bpy, PdMe and OMe resonances downfield of the starting palladium(II) complex, and by a colour change from a clear orange to a clear, dark red solution. Although the aromatic region of the spectrum was complex, a new H6/6' bpy signal could be clearly seen 0.13 ppm downfield of the equivalent proton of the starting complex. The OMe signal shifted downfield by 0.08 ppm and the PdMe resonance by 2.16 ppm. The appearance of only one set of new signals indicated that only one isomeric form of the palladium(IV) species was present. The chemical shift equivalence of the two 4-chlorophenyl selenolate moieties suggested that it was the *trans*-addition product, $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ (**31**) (Scheme 4.4). Details of the characterisation of **31** are discussed in Section 4.2.4.1.

When there was no further reaction detected, the solution was warmed slowly. Interestingly, decomposition products were not observed initially. Rather, the reagents PdMe(Anis)(bpy) and $(ClC_6H_4Se)_2$ were reformed, and when the temperature was lowered again **31** was regenerated. This, and the above observation that the reaction did not appear to go to completion, suggested that an equilibrium between the reagents and the intermediate palladium(IV) species existed (Scheme 4.4). This equilibrium is discussed further in Section 4.2.1.2, and estimations of equilibrium constants and thermodynamic parameters presented in Section 4.2.1.3.

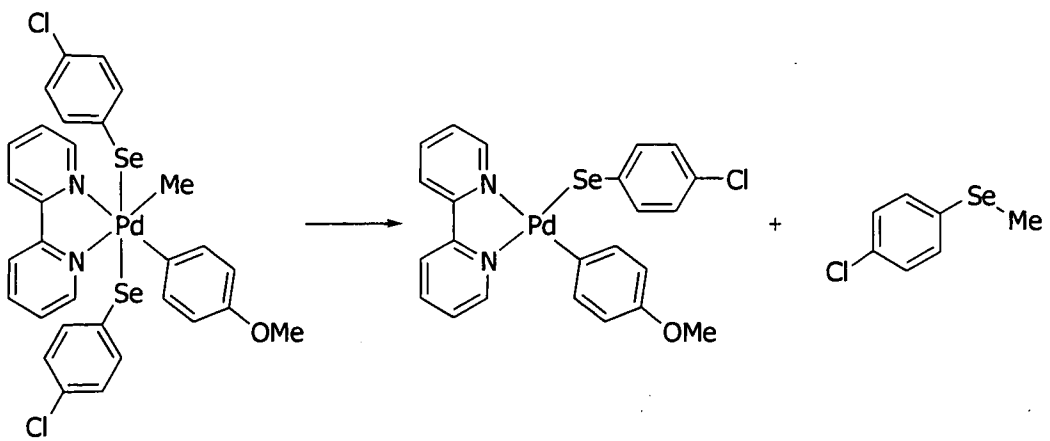
Scheme 4.4: Equilibrium between reagents PdMe(Anis)(bpy) and $(ClC_6H_4Se)_2$ and the Pd(IV) intermediate $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ (**31**).



31

When the temperature was raised slowly above *ca.* –25 °C, a gradual decomposition of **31** was observed with Me-SeC_6H_4Cl and $Pd(SeC_6H_4Cl)(Anis)(bpy)$ as the major products (> 95 %) formed (Scheme 4.5). This suggests that reductive elimination from **31** is almost selective for selenium-methyl coupling. Over time, the signals caused by $Pd(SeC_6H_4Cl)(Anis)(bpy)$ broadened and eventually disappeared. The disappearance of these resonances may be due to the gradual precipitation and/or decomposition of $Pd(SeC_6H_4Cl)(Anis)(bpy)$.

Scheme 4.5: Reductive elimination of a C-Se bond from $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ (**31**).

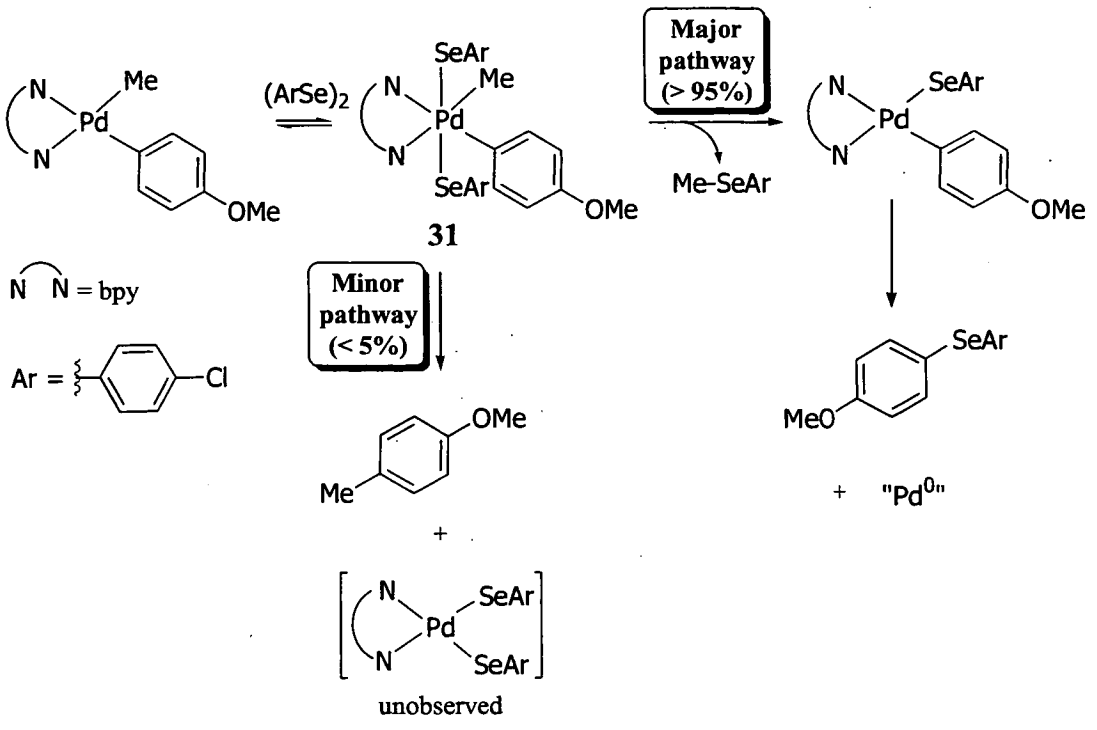


31

A small amount (< 5 %) of 4-methoxytoluene (Me-Anis) was also observed at this stage of the reaction (> *ca.* –25 °C). It is likely that this originated by carbon-carbon bond forming reductive elimination from the palladium(IV) intermediate (Scheme 4.6). Consequently, the inorganic palladium(II) species $Pd(SeC_6H_4Cl)_2(bpy)$ was presumably produced, but was not identified by ^1H NMR studies due to the high complexity of the aromatic region and the low level of the complex expected to be present. It is also possible that this species is insoluble and precipitates from solution or that it decomposes in solution. 4-Methoxytoluene (Me-Anis) could also potentially form by the decomposition of PdMe(Anis)(bpy). However, observations of this complex in CD_2Cl_2 showed it to be stable for at least 24 hours at room temperature. Over extended periods, decomposition occurred slowly to give Me-Anis, 4,4'-dimethoxybiphenyl and free bpy along with some unidentified products.

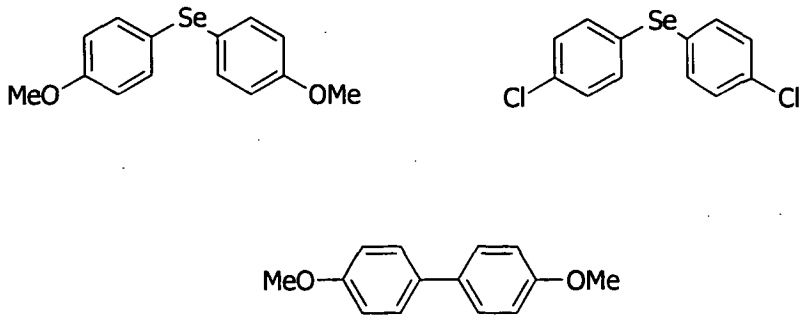
When the reaction of PdMe(Anis)(bpy) with $(ClC_6H_4Se)_2$ was kept at room temperature for longer periods, other products began to form. Included, amongst others, was Anis-SeC_6H_4Cl. The appearance of this compound *after* the decomposition of the palladium(IV) intermediate was nearly complete suggested that aryl-selenium coupling *did not* occur *via* reductive elimination from **31**. Moreover, there was no evidence for the presence of $Pd(SeC_6H_4Cl)Me(bpy)$, which would be expected if Anis-SeC_6H_4Cl was forming by reductive elimination from the observed palladium(IV) species. It can be envisaged that reductive elimination might occur from the palladium(II) species $Pd(SeC_6H_4Cl)(Anis)(bpy)$ to give Anis-SeC_6H_4Cl and an unidentified palladium(0) species as shown in Scheme 4.6. This may also help to explain why free bpy is observed as a product. Therefore, it is likely that the reaction observed between PdMe(Anis)(bpy) and $(ClC_6H_4Se)_2$ follows the reaction sequence shown in Scheme 4.6.

Scheme 4.6: Possible reaction sequence for the reaction of PdMe(Anis)(bpy) with $(ClC_6H_4Se)_2$ to form C-Se and C-C bonds (at temperatures above *ca.* –25 °C).



Other compounds present at the end of the reaction were formed in minor quantities, and were unobserved in some trials of this reaction. These included 4,4'-dimethoxybiphenyl [$(Anis)_2$], $Se(C_6H_4Cl)_2$ and $Se(Anis)_2$ (Figure 4.1). Their presence was detected by a combination of ^1H NMR and GC-MS analysis. Although all were observed by GC-MS, the complexity of the ^1H NMR spectra and the small amounts present meant that not all compounds were conclusively identified in the ^1H NMR spectra. Furthermore, the relative amounts of product seen by GC-MS did not always agree with those seen by NMR. Thus, the possibility that some products were, at least partly, formed during CG-MS cannot be ruled out.

Figure 4.1: Minor products of the reaction of PdMe(Anis)(bpy) and $(ClC_6H_4Se)_2$ in CD_2Cl_2.



As discussed in Chapter Two, biaryl formation is commonly seen in palladium mediated reactions. Hence, the observation of $(Anis)_2$ as a product is not surprising. The mechanism by which it is formed is not obvious from these reactions, but it could be related to the route proposed by Yamamoto *et al.* in which biaryl formation occurs *via* organic group exchange reactions between palladium(II) centres followed by decomposition of an unstable $Pd^{II}Ar_2(bpy)$ species (Scheme 2.9, Section 2.2.2.1).[13]

Compounds analogous to $Se(C_6H_4Cl)_2$ and $Se(Anis)_2$ have been observed in comparable reactions of palladium(II) complexes with $(PhE)_2$ (E = S, Se).[9] Canty and coworkers observed the formation of SPh_2 from the reactions of $(PhS)_2$ with $PdMe_2(bpy)$ and $Pd(CH_2CH_2CH_2CH_2)(bpy)$ and the formation of $SePh_2$ from the reactions of $PdMe_2(L_2)$ (L_2 = bpy, phen) with $(SePh)_2$.[9] It was postulated that such products could form from the reaction of decomposition products of the form R-EPh with palladium(II) products, '$Pd^{II}EPh$', to give '$Pd^{IV}(EPh)(ER)Ph$', which could then reductively eliminate $E(Ph)_2$.[9] The oxidative addition of carbon-chalcogen bonds to palladium(0) centres is known, with the addition of carbon-tellurium bonds shown to occur at a faster rate than the addition of highly reactive carbon-iodine bonds.[14] Carbon-selenium bonds are less reactive but do undergo oxidative addition to $Pt(PEt_3)_4$ at 50 °C.[14]

There is no evidence for the involvement of the solvent, CD_2Cl_2, in the reaction. This is in contrast to similar reactions with tmeda analogues (discussed in Section

4.2.2) and some other reported reactions in which minor side products forming from the reaction of intermediates with dichloromethane were observed.[3,4] This is discussed in greater detail in Section 4.2.2.

When the reaction of PdMe(Anis)(bpy) with $(ClC_6H_4Se)_2$ was carried out at 40 °C, the palladium(IV) intermediate was not observed, and within 30 minutes, the reaction had gone to completion. The major products were Me-SeC_6H_4Cl and an orange solid. Small amounts of other decomposition products were also observed.

The reaction of PdMe(Anis)(bpy) with excess $(ClC_6H_4Se)_2$ at room temperature led to a less complicated ^1H NMR spectrum than that observed for the reaction where a 1:1 ratio of reagents was used. The main products seen by ^1H NMR were Me-SeC_6H_4Cl, Anis-SeC_6H_4Cl, free bpy and unreacted $(ClC_6H_4Se)_2$, together with an insignificant amount of Me-Anis. GC-MS also showed $Se(C_6H_4Cl)_2$ as a major product. This was not seen by ^1H NMR spectroscopy, suggesting that it probably formed on the GC column. It is possible to rationalise the absence of the other side products observed previously through consideration of the proposed mechanism. The presence of excess $(ClC_6H_4Se)_2$ would force the equilibrium towards palladium(IV). Therefore, no palladium(II) reagent would be available to undergo any side reactions. It is also possible that the decomposition product, Pd(SeC_6H_4Cl)(Anis)(bpy), can undergo further reaction with the excess diselenide to form Pd$(SeC_6H_4Cl)_2$(bpy) and Anis-SeC_6H_4Cl. A similar reaction has been shown to occur between Pd(SeC_6H_4Cl)Tol(dmpe) and $(ClC_6H_4Se)_2$ (see Section 4.2.3.2), and it would also be analogous to the reactions of Pd(O_2CAr)Tol(bpy) (Ar = Ph, Ar_F) with diaroyl peroxides discussed in Chapter Two. If such a reaction is taking place, it might also be acting as a competing side process in the reactions of PdMe(Anis)(bpy) with $(ClC_6H_4Se)_2$ and also in the reactions of Pd$(SeC_6H_4Cl)_2$Me(Anis)(bpy) (Section 4.2.1.2), particularly at higher temperatures.

4.2.1.2 Reactions of $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$

In order to further study the equilibrium involving $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ (**31**) and its decomposition, the palladium(IV) species was prepared by an independent method (see Section 4.2.4.1).

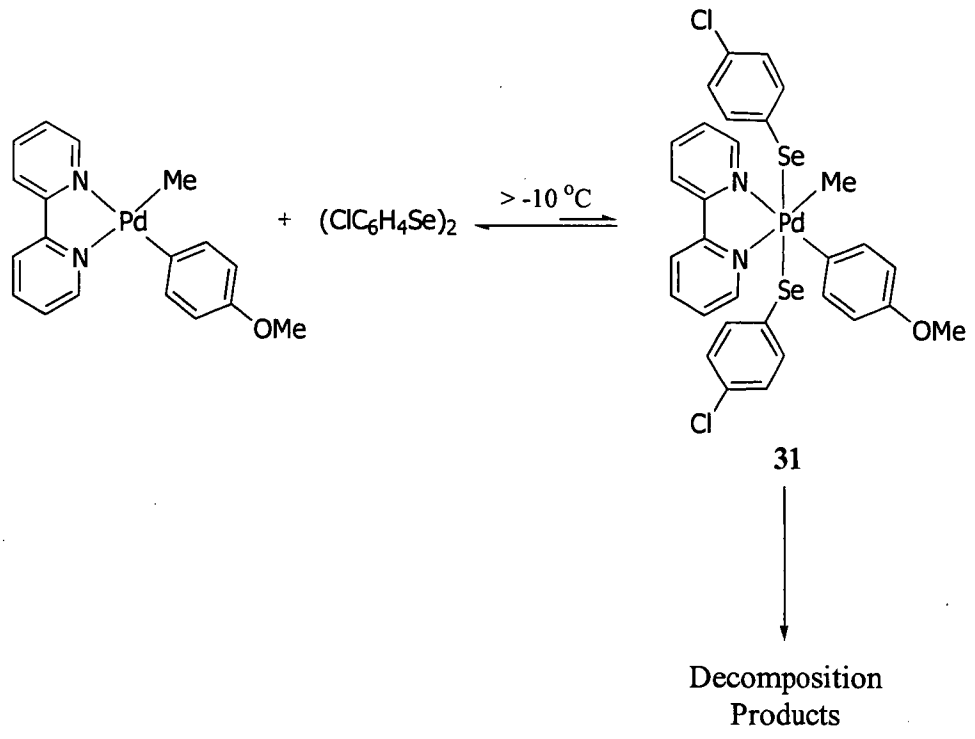
The behaviour of **31** at various temperatures in solution demonstrates the reversible nature of the oxidative addition of $(ClC_6H_4Se)_2$ to PdMe(Anis)(bpy). When a solution of **31** was monitored at –40 °C in CD_2Cl_2, a slow reaction to form a small amount of PdMe(Anis)(bpy) and $(ClC_6H_4Se)_2$ was observed. At –20 °C, the equilibrium still lay towards the palladium(IV) species, but the palladium(II) species was present in an almost equivalent concentration. Between –20 and –10 °C, the equilibrium shifted to favour the palladium(II) species.

A ^1H NMR spectrum of **31** measured immediately after the complex was dissolved in CD_2Cl_2 at room temperature showed the presence of a significant amount of PdMe(Anis)(bpy) and $(ClC_6H_4Se)_2$ and minor amounts of decomposition products. After 30 minutes, the mixture was predominantly PdMe(Anis)(bpy) and $(ClC_6H_4Se)_2$ with small amounts of **31** and decomposition products also present. The solution had also changed from a clear dark red to a clear orange colour similar to that noted when PdMe(Anis)(bpy) and $(ClC_6H_4Se)_2$ are first mixed. The reaction then proceeded in an identical manner to the reaction of PdMe(Anis)(bpy) with $(ClC_6H_4Se)_2$ at room temperature, as described in the previous section.

When **31** was followed at higher temperature (40 °C), a similar reaction pattern was observed. Within 10 minutes, the colour had changed to orange and ^1H NMR studies showed that the palladium(IV) species had been converted to predominantly PdMe(Anis)(bpy) and $(ClC_6H_4Se)_2$. After a further 50 minutes at this temperature, several 'decomposition' products had formed and an orange solid had started to precipitate.

The above results indicate that at higher temperatures the equilibrium between PdMe(Anis)(bpy) and $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ lies significantly towards the palladium(II) species. At temperatures where the decomposition of the palladium(IV) species is facile, the equilibrium lies almost completely towards the palladium(II) complex. As palladium(IV) is formed, it decomposes quickly driving the reaction to produce more palladium(IV). This explains why, when carried out at higher temperatures, the palladium(IV) intermediate is not seen (Scheme 4.7).

Scheme 4.7: The behaviour of the equilibrium between PdMe(Anis)(bpy) and $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ (**31**) at temperatures above *ca.* –10 °C.

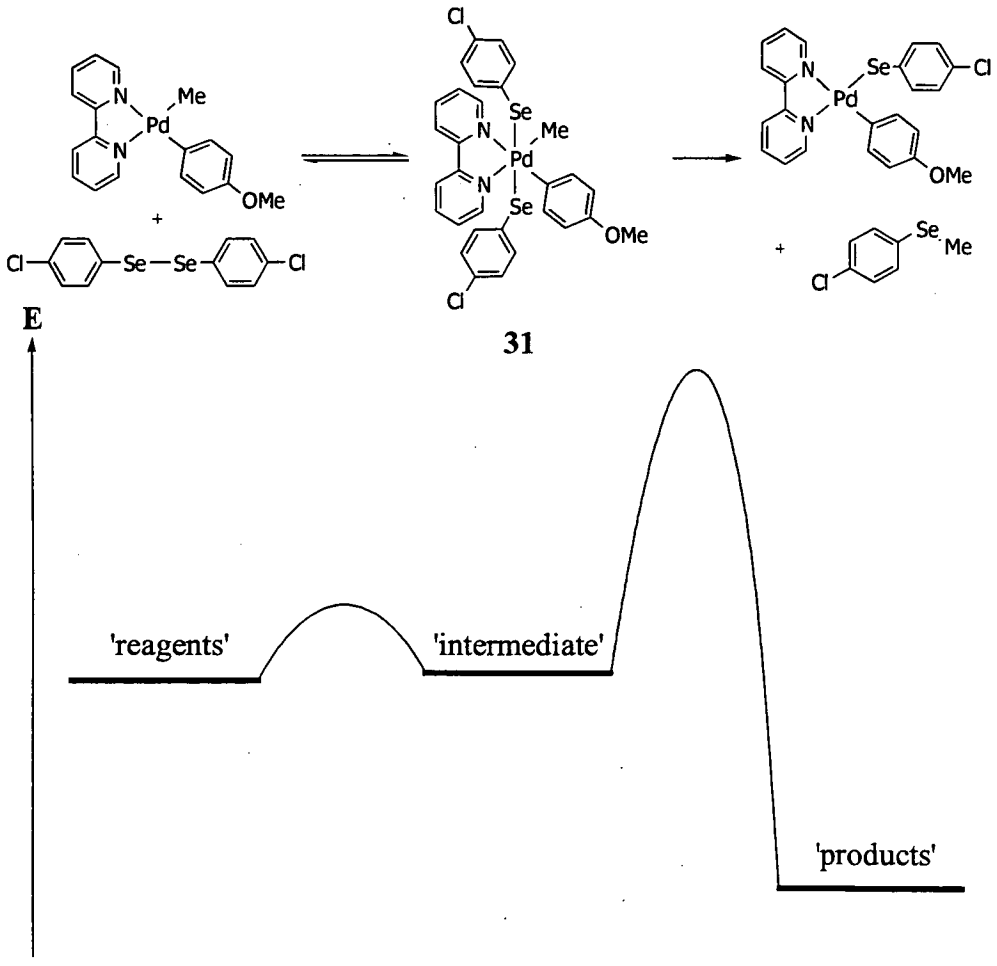


4.2.1.3 Estimation of Equilibrium Constants and Thermodynamic Parameters

Taking into consideration the behaviour of the reaction of PdMe(Anis)(bpy) with $(ClC_6H_4Se)_2$ at different temperatures, it is possible to form a qualitative view of the relative energy levels of the reagents, intermediates and products. The reversible nature of the initial oxidative addition suggests that the 'reagents', PdMe(Anis)(bpy) and $(ClC_6H_4Se)_2$, and the 'intermediate', $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$, are close in energy and there is a relatively low activation energy for the equilibrium (Figure

4.2). The reluctance of the palladium(IV) intermediate to decompose to the 'products', $Pd(SeC_6H_4Cl)(Anis)(bpy)$ and $Me\text{-}SeC_6H_4Cl$, at low temperature suggests this step of the reaction has a relatively high activation energy. The irreversibility of the decomposition suggests that the 'products' are low in energy compared with the 'intermediate' and 'reagents' (Figure 4.2).

Figure 4.2: Qualitative representation of relative energies of involved species and activation energies for the formation of $Me\text{-}SeC_6H_4Cl$ from the reaction of $PdMe(Anis)(bpy)$ with $(ClC_6H_4Se)_2$.



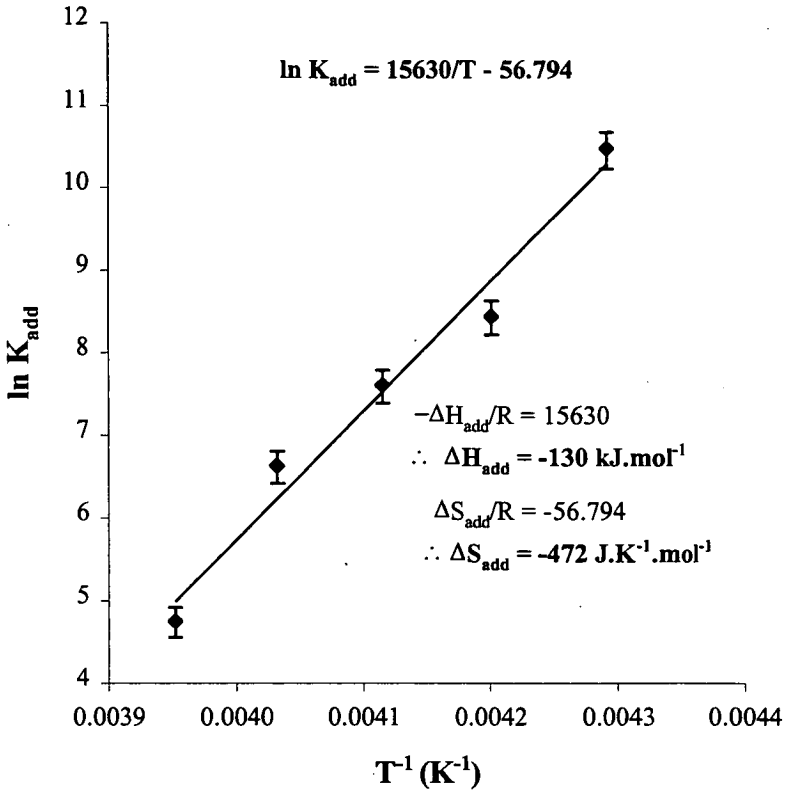
The equilibrium between $PdMe(Anis)(bpy)$ and $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ was studied in more detail, allowing equilibrium constants (K_{add}) at various temperatures to be determined and, consequently, thermodynamic parameters to be estimated. The equilibrium was studied by monitoring reductive elimination from $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ (**31**) to $PdMe(Anis)(bpy)$ and $(ClC_6H_4Se)_2$, or by

monitoring the oxidative addition of $(ClC_6H_4Se)_2$ to PdMe(Anis)(bpy) in 1:1 mole ratio in CD_2Cl_2 by ^1H NMR. The use of the isolated palladium(IV) species had the advantage that the reagents could not be present in ratios even slightly different from 1:1. The range of temperatures within which the equilibrium constant could be determined was limited to temperatures where the decomposition of **31** did not occur too rapidly and at which the equilibrium reactions proceeded at a reasonable rate. With this in mind, the equilibrium constant was determined at several temperatures between –40 and –20 °C (Table 4.1). In accordance with the equation $\ln K_{add} = -\Delta H_{add}/RT + \Delta S_{add}/R$ ($R = 8.314$ J.mol^{-1}.K^{-1}), a plot of $\ln K_{add}$ (y-axis) against T^{-1} (x-axis) allowed ΔH_{add} and ΔS_{add} to be estimated. The parameter ΔH_{add} was determined from the gradient of the line of best fit, to be -130 ± 12 kJ.mol^{-1} and ΔS_{add}, from the y-intercept, to be -472 ± 49 J.K^{-1}.mol^{-1} (Figure 4.3). The value determined for ΔH_{add} was approximately double that for the related platinum reactions and ΔS_{add} was almost four times that of the other reactions (Table 4.2).

Table 4.1: Estimated equilibrium constants for the reaction PdMe(Anis)(bpy) + $(ClC_6H_4Se)_2 \rightarrow Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ at various temperatures.

Temperature (°C)	K_{add}
-40	35408 ± 7750
-35	4628 ± 950
-30	2010 ± 400
-25	754 ± 145
-20	116 ± 20

Figure 4.3: Graph of ln K_{add} *versus* T^{-1} with the equation for the line of best fit and calculations for ΔH_{add} and ΔS_{add} shown.



The values given for K_{add}, ΔH_{add} and ΔS_{add} can only be considered as estimates for a number of reasons. The main source of error in these experiments arises from the integration of resonances in NMR spectra. As such, a 5 % error on integration was allowed, as done by Panunzi *et al.* in studying a related system.[8] The propagation of error was considered, and the values for the equilibrium constants calculated to have errors of *ca.* 18 - 22 %. This was comparable with the errors reported by Panunzi *et al.* of 20 – 25 %.[8] The reactions were very slow to reach equilibrium, particularly at the lower temperatures. Consequently, in some cases it was difficult to be certain that equilibrium had been reached, and that the reaction was not simply proceeding at a very slow rate. At –20 and –25 °C, very small amounts of decomposition products were observed. However, these appeared very slowly, and hence should have minimal effect on the equilibrium constants determined.

Table 4.2: Approximate ΔH_{add} and ΔS_{add} values for the reaction of PdMe(Anis)(bpy) with $(ClC_6H_4Se)_2$, and for related reactions of Pt(0) and Pt(II) complexes.

Complex	$(RSe)_2$	ΔH_{add} [a]	ΔS_{add} [b]
PdMe(Anis)(bpy)	$(ClC_6H_4Se)_2$	-130	-472
Pt(CH(CO_2Me)$_2$)(Anis)(Bu^{t}bpy) [8]	$(PhSe)_2$	59[d]	-184
Pt(Pr^i-fu)(dmphen)[c] [1]	$(MeSe)_2$	-63	-151
Pt(Et-fu)(dmphen)[c] [1]	$(MeSe)_2$	-65	-159
Pt(Me-fu)(dmphen)[c] [1]	$(MeSe)_2$	-56	-130

[a] in kJ.mol^{-1}
[b] in J.K^{-1}.mol^{-1}
[c] fu = fumarate
[d] Reported as a positive value but assumed to actually be –59 kJ.mol^{-1}.

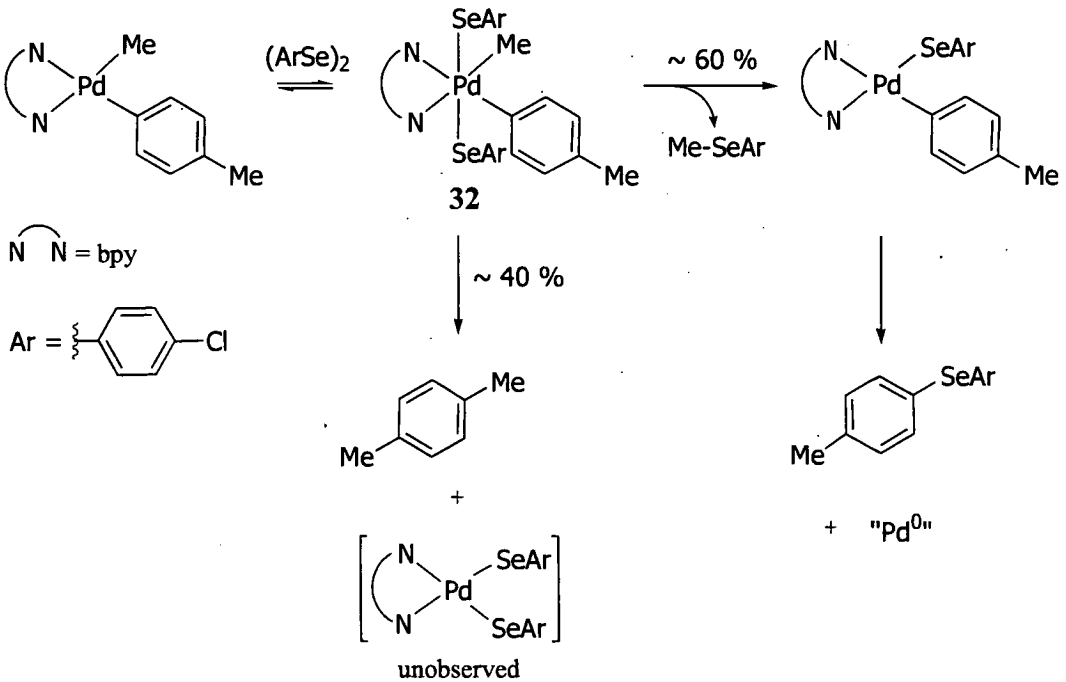
4.2.1.4 The Reaction of PdMeTol(bpy) with $(ClC_6H_4Se)_2$

The reaction of PdMeTol(bpy) with $(ClC_6H_4Se)_2$ was investigated by ^{1}H NMR spectroscopy in order to determine whether it occurs in a similar manner as described for the reaction with PdMe(Anis)(bpy). It also provided a means for direct comparison of the reactions of PdMeTol(bpy) with $(ClC_6H_4Se)_2$ and with $(ArCO_2)_2$ (discussed in Chapter Two). The use of PdMeTol(bpy) as the starting complex had the drawback that, in addition to a complex aromatic region, the products shared similar shifts in the aliphatic region. Consequently, the spectra were somewhat more difficult to interpret than those of those involving PdMe(Anis)(bpy).

It was clear, nevertheless, that this reaction behaved similarly to the one using PdMe(Anis)(bpy) as reagent. When kept at –40 °C, a 1:1 mixture of reagents reacted slowly to form the palladium(IV) species, Pd(SeC_6H_4Cl)$_2$MeTol(bpy) (**32**). As noted for the previous reaction, the addition was not quantitative, with the palladium(IV) species existing in equilibrium with the reagents. When warmed to room temperature, the equilibrium shifted almost completely back to the reagents before 'decomposition' products were observed. Initially, the only products formed had resonances consistent with the presence of Me-SeC_6H_4Cl, Pd(SeC_6H_4Cl)Tol(bpy), Tol-Me and some free bpy. The formation of Tol-SeC_6H_4Cl was not apparent until later in the reaction, suggesting that the decomposition of **32** occurs preferentially by

alkyl-selenium coupling, and that Tol-SeC_6H_4Cl formation may occur *via* reductive elimination from $Pd(SeC_6H_4Cl)Tol(bpy)$. These observations suggest a reaction sequence similar to that of the reaction with PdMe(Anis)(bpy) (Scheme 4.8), although the extent of carbon-carbon (*ca.* 40 %) coupling was greater than that seen in the reaction with PdMe(Anis)(bpy) (< 5 %).

Scheme 4.8: Possible mechanism for the reaction of PdMeTol(bpy) with $(ClC_6H_4Se)_2$



4.2.2 ^{1}H NMR Studies of the Reaction of PdMeR(tmeda) (R = Me, Tol) and $(ClC_6H_4Se)_2$

As discussed earlier, it has been reported that the reaction between $PdMe_2(bpy)$ and $(PhSe)_2$ led to the isolation of the palladium(IV) intermediate, $Pd(SePh)_2Me_2(bpy)$.[9] The latter complex was shown to decompose *via* both carbon-carbon and carbon-selenium bond formation to form Me-SePh and ethane as the major products, along with unidentified palladium(II) products.[9] Similarly, the reactions discussed in Section 4.2.1 demonstrate that reactions between PdMeAr(bpy) (Ar = Anis, Tol) and $(ClC_6H_4Se)_2$ lead to the formation of

palladium(IV) species, $Pd(SeC_6H_4Cl)_2MeAr(bpy)$, which decompose *via* both carbon-carbon and carbon-selenium bond formation. In order to investigate related systems containing a flexible, aliphatic ancillary ligand, the reactions of PdMeR(tmeda) (R = Me, Tol) with $(ClC_6H_4Se)_2$ were studied. These reactions were also carried out in order to test their suitability as a model for analogous reactions with $(ArCO_2)_2$ (Chapter Two).

4.2.2.1 The Reaction of $PdMe_2$(tmeda) with $(ClC_6H_4Se)_2$

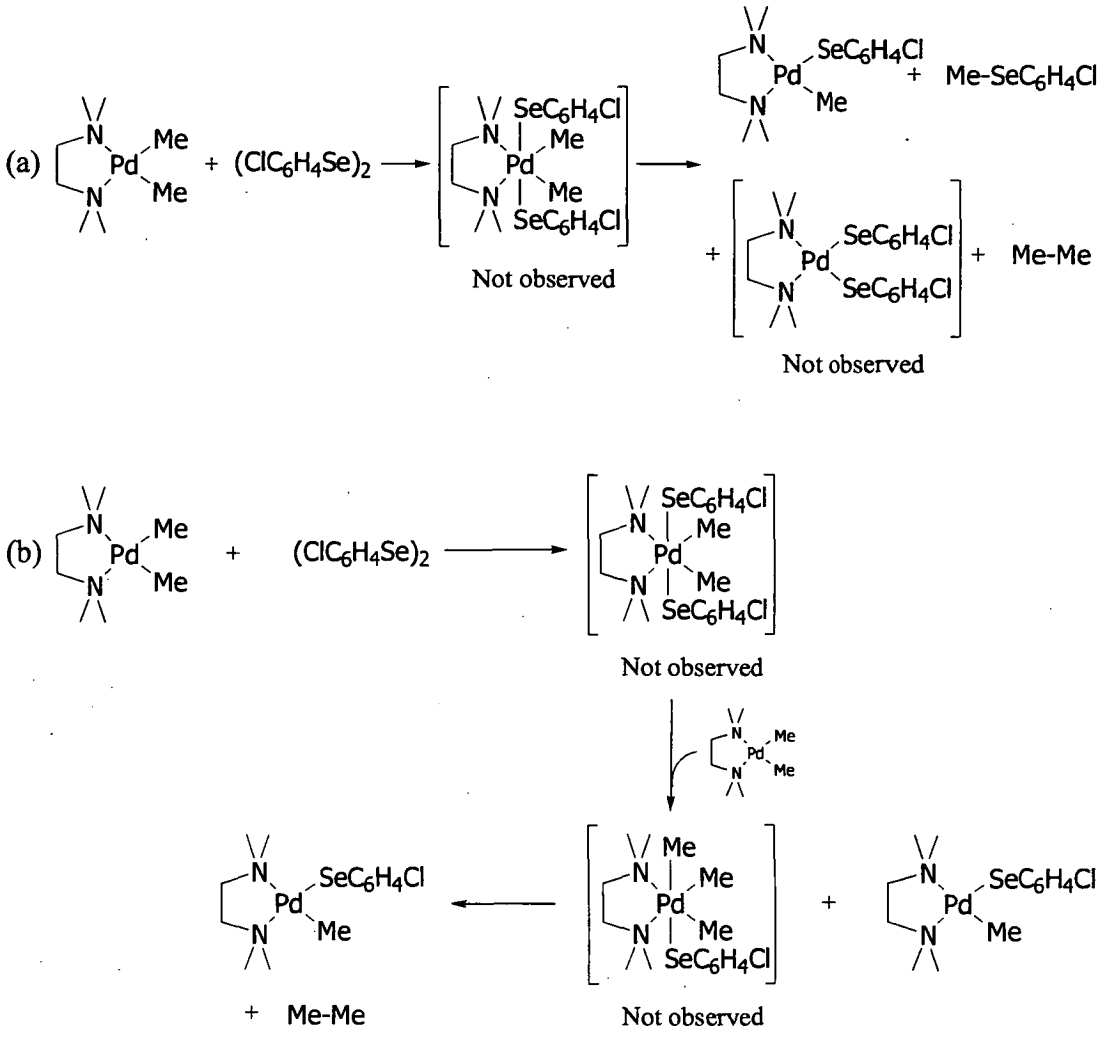
When $PdMe_2$(tmeda) and $(ClC_6H_4Se)_2$ were allowed to react in equivalent amounts in CD_2Cl_2 at room temperature, the products observed by GC-MS and/or ^1H NMR were $Me\text{-}SeC_6H_4Cl$, $Pd(SeC_6H_4Cl)Me$(tmeda), ethane and free tmeda. An insoluble orange/brown solid also formed overnight. Some $(ClC_6H_4Se)_2$ remained unreacted, suggesting that the reaction might not proceed with 1:1 stoichiometry. Low temperature studies revealed that the reaction was already proceeding slowly at –20 °C with all products appearing simultaneously. No palladium(IV) intermediates could be identified.

Complete consumption of the reagents was observed when the reaction was carried out using two equivalents of $PdMe_2$(tmeda) and one of $(ClC_6H_4Se)_2$. The products were the same as those outlined above. The similarities between the products formed by this reaction with those formed in the reaction involving the bpy analogue, reported by Canty *et al.*,[9] raises the possibility that a similar reaction mechanism may be involved. This would entail reductive elimination from $Pd^{IV}(SeC_6H_4Cl)_2Me_2$(tmeda) by carbon-carbon and carbon-selenium bond formation to give the products shown in Scheme 4.9a. A problem with this mechanism for the formation of ethane is that the inorganic species $Pd(SeC_6H_4Cl)_2$(tmeda) is not observed and free tmeda is. It is possible that $Pd(SeC_6H_4Cl)_2$(tmeda) precipitates from solution or that it decomposes to form tmeda. In addition, this mechanism does not explain the observed 2:1 stoichiometry of reagents required. Consequently, other mechanisms operating instead of, or in addition to, this one cannot be excluded.

The process also bears some resemblance to the reaction of $PdMe_2$(tmeda) with $(PhCO_2)_2$, described in Section 2.2.1, in which an unobserved palladium(IV) intermediate, '$Pd(O_2CPh)Me_2$(tmeda)', is assumed to undergo an exchange reaction with a second equivalent of $PdMe_2$(tmeda) to form $Pd(O_2CPh)Me_3$(tmeda) (**14**) and $Pd(O_2CPh)Me$(tmeda) (**6**) (Scheme 2.14). Ethane is then formed by reductive elimination from $Pd(O_2CPh)Me_3$(tmeda) (**14**). A similar mechanism here would provide an alternative route to ethane formation and might help explain the observed 2:1 stoichiometry of the reaction (Scheme 4.9b). The presence of free tmeda in the reaction mixture is still puzzling but could possibly stem from the decomposition of $Pd(SeC_6H_4Cl)Me$(tmeda) through the elimination of $Me\text{-}SeC_6H_4Cl$.

The mechanisms shown in Scheme 4.9 present ways in which palladium(IV) may be involved in the formation of the observed products. Although the observed reaction seems to behave similarly to related reactions in which the involvement of palladium(IV) has been proven, care must be taken in implicating equivalent mechanisms in this case. The lack of observation of palladium(IV) intermediates means that the potential involvement of palladium intermediates in other oxidation states [*e.g.* Pd(II) $\rightarrow$ Pd(0) $\rightarrow$ Pd(II)] cannot be disregarded.

Scheme 4.9: Possible mechanisms by which Pd(IV) could be involved in the reaction of $PdMe_2$(tmeda) with $(ClC_6H_4Se)_2$ in CD_2Cl_2.



When kept for prolonged periods in CD_2Cl_2 at room temperature, a number of changes in the ^1H NMR spectrum occurred. Resonances due to Pd(SeC_6H_4Cl)Me(tmeda) and tmeda slowly disappeared and were replaced by several new signals. Singlets at 0.34, 2.50 and 2.61 ppm and multiplets at about 2.65 and 2.48 ppm shared similar shifts with resonances expected for PdClMe(tmeda).[15] Analogous products were observed in the reactions of $Pd(PPh_3)_4$ with $(PhSe)_2$ and $(ThSe)_2$ in dichloromethane, where $PdCl(SePh)(PPh_3)_2$ and $PdClTh(PPh_3)_2$, respectively, formed as minor side products.[3,4] These resulted from the involvement of the solvent in the reaction and, in the latter, by reaction of a selenium-carbon bond.[3,4]

In addition to the appearance of suspected PdClMe(tmeda), ^{1}H NMR indicated the presence of a set of signals arising from a tmeda ligand with chemically non-equivalent halves. These occurred at 3.85 (m), 3.45 (s), 2.72 ('t') and 2.27 ppm (s). The signals at 3.85 and 3.45 ppm are significantly downfield of resonances normally expected for 'Pd^{II}(tmeda)' complexes. Two unidentified small doublets also appeared at 7.73 and 7.39 ppm.

In an attempt to determine the identity and source of this unidentified compound(s), free tmeda in CD_2Cl_2 was allowed to react at room temperature. After several hours, ^{1}H NMR clearly showed the appearance of new signals in the aliphatic region with similar shifts to those reported above. However, no new resonances were seen in the aromatic region. Considering this reaction was not observed in acetone-d_6, a likely explanation is that the presence of trace amounts of acid in the CD_2Cl_2 leads to the protonation of one end of the tmeda molecule to give $[NMe_2CH_2CH_2NDMe_2]^+$. This compound is known to exist.[16,17]

In an endeavor to avoid the involvement of solvent in the reaction, acetone-d_6 was used as an alternative to CD_2Cl_2. The initial stage of the reaction proceeded in the same manner as observed previously, with Pd(SeC_6H_4Cl)Me(tmeda), Me-SeC_6H_4Cl, ethane and free tmeda formed as products. However, when kept for an extended period, the reaction behaved quite differently than in CD_2Cl_2. Some further reaction did take place slowly to give a minor amount of an unidentified complex. This complex gave rise to resonances consistent with the presence of a Pd-Me group and an asymmetric tmeda ligand.

A possible explanation for the formation of these new products in acetone-d_6 is the reaction of Me-SeC_6H_4Cl with Pd(SeC_6H_4Cl)Me(tmeda), or with unreacted $PdMe_2$(tmeda) if present. This could feasibly occur by cleavage of either of the carbon-selenium bonds. Cleavage of the methyl-selenium bond would not lead to any products that have not been formed already. However, reaction of the aryl-selenium bond could potentially lead to a number of previously unobserved species. As discussed in Section 4.2.1.1, the oxidative addition of carbon-chalcogenide bonds

of diorganyl chalcogenides to platinum(0) and palladium(0) complexes has been reported.[14]

4.2.2.2 The Reaction of PdMeTol(tmeda) with $(ClC_6H_4Se)_2$

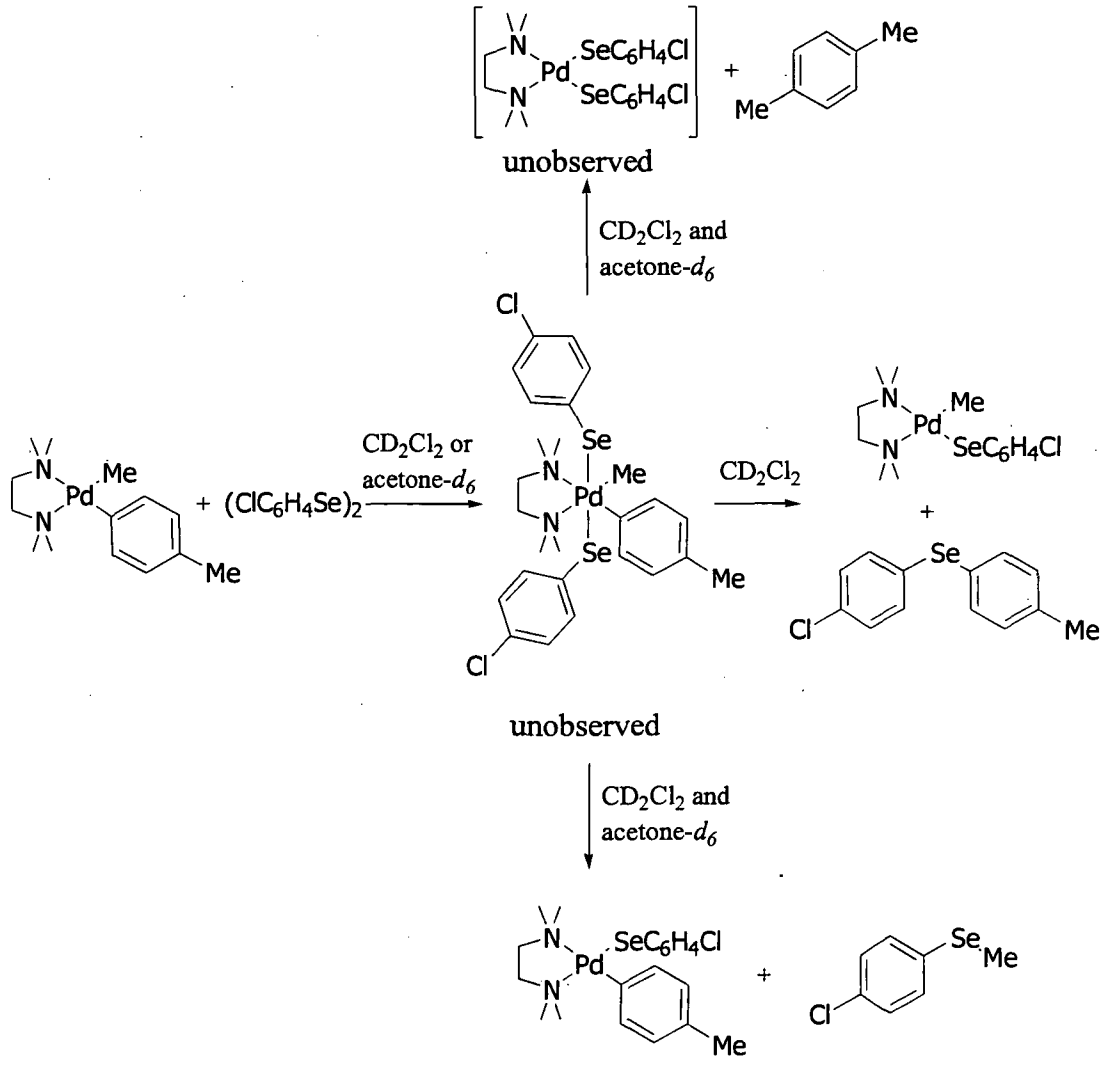
Unlike the analogous reaction with $PdMe_2$(tmeda), the 1:1 reaction of PdMeTol(tmeda) with $(ClC_6H_4Se)_2$ led to the complete consumption of both reagents. The reaction was initially carried out in acetone-d_6 in order to try to avoid the involvement of the solvent as was seen in Section 4.2.2.1. The reaction proceeded reasonably cleanly and the resonances present at the end of the reaction were consistent with the presence of 1,4-xylene (Tol-Me), free tmeda, Me-SeC_6H_4Cl and Pd(SeC_6H_4Cl)Tol(tmeda). An orange solid also formed. There was no evidence for the formation of Tol-SeC_6H_4Cl or Pd(SeC_6H_4Cl)Me(tmeda), suggesting that the reaction in acetone-d_6 selectively undergoes selenium-alkyl coupling in preference to selenium-aryl coupling.

When the same reaction was carried out in CD_2Cl_2, the resulting ^1H NMR spectrum was somewhat more complicated. In addition to those products seen in acetone-d_6, Tol-SeC_6H_4Cl and Pd(SeC_6H_4Cl)Me(tmeda) were both formed. This implies that the solvent plays a significant role in the selectivity of the reaction. When kept for extended periods, further reactions similar to those seen in Section 4.2.2.1 during the reaction of $PdMe_2$(tmeda) with $(ClC_6H_4Se)_2$, were observed. In addition to the formation of the suspected $[NMe_2CH_2CH_2NDMe_2]^+$ and PdClMe(tmeda), signals consistent with those expected for PdClTol(tmeda) were also observed. These results are in contrast to the analogous reactions with bpy complexes in which Pd(SeC_6H_4Cl)Me(bpy) is not seen at any time during the reaction, and in which there is no evidence of solvent undergoing reaction with any of the products.

The formation of all of the products above can be envisaged to occur from a common palladium(IV) intermediate as shown in Scheme 4.10. However, as discussed in a previous section, the lack of conclusive evidence for such an

intermediate means that other routes cannot be excluded. The presence of free tmeda is still puzzling, but it could potentially form by the decomposition of any of the palladium complexes present. The orange solid may be the unobserved inorganic complex, $Pd(SeC_6H_4Cl)_2(tmeda)$.

Scheme 4.10: The possible involvement of a Pd(IV) intermediate in the reaction of PdMeTol(tmeda) with $(ClC_6H_4Se)_2$.



4.2.3 ^{1}H and ^{31}P NMR Studies of the Reaction of PdMeR(dmpe) (R = Me, Tol) and $(ClC_6H_4Se)_2$

The complexes PdMeR(dmpe) (R = Me, Tol) were chosen in order to study the reactions of simple systems containing a bidentate phosphine ligand, and as a phosphine analogues of PdMeR(tmeda) (R = Me, Tol). The choice of dmpe as ligand was logical for a number of reasons. Foremost, it is a direct analogue of tmeda and forms a five-membered ring with palladium as in the bpy and tmeda species. It also has less steric effects than other commonly used bidentate phosphine ligands such as dppe [1,2-bis(diphenylphosphino)ethane], depe [1,2-bis(diethylphosphino)ethane] and dppbz [1,2-bis(diphenylphosphino)benzene]. In addition, the decomposition of octahedral platinum(IV) species bearing bidentate phosphine ligands have been shown to lead to both carbon-carbon and carbon-oxygen bond formation (see Sections 2.1 and 2.2.4).[18,19]

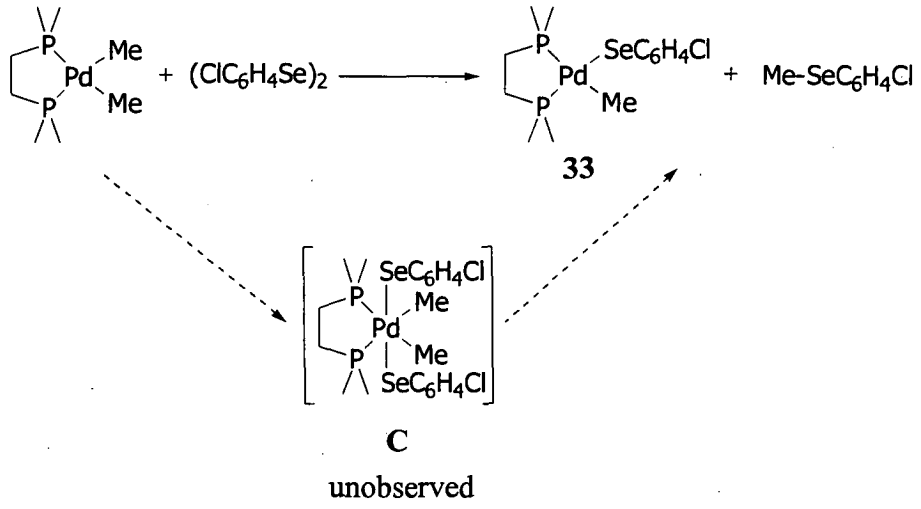
4.2.3.1 The Reaction of $PdMe_2$(dmpe) with $(ClC_6H_4Se)_2$

The reaction of a 1:1 ratio of $PdMe_2$(dmpe) with $(ClC_6H_4Se)_2$ in CD_2Cl_2 was monitored at various temperatures by ^{1}H and ^{31}P NMR spectroscopy. The reaction proceeded cleanly with full consumption of reagents. As the reaction progressed, ^{31}P NMR signals changed from a singlet at 21.8 ppm, arising from $PdMe_2$(dmpe), to two doublets at 34.2 and 24.0 ppm. The appearance of the two doublets suggested the formation of a complex incorporating a dmpe ligand with two chemically inequivalent phosphorus atoms. This was supported by ^{1}H NMR spectroscopy in which two signals appeared for the PMe_2 groups. The integration of these resonances compared with others in the spectrum suggested that the monoorganopalladium(II) complex Pd(SeC_6H_4Cl)Me(dmpe) (**33**) was present. This complex was subsequently isolated and X-ray crystallographic analysis performed (see Section 4.2.4.2). Signals consistent with the presence of Me-SeC_6H_4Cl were also identified with a 1:1 ratio of products observed. Unlike reactions involving $PdMe_2(L_2)$ (L_2 = tmeda, bpy), no products arising from carbon-carbon coupling were

detected, suggesting that this reaction was selective for carbon-selenium coupling (Scheme 4.11).

The formation of the observed products by reductive elimination from an intermediate such as '$Pd^{IV}(SeC_6H_4Cl)_2Me_2(dmpe)$' (**C**, Scheme 4.11) can be easily envisaged. However, no palladium(IV) intermediates were observed during the reaction and, as such, no conclusive evidence for the involvement of this species currently exists.

Scheme 4.11: The reaction between $PdMe_2(dmpe)$ and $(ClC_6H_4Se)_2$ indicating the potential for involvement of an unobserved Pd(IV) species, $Pd(SeC_6H_4Cl)_2Me_2(dmpe)$, **C**.

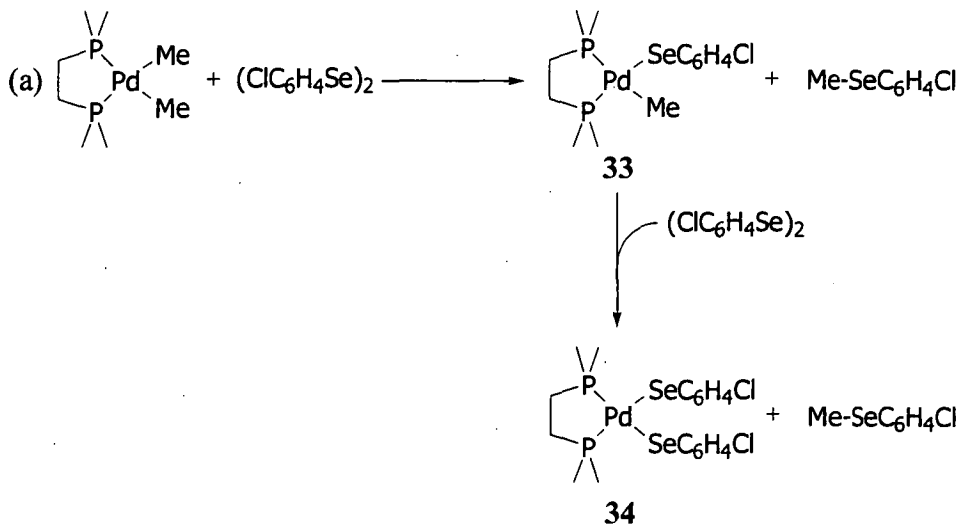


When a slight excess of diselenide was added, the reaction progressed further and a third product was identified. This product displayed broad signals in both ^1H and ^{31}P NMR spectra. ^{31}P NMR spectroscopy revealed a singlet at 37.6 ppm indicating the presence of dmpe with chemically equivalent phosphorus atoms. This was verified by ^1H NMR spectroscopy in which doublets appeared for the PMe_2 and PCH_2 groups. Two doublets arising from a SeC_6H_4Cl group also appeared in the aromatic region. Integration of these signals indicated the presence of two SeC_6H_4Cl moieties for each dmpe ligand. Subsequently, the product was identified, by ^1H NMR and elemental analysis, as $Pd(SeC_6H_4Cl)_2(dmpe)$ (**34**). A related complex, $Pd(SePh)_2(dppe)$, has been reported previously, where one group reported a singlet in

^{31}P NMR spectra at 48.12 ppm,[20] while the other reported a singlet of 55.0 ppm.[21] The appearance of **34** coincided with an increase in Me-SeC_6H_4Cl and a decrease in Pd(SeC_6H_4Cl)Me(dmpe).

In order to clarify the source of Pd(SeC_6H_4Cl)$_2$(dmpe), a second equivalent of (ClC_6H_4Se)$_2$ was added to the completed reaction of $PdMe_2$(dmpe) with (ClC_6H_4Se)$_2$ shown in Scheme 4.11. This led to full consumption of the diselenide and Pd(SeC_6H_4Cl)Me(dmpe) (**33**) and an increase in the amount of Me-SeC_6H_4Cl, with a final product ratio of 1:2, **34**:Me-SeC_6H_4Cl. This confirms that the formation of **34** results from the reaction of **33** with one equivalent of (ClC_6H_4Se)$_2$. No palladium(IV) intermediates were seen, but this does not rule out their involvement. This reaction shares similar features to the carbon-oxygen bond forming reactions discussed in Chapter Two, in which monoorganopalladium(II) aroate complexes reacted with diaroyl peroxides to form an inorganic palladium(II) complex and a compound formed *via* carbon-oxygen bond formation. The sequence of reactions and the overall reaction (eq 4.1) for the addition of two equivalents of (ClC_6H_4Se)$_2$ to $PdMe_2$(dmpe) are shown in Scheme 4.12 as (a) and (b) respectively.

Scheme 4.12: The reaction of $PdMe_2$(dmpe) with two equivalents of (ClC_6H_4Se)$_2$ in CD_2Cl_2. (a) Reaction sequence. (b) Overall equation.



(b) $PdMe_2$(dmpe) + 2 (ClC_6H_4Se)$_2$ → Pd(SeC_6H_4Cl)$_2$(dmpe) + 2 Me-SeC_6H_4Cl (4.1)

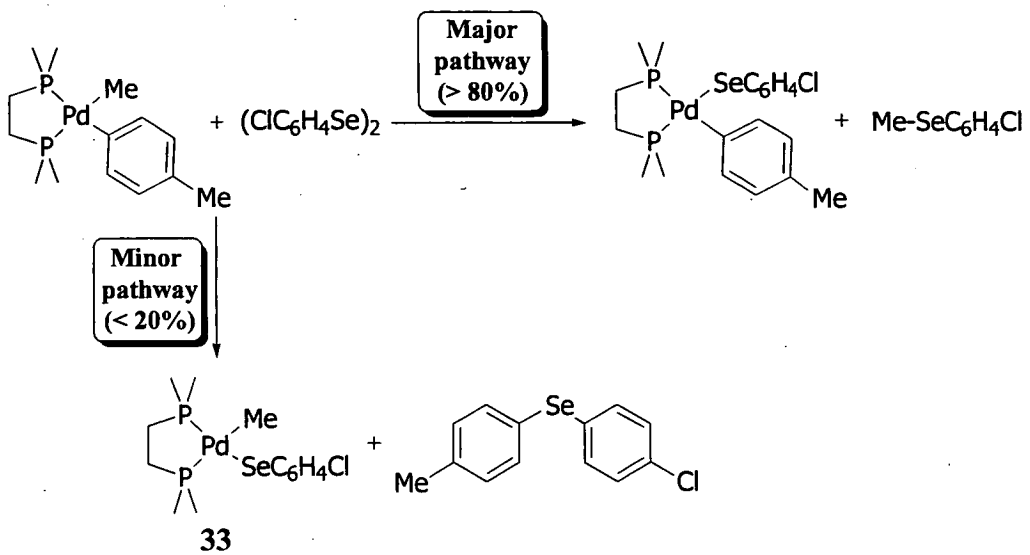
When the reaction using a 1:1 ratio of reagents was carried out at temperatures above *ca.* 5 °C, the reaction of $(ClC_6H_4Se)_2$ with $Pd(SeC_6H_4Cl)Me(dmpe)$ (**33**) occurred in competition with its reaction with $PdMe_2(dmpe)$ to a small extent. Consequently, $Pd(SeC_6H_4Cl)_2(dmpe)$ (**34**) appeared as a minor product in some reactions.

4.2.3.2 The Reaction of PdMeTol(dmpe) with $(ClC_6H_4Se)_2$

The reaction of PdMeTol(dmpe) with $(ClC_6H_4Se)_2$ was investigated in order to probe for selectivity in aryl-selenium and alkyl-selenium bond formation in complexes containing flexible bidentate phosphine ligands. 4-Tolyl was chosen as the aryl ligand due to its straightforward ^1H NMR spectrum and extra signal in the aliphatic region in comparison with phenyl. It also allows this reaction to be compared directly with the analogous reaction of PdMeTol(tmeda).

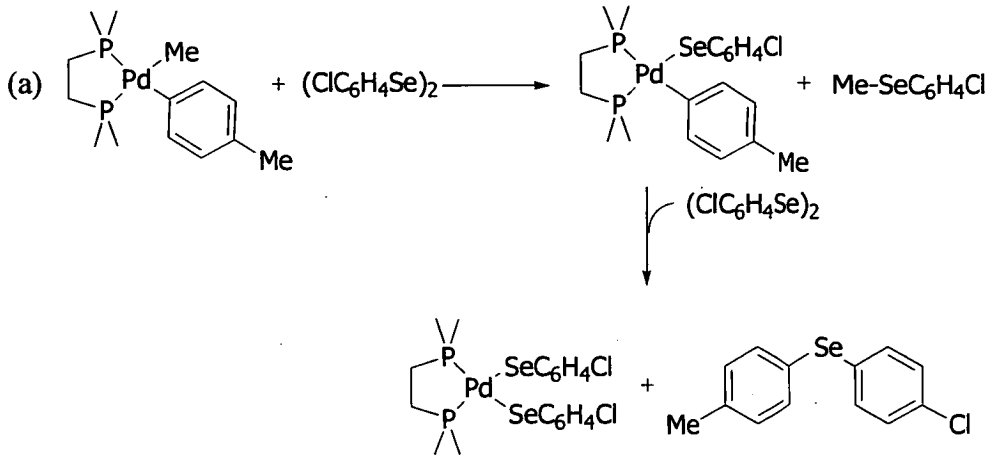
This reaction shows many similarities to the reaction with $PdMe_2(dmpe)$ described in Section 4.2.3.1 above. When carried out in a 1:1 ratio, $Me\text{-}SeC_6H_4Cl$ and ^1H NMR resonances consistent with the presence of $Pd(SeC_6H_4Cl)Tol(dmpe)$ appeared. A small (< 20 %) amount of $Pd(SeC_6H_4Cl)Me(dmpe)$ (**33**), $Tol\text{-}SeC_6H_4Cl$ and $Pd(SeC_6H_4Cl)_2(dmpe)$ (**34**) were also observed. However, the reaction highly favoured alkyl-selenium over aryl-selenium coupling (Scheme 4.13). As noted for the reaction with $PdMe_2(dmpe)$, and in contrast to analogous reactions with $PdMeAr(L_2)$ (Ar = Tol, Anis; L_2 = tmeda, bpy), there was no evidence of carbon-carbon coupling. The production of $Pd(SeC_6H_4Cl)_2(dmpe)$ (**34**) at this stage of the reaction is likely to be due to the competing reaction of $(ClC_6H_4Se)_2$ with $Pd(SeC_6H_4Cl)R(dmpe)$ (R = Tol, Me). Again, no palladium(IV) intermediates were detected, but the involvement of species such as '$Pd(SeC_6H_4Cl)_2MeTol(dmpe)$' cannot be ruled out.

Scheme 4.13: Reaction of PdMeTol(dmpe) and $(ClC_6H_4Se)_2$ in CD_2Cl_2. Major and minor reaction routes are shown.



As for the reaction with $PdMe_2$(dmpe), excess diselenide caused the formation of additional products. Addition of a second equivalent of $(ClC_6H_4Se)_2$ to the completed reaction of PdMeTol(dmpe) with $(ClC_6H_4Se)_2$ (Scheme 4.13), led to the formation of $Pd(SeC_6H_4Cl)_2$(dmpe) (**34**) and Tol-SeC_6H_4Cl (identified by ^1H NMR and GC-MS) (Scheme 4.14). In conjunction with this, resonances due to Pd(SeC_6H_4Cl)Tol(dmpe) diminished. Overall, the final ratio of products was 1:1:1, **34**:Me-SeC_6H_4Cl:Tol-SeC_6H_4Cl. This indicates that one equivalent of $(ClC_6H_4Se)_2$ reacts with Pd(SeC_6H_4Cl)Tol(dmpe) to form Tol-SeC_6H_4Cl and **34**. Once more, no palladium(IV) intermediates were identified, but intermediates such as 'Pd$(SeC_6H_4Cl)_3$Tol(dmpe)', analogous to $Pt(O_2CPh)_3$(NCN) discussed in Chapter Three, cannot be discounted. The likely sequence and overall reaction (eq 4.2) for the interaction of PdMeTol(dmpe) with two equivalents of $(ClC_6H_4Se)_2$ are shown in Scheme 4.14. A minor amount of 4,4'-bitolyl was also observed. As discussed previously, this is not surprising and possible mechanisms for its production are discussed in Sections 4.2.1.1 and 2.2.2.1.

Scheme 4.14: The reaction of PdMeTol(dmpe) with two equivalents of $(ClC_6H_4Se)_2$. (a) Reaction sequence (only the major reaction pathway is shown). (b) Overall equation.



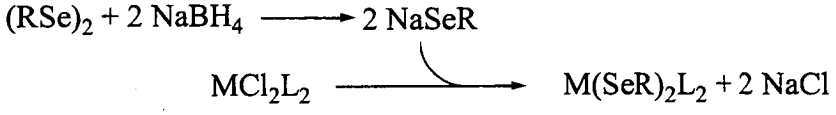
34

(b) $PdMeTol(dmpe) + 2\ (ClC_6H_4Se)_2 \rightarrow Pd(SeC_6H_4Cl)_2(dmpe) + Me\text{-}SeC_6H_4Cl + Tol\text{-}SeC_6H_4Cl$ (4.2)

4.2.4 Synthesis and Characterisation of Complexes

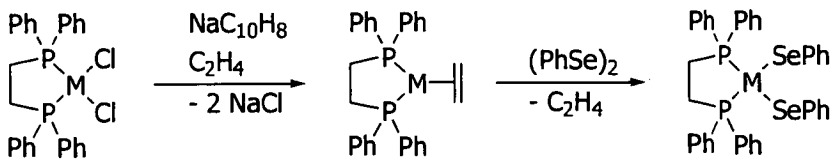
Palladium and platinum complexes incorporating selenolate ligands (RSe^-) have been known for some time, and several synthetic avenues to such complexes have been reported.[1-4,8,9,12,20-26] One of the most common methods, particularly for the synthesis of complexes of the form $M^{II}(SeR)_2(L)_2$, involves a metathesis reaction between a $M^{II}Cl_2(L)_2$ complex and sodium selenolate salts (NaSeR).[20,22-25] The selenolate salts are prepared *in situ* by sodium borohydride reduction of diorganyl diselenides (Scheme 4.15).[20,22-25] To date, the utilisation of this method seems to have been restricted to the synthesis of complexes incorporating phosphine ligands.

Scheme 4.15: The preparation of organyl(selenolato)palladium(II) and platinum(II) complexes by the reaction of a metal(II) dichloride and a sodium selenolate reagent.



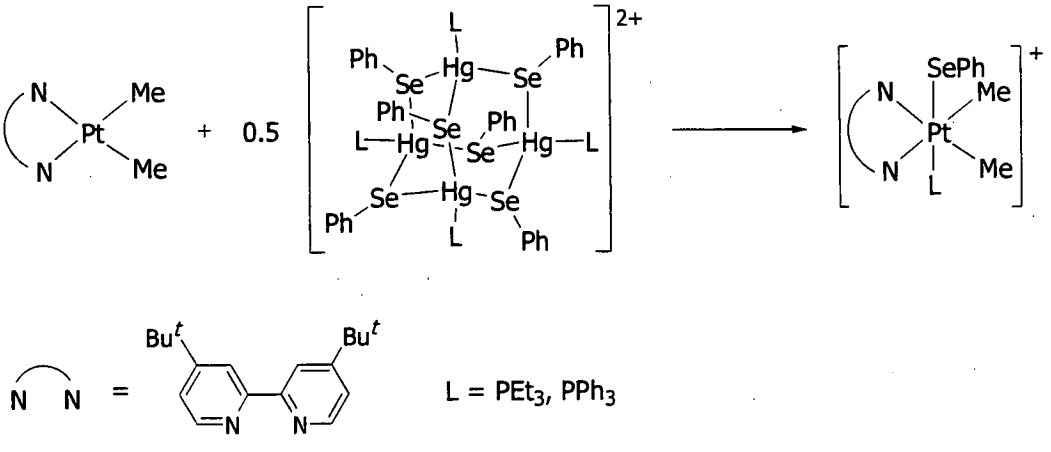
As discussed in Section 4.1, M(II) and M(IV) (M = Pd, Pt) complexes can also be synthesised by the oxidative addition of diorganyl diselenides to M(0) and M(II) complexes, respectively. In addition to those examples discussed previously, addition to (ethene)metal(0) complexes has also been used as a gateway to metal(II) selenolate complexes.[21] In the example shown in Scheme 4.16, a metal(II) chloride is reduced by sodium naphthalenide in the presence of ethylene and followed by oxidative addition of diphenyl diselenide.[21] This method has the disadvantage that the product requires chromatographic purification and results in only moderate yields.

Scheme 4.16: Synthesis of $M(SePh)_2(dppe)$ (M = Pd, Pt) *via* a $M^0(C_2H_4)(dppe)$ intermediate.[21]



Janzen *et al.* were successful in isolating the first examples of cationic selenolate complexes of platinum(IV).[26] They demonstrated that the reaction of adamantoid mercury(II) compounds with diorganoplatinum(II) complexes led to the formation of cationic complexes of the form $[Pt(EPh)Me_2L(Bu^tbpy)][ClO_4]$, as shown in Scheme 4.17. The mechanism involved appears to be complex. Nevertheless, the reaction provides a simple route to the desired product.[26]

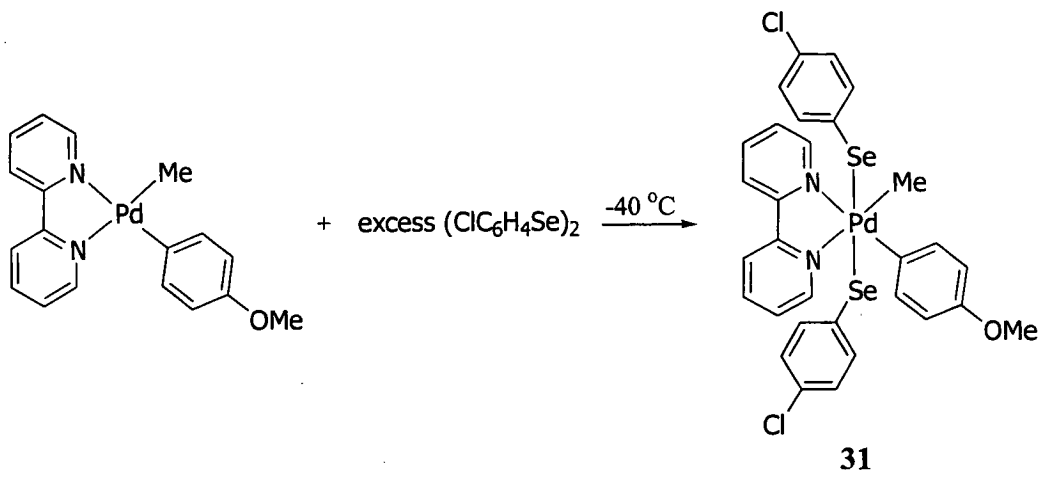
Scheme 4.17: Synthesis of cationic Pt(IV) selenolate complexes.[26]



4.2.4.1 Synthesis and Characterisation of $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$

In order to carry out detailed studies into the equilibrium involving $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ (**31**) and to examine its decomposition, a synthetic method leading to the isolation of **31** was sought. As shown in Section 4.2.1, complex **31** exists in equilibrium with PdMe(Anis)(bpy) and $(ClC_6H_4Se)_2$, and attempts to isolate **31** from this mixture inevitably led to contamination by PdMe(Anis)(bpy). When the reaction was carried out in the presence of excess diselenide at –40 °C, complete conversion of the palladium(II) reagent was observed and **31** was isolated as a red solid in high yield (Scheme 4.18). The product decomposed in solution at temperatures above *ca.* –25 °C, but could be stored as a solid at –20 °C for several months.

Scheme 4.18: Synthesis of $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ (**31**).



31

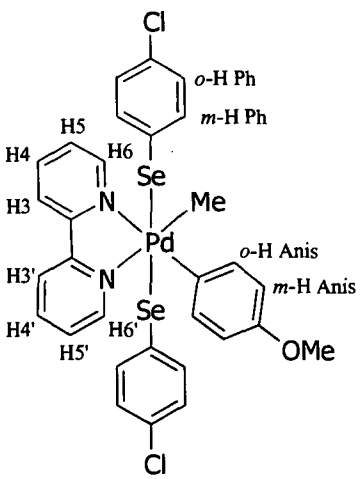
93 %

Characterisation of **31** was carried out through NMR studies in CD_2Cl_2 and elemental analysis. ^1H NMR and gCOSY studies were carried out at –40 °C in order to minimise decomposition of the complex. One isomeric form was present as indicated by the appearance of only one set of resonances for each group, *i.e.* one PdMe, one Pd(Anis), one SeC_6H_4Cl and two pyridyl group resonances. The presence of eight signals arising from the 2,2'-bipyridyl ligand indicated that groups *trans* to the nitrogen atoms of bpy must be different. Furthermore, the two ClC_6H_4Se groups

were chemically equivalent. Thus they must be mutually *trans*, occupying the axial positions, as they cannot be in a mutually *cis* arrangement opposite the bpy ligand since this arrangement would generate symmetrical bpy.

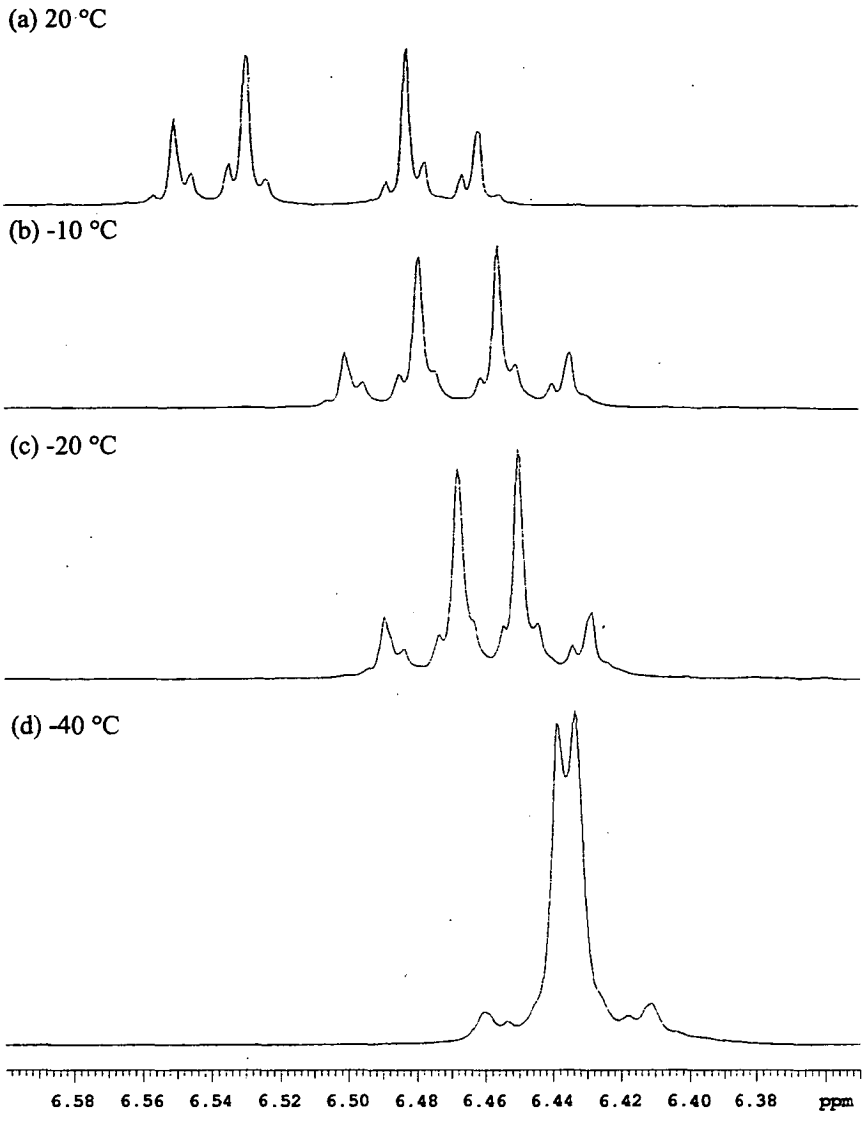
As noted in Chapter Two, doublets arising from H6' and H6 (for numbering scheme, see Figure 4.4) were easy to distinguish due to their small coupling constants (5.2 and 4.4 Hz respectively). In accordance with the observation made for $Pd(O_2CPh)Me(bpy)$ (**5**) (Section 2.2.5.2) that the bpy proton adjacent to the aryl group occurs upfield of the one adjacent to the methyl, the higher field H6/6' resonance was assigned to H6'. This is also consistent with the suggestion by Markies *et al.* that the π-electrons of the palladium-bonded aryl ring shield the H6' proton of the adjacent bpy ring.[27] Subsequently, the remainder of the bpy protons could be assigned using gCOSY experiments.

Figure 4.4: ^{1}H NMR numbering scheme for $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ (**31**).



At –40 °C, the *ortho-* and *meta-* protons of the phenyl group were nearly coincident, but expansion of the region revealed the pattern of an AA'BB' system ($\Delta\nu/J \approx 1$). As the temperature was increased the two doublets became more separated and at room temperature they were well resolved ($\Delta\nu/J \approx 3$) (Figure 4.5).

Figure 4.5: Changes in the AA'BB' pattern of the SeC_6H_4Cl resonances of **31** on going from (a) 20 °C to (d) -40 °C.

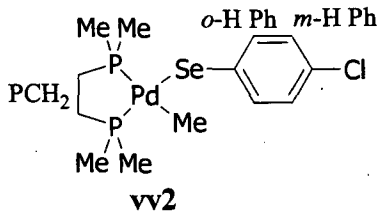


4.2.4.2 Synthesis and Characterisation of $Pd(SeC_6H_4Cl)Me(dmpe)$

The clean and straightforward reaction between $PdMe_2(dmpe)$ and $(ClC_6H_4Se)_2$ allowed the isolation of $Pd(SeC_6H_4Cl)Me(dmpe)$ (**33**) from this reaction (Scheme 4.11). In order to avoid the formation of $Pd(SeC_6H_4Cl)_2(dmpe)$ (**34**) as described in Section 4.2.3.1, the reaction was started at –50 °C and allowed to come slowly to room temperature. The product was isolated as an orange solid in high yield and was characterised by ^1H NMR, ^{31}P NMR, elemental analysis and X-ray crystallography.

NMR spectroscopy was carried out at room temperature in CD_2Cl_2 and in $CDCl_3$ (Figure 4.6). In CD_2Cl_2, ^{31}P NMR showed the presence of two doublets at 33.76 and 23.80 ppm. The signals are seen as doublets due to the coupling of one phosphorus with the other and have $^3J_{PP}$ coupling constants of 21 and 22 Hz, respectively. The ^1H NMR spectrum in CD_2Cl_2 was also quite straightforward. Resonances due to Pd-Me, PMe_2 and PCH_2 all appeared with phosphorus coupling. Pd-Me protons gave rise to a broad 'triplet', PMe_2 protons to two doublets and PCH_2 resonances appeared as complex multiplets. The aromatic protons of the ClC_6H_4Se moiety appeared as doublets at 7.52 and 7.00 ppm.

Figure 4.6: ^1H NMR numbering scheme for $Pd(SeC_6H_4Cl)Me(dmpe)$ **(33)**.



vv2

X-ray crystallographic studies were carried out on single crystals grown by recrystallisation from CH_2Cl_2/diethyl ether. The molecular structure of this complex is shown in Figure 4.7 with pertinent bond distances and angles in Table 4.3. The complex is mononuclear and the palladium centre is four-coordinate with its coordination sites occupied by the *cis*-bidentate phosphorus donor ligand, a unidentate 4-(chlorophenyl)selenolate moiety and a methyl group. The metal atom environment is close to square planar and the aryl ring makes an approximate right angle with the 'P_2SeC' coordination plane (97.16°). Disorder is apparent in the dmpe ligand and was resolvable in one of the bridging methylene groups. This impacted on the displacement parameters of the ligand methyl groups, the disorder in which was not resolvable.

Only a limited number of crystal structures of mononuclear palladium(II) complexes incorporating non-bridging selenolate ligands have been reported. The Pd-Se bond distance for **33** [2.4483(8) Å] is comparable with those reported for *trans*-PdCl(SePh)$(PPh_3)_2$ [2.4200(6) Å][3] and *trans*-Pd$(SePh)_2\{P(Bu^n)_3\}_2$ [2.4609(4) Å] even though the groups *trans* to Se are different.[23] Octahedral complexes are reported with slightly longer Pd-Se distances, ranging from 2.487(1) to 2.506(1) Å.[9]

Figure 4.7: Structure of complex Pd(SeC_6H_4Cl)Me(dmpe) (**33**). Ellipsoids are shown at the 50% probability level.

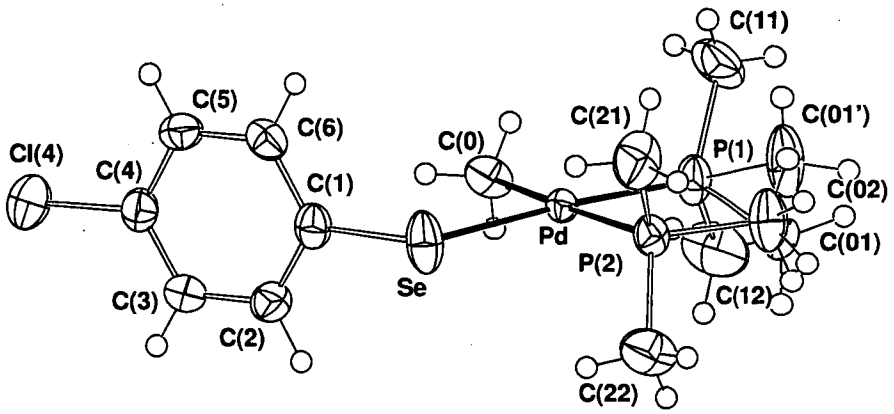


Table 4.3: Selected bond distances (Å) and angles (°) for **33**.

	33		
	Bond Distances (Å)		
Pd-C(0)	2.116(6)	Pd-Se	2.4483(8)
Pd-P(1)	2.230(1)	Se-C(1)	1.916(6)
Pd-P(2)	2.305(2)		
	Bond Angles (deg.)		
C(0)-Pd-P(1)	89.4(2)	P(1)-Pd-Se	173.78(6)
C(0)-Pd-P(2)	175.2(2)	P(2)-Pd-Se	88.20(4)
C(0)-Pd-Se	96.6(2)	Pd-Se-C(1)	110.7(2)
P(1)-Pd-P(2)	85.79(8)		
	Interplanar Dihedral Angle (deg.)[a]		
θ	97.16		

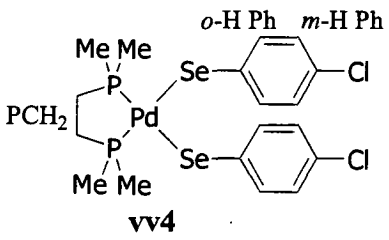
[a] θ is the angle between the P_2Se_2 and the SeC_6H_4Cl coordination plane.

4.2.4.3 Synthesis and Characterisation of $Pd(SeC_6H_4Cl)_2(dmpe)$

$Pd(SeC_6H_4Cl)_2(dmpe)$ (**34**) was isolated from the room temperature reaction of $PdMe_2(dmpe)$ with two equivalents of $(ClC_6H_4Se)_2$ (Scheme 4.12) as an orange solid in moderate yield. The product was characterised by ^1H and ^{31}P NMR spectroscopy and elemental analysis.

^{31}P NMR spectroscopy showed only a single resonance at 37.59 ppm. This indicated that the same chemical environment existed for each phosphorus atom and is consistent with the proposed square planar structure of a *cis*-coordinated bidentate phosphorus ligand opposite two *cis*-oriented 4-(chlorophenyl)selenolate groups (Figure 4.8). The ^1H NMR spectrum was straightforward owing to the high degree of symmetry in the molecule. As seen for $Pd(SeC_6H_4Cl)Me(dmpe)$ (**33**), phosphorus coupling was observed for resonances arising from PCH_2 and PMe_2 with a doublet appearing for each.

Figure 4.8: ^1H NMR numbering scheme for $Pd(SeC_6H_4Cl)_2(dmpe)$ (**34**).



vv4

4.3 Conclusions

The investigation of reactions of palladium(II) complexes with $(ClC_6H_4Se)_2$ has allowed a number of interesting comparisons to be made with analogous reactions of diaroyl peroxides.

In contrast to the reaction of PdMeR(bpy) (R = Me, Tol) with $(Ar'CO_2)_2$ (Ar' = Ph, Ar_F), in which the suspected palladium(IV) intermediate, '$Pd(O_2CAr)_2MeR(bpy)$', was not able to be detected spectroscopically, the reactions of PdMeAr(bpy) (Ar = Tol, Anis) with $(ClC_6H_4Se)_2$ resulted in the observation of $Pd(SeC_6H_4Cl)_2MeTol(bpy)$ and isolation of $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$. The characterisation of species such as these, and previously reported $Pd(SePh)_2Me_2(bpy)$,[9] and studies of their reactions provides an insight into the possible reactions of, as yet undetectable, species such as $Pd(O_2CAr')_2MeR(bpy)$. The complexes $Pd(SeC_6H_4Cl)_2MeAr(bpy)$ do not undergo exchange reactions with PdMeAr(bpy) as is suspected to occur between '$Pd(O_2CAr')_2MeR(bpy)$' and PdMeR(bpy). However, $Pd(SeC_6H_4Cl)_2MeAr(bpy)$ represents a model for unobserved '$Pd(O_2CAr')_2MeR(bpy)$', and its decomposition may mirror that of '$Pd(O_2CAr')_2MeR(bpy)$' if it were able to be isolated free from PdMeR(bpy), *i.e. via* both carbon-carbon and carbon-oxygen coupling.

The existence of $Pd(SeC_6H_4Cl)_2MeAr(bpy)$ in equilibrium with PdMeAr(bpy) and $(ClC_6H_4Se)_2$ is a rare example of a reversible oxidative addition-reductive elimination reaction, and the first example of reversible oxidative addition of a diorganyl dichalcogenide to a palladium(II) complex.

Contrary to their bpy analogues, no palladium(IV) species were observed in the reactions between PdMeR(tmeda) and $(ClC_6H_4Se)_2$. Previous unsuccessful attempts to observe '$Pd^{IV}Ar(tmeda)$' complexes suggest that the elusive nature of a similar species in this ligand environment is not surprising (see also Section 2.2.3).[28] However, there are a number of examples of complexes of the form '$Pd^{IV}Me_2(tmeda)$', and observation of a species such as '$Pd(SeC_6H_4Cl)_2Me_2(tmeda)$' might have been expected. This could reflect the importance of the presence of a rigid ancillary ligand, and lack of steric congestion at the Pd-N donor bond, to the stability of palladium(IV) complexes incorporating selenolato ligand(s).

In all of the systems studied there was a preference for methyl-selenium over aryl-selenium coupling. Although aryl-selenium coupling was observed, it was formed either in minor quantities, or after methyl-selenium bond formation where Pd-Me bonds were no longer present. These observations are consistent with those in Chapters Two and Three in which aryl-oxygen coupling was shown to occur less readily than methyl-oxygen coupling. Reactions of $(ArCO_2)_2$ with $Pd(O_2CAr)Tol(bpy)$ required higher temperatures and longer reaction times to form $Tol\text{-}O_2CAr$ than the analogous reaction to form $Me\text{-}O_2CAr$, while aryl-oxygen coupling was not seen at all in the reaction of $Pd(O_2CAr)Tol(tmeda)$ (Chapter Two). In Chapter Three it was shown that while methyl-oxygen coupling occurred readily from $Pt(O_2CPh)_2Me(NCN)$, no aryl-oxygen coupling was observed from $Pt(O_2CPh)_2Tol(NCN)$. It was also suggested that accessibility and orientation of the aryl ligand prior to coupling is important. Therefore, in light of these observations, it is not surprising that aryl-chalcogen coupling was not as facile as methyl-chalcogen coupling. This may be due to increased congestion around the metal centre hindering the approach of the free benzoate ion, and/or restricting movement of the aryl group to the orientation required for coupling. Similar considerations would apply if $C(sp^2)$-O coupling were to occur by a mechanism not involving initial dissociation of a benzoate group.

It is clear that the formation of carbon-selenium bonds through reactions of PdMeAr(bpy) (Ar = Tol, Anis) and PdMeR(tmeda) (R = Me, Anis) with $(ClC_6H_4Se)_2$, described in Section 4.2, proceeds *via* different routes than the analogous reactions with diaroyl peroxides discussed in Chapter Two. However, the use of diselenide reagents as a model for diaroyl peroxides has allowed access to some palladium(IV) species analogous to inaccessible intermediates implicated in some of the reactions discussed in Chapter Two.

4.4 Experimental

4.4.1 General Experimental

4.4.1.1 Instrumentation

Elemental analysis, GC-MS and ^{1}H NMR spectroscopy were carried out as described in Section 2.3.1.1. ^{31}P NMR spectroscopy was performed on a Varian INOVA-400 NMR operating at 161.80 MHz and shifts are reported in ppm relative to an external H_3PO_4 reference.

4.4.1.2 Reagents and Solvents

All reactions and manipulations of air and moisture sensitive compounds were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were purified and dried in the normal manner.[29] The reagents PdMe(Anis)(bpy),[30] PdMeTol(L_2) (L_2 = bpy, tmeda)[30] and $PdMe_2(L_2)$ (L_2 = tmeda, dmpe)[31] were prepared as described. PdMeTol(dmpe) was prepared as described for $PdMe_2$(dmpe) but using PdMeTol(tmeda) as reagent.[31] Other reagents were used as received.

4.4.2 Synthesis of Complexes

$Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ (31). A solution of $(ClC_6H_4Se)_2$ (0.060 g , 0.157 mmol) in a minimum of CH_2Cl_2 (~ 2 mL) was added to a sample of solid PdMe(Anis)(bpy) (0.0378 g, 0.0982 mmol) precooled to –40 °C. The solution quickly became dark red in colour and stirring was continued for two hours at –40 °C. The solution was concentrated *in vacuo* at low temperature to near dryness, and *n*-pentane added to precipitate the red product. The solid was rinsed twice with *n*-pentane (2 x 3 mL) and once with diethyl ether (2 mL), then dried *in vacuo*. The product was stored at –20 °C. Yield: 0.070 g (93 %). ^{1}H NMR (CD_2Cl_2, -40 °C): δ 8.85 (d, 1H, ^3J = 4.4 Hz, H6), 8.19 (d, 1H, ^3J = 5.2 Hz, H6'), 7.89 (t, 1H, ^3J = 8.0 Hz,

H4), 7.72 (t, 1H, ^3J = 8.0 Hz, H4'), 7.66 (d, 1H, ^3J = 8.0 Hz, H3), 7.54-7.48 (m, 2H, H3' and H5), 7.46 (d, 2H, ^3J = 8.8 Hz, *o*-H Anis), 7.22 (t, 1H, ^3J = 6.8 Hz, H5'), 6.83 (d, 2H, ^3J = 8.8 Hz, *m*-H Anis), 6.43 (m, 8H, C_6H_4), 3.81 (s, 3H, OMe), 2.50 (s, 3H, PdMe). Anal. Calcd: C, 47.05; H, 3.42; N, 3.66. Found: C, 46.98; H, 3.36; N, 3.58.

Pd(SeC$_6$H$_4$Cl)Me(dmpe) (33). A solution of $(ClC_6H_4Se)_2$ (0.0143 g, 0.0375 mmol) in CH_2Cl_2 (2 mL) was added to a stirred solution of $PdMe_2$(dmpe) (0.0107 g, 0.037 mmol) in CH_2Cl_2 (2 mL) at –50 °C. The solution was allowed to warm slowly to ambient temperature with stirring. The volume was reduced to near dryness *in vacuo*, and *n*-pentane added to precipitate the product, an orange solid, which was collected by filtration, rinsed with *n*-pentane (3 x 5 mL) and dried *in vacuo*. Yield: 0.016 g (95 %). Crystals suitable for X-ray crystallography were obtained by recrystallisation from CH_2Cl_2/diethyl ether. ^{1}H NMR ($CDCl_3$): δ 7.60 (d, 2H, ^3J = 8.4 Hz, C_6H_4), 7.01 (d, 2H, ^3J = 8.4 Hz, C_6H_4), 1.88-1.58 (m, 4H, PC*H*$_2$), 1.48 (d, 6H, $^2J_{PH}$ = 10.0 Hz, PMe), 1.13 (d, 6H, $^2J_{PH}$ = 8.4 Hz, PMe), 0.15 ('t', 3H, $^3J_{PH}$ = 6.8 Hz and 6.0 Hz, PdMe). ^{31}P NMR ($CDCl_3$): δ 21.39 (d, $^3J_{PP}$ = 21 Hz), 31.40 (d, $^3J_{PP}$ = 22 Hz). Anal. Calcd: C, 33.79; H, 5.02. Found: C, 33.78; H, 5.08.

Pd(SeC$_6$H$_4$Cl)$_2$(dmpe) (34). A solution of $PdMe_2$(dmpe) (0.0103 g, 0.0359 mmol) and $(ClC_6H_4Se)_2$ (0.0347 g, 0.0911 mmol) in a minimum of CH_2Cl_2 (~ 0.8 mL) were allowed to react for several hours at room temperature. *n*-Pentane was added to the resulting orange solution in order to precipitate the product. The suspension was centrifuged and the yellow supernatant removed. The orange product was rinsed with *n*-pentane (2 x 1 mL) and diethyl ether (2 mL), and dried *in vacuo*. Yield: 0.0102 g (44 %). ^{1}H NMR (CD_2Cl_2): δ 7.51 (d, 4H, ^3J = 8.0 Hz, C_6H_4), 6.97 (d, 4H, ^3J = 8.0 Hz, C_6H_4), 1.80 (d (br), 4H, $^2J_{PH}$ = 20.0 Hz, PC*H*$_2$), 1.42 (d, 12H, $^2J_{PH}$ = 10.8 Hz, PMe). ^{31}P NMR (CD_2Cl_2): δ 37.59. Anal. Calcd: C, 33.91; H, 3.79. Found: C, 33.77; H, 3.98.

4.4.3 ^{1}H and ^{31}P NMR Studies of the Reaction of Palladium(II) Complexes with $(ClC_6H_4Se)_2$

PdMeAr(bpy) (Ar = Anis, Tol) with $(ClC_6H_4Se)_2$. In a typical experiment, a solution of PdMeAr(bpy) (0.01 – 0.03 mmol) in CD_2Cl_2 (0.2 mL) was cooled to –40 °C. To this was added one equivalent of $(ClC_6H_4Se)_2$ in CD_2Cl_2 (0.4 mL). The reaction was monitored by ^{1}H NMR for several hours. The reaction was allowed to come to room temperature and was monitored over several days. The reaction mixture was also analysed by GC-MS. This reaction was carried out at several temperatures between –40 and 40 °C.

$PdMe_2$(tmeda) with $(ClC_6H_4Se)_2$. In a typical experiment, a solution of $(ClC_6H_4Se)_2$ (0.0059 g, 0.0155 mmol) in CD_2Cl_2 (0.4 mL) was added to a solution of $PdMe_2$(tmeda) (0.0078 g, 0.0309 mmol) in CD_2Cl_2 (0.2 mL). The reaction was monitored for *ca.* two hours after mixing, then daily for several days. The reaction mixture was also analysed by GC-MS. This reaction was also carried out in acetone-d_6.

PdMeTol(tmeda) with $(ClC_6H_4Se)_2$. In a typical experiment, a solution of $(ClC_6H_4Se)_2$ (0.0040 g, 0.0105 mmol) in CD_2Cl_2 (0.4 mL) was added to a solution of PdMeTol(tmeda) (0.0035 g, 0.0106 mmol) in CD_2Cl_2 (0.2 mL). The reaction was monitored for *ca.* two hours after mixing, then daily for several days. The reaction mixture was also analysed by GC-MS. This reaction was also carried out in acetone-d_6.

PdMeR(dmpe) (R = Me, Tol) with $(ClC_6H_4Se)_2$. In a typical experiment, a solution of $(ClC_6H_4Se)_2$ (0.0040 g, 0.0105 mmol) in CD_2Cl_2 (0.4 mL) was added to a solution of PdMeR(dmpe) (0.0105 mmol) in CD_2Cl_2 (0.2 mL). The sample was monitored by ^{1}H and/or ^{31}P NMR to the completion of the reaction. To this was added a second equivalent of $(ClC_6H_4Se)_2$ (0.0040 g, 0.0105 mmol) and the reaction monitored to its completion.

4.4.4 Determination of Equilibrium Constants

In a typical experiment, a sample of $Pd(SeC_6H_4Cl)_2Me(Anis)(bpy)$ (0.0040 g, 0.0052 mmol) was cooled to the required temperature then dissolved in CD_2Cl_2 (600 μL). The sample was kept at the required temperature for several hours then monitored in a precooled NMR probe for several hours until equilibrium was reached. The concentration of each compound was determined through integration of appropriate peaks. A 5 % error on integration was assumed.

4.4.5 Other Reactions

Tmeda with CD_2Cl_2. A solution of tmeda (2 μL, 0.0133 mmol) in CD_2Cl_2 (0.6 mL) was monitored by ^1H NMR over several days.

4.4.6 X-Ray Data Collection, Structure Determination and Refinement

Structures were solved by Prof Allan H. White and Dr Brian W. Skelton, School of Biomedical and Chemical Sciences, University of Western Australia, as described in Section 2.3.7. Crystal data and details of the structure determination of **33** are presented in Table 4.4.

Table 4.4: Specific crystallographic details for $Pd(SeC_6H_4Cl)Me(tmeda)$ (**33**).

	33
formula	$C_{13}H_{23}ClP_2PdSe$
fw	462.11
cryst size, mm^3	0.2 x 0.17 x 0.14
cryst system	orthorhombic
space group	$Pna2_1$
a, Å	16.919(3)
b, Å	6.1734(3)
c, Å	16.906(3)
V, $Å^3$	1766
Z	4
ρ_{calcd}, $g.cm^{-3}$	1.73_8
μ_{Mo}, cm^{-1}	34
$2\theta_{max}$, deg	75
$T_{min/max}$	0.70, 0.80
N_t	36023
N	4731
N_0	2953
R_{int}	0.051
R	0.034
R_w	0.037

Within the space group, one of the bidentate methylene groups was modeled as being disordered over a pair of sites with occupancies set at 0.5 after trial refinement. 'Friedel' data were preserved distinct, x_{abs} refining to 0.02(1).

4.5 References

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Appendix A:

Publication Arising from Work Reported in this Thesis*

"Canty, A.J.; Done, M. C.; Skelton, B. W.; White, A. H. Carbon-oxygen bond formation at organopalladium centres. *Inorg. Chem. Commun.* **2001**, *4*, 648-650."

* The candidate has previously published work under her maiden name, Melanie C. Done.

ELSEVIER

Inorganic Chemistry Communications 4 (2001) 648–650

INORGANIC CHEMISTRY COMMUNICATIONS

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Carbon–oxygen bond formation at organopalladium centres

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Received 20 April 2001; accepted 15 August 2001

Abstract

The reaction of $PdMe_2(bpy)$ (bpy = 2,2′-bipyridine) with diaroyl peroxides is a complex process in which initial oxidation of Pd(II) is followed by methyl group exchange between an undetected Pd(IV) intermediate and $PdMe_2(bpy)$ to give $PdMe(O_2CAr)(bpy)$ and $PdMe_3(O_2CAr)(bpy)$; the latter Pd(IV) complex decomposes by elimination of Me–Me to give additional $PdMe(O_2CAr)(bpy)$ which reacts with $(ArCO_2)_2$ to give $Me–O_2CAr$ and $Pd(O_2CAr)_2(bpy)$. The complexes $Pd(O_2CPh)_2(L_2)$ (L_2 = bpy, *N,N,N′,N′*-tetramethylethylenediamine) have been characterised by X-ray diffraction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Organopalladium(IV); 2,2′-bipyridine; *N,N,N′,N′*-tetramethylethlenediamine; Catalysis; Peroxide; Crystal structure

1. Introduction

The formation of carbon–oxygen bonds at palladium centres is a process of considerable current interest, in particular for the palladium catalysed acetoxylation of arenes [1] and the formation of carbon–oxygen bonds on the reaction of organopalladium(II) complexes with *m*-chloroperbenzoic acid [2], *tert*-butylhydroperoxide [3,4], molybdenum peroxides [5], pentafluoroiodosylbenzene [6], and hydrogen peroxide catalysed by an iron(III) porphyrin catalyst [7]. Organopalladium(IV) species have been suggested as intermediates in these processes, although they have not been detected spectroscopically. However, for closely related carbon–selenium coupling the intermediacy of Pd(IV) has been demonstrated in the reaction of $PdMe_2(bpy)$ (bpy = 2,2′-bipyridine) with diphenyldiselenide to form isolable crystalline *trans*-$PdMe_2(SePh)_2(bpy)$ which decomposes when redissolved in $CDCl_3$ to form C–C bonds (Me–Me) and C–Se bonds (Me–SePh) in ~1:1 ratio together with Pd(II) products (Eq. 1) [8]. In the same report it was noted that dibenzoyl peroxide, $(PhCO_2)_2$, reacts with $PdMe_2(bpy)$ to form inorganic product(s), ethane, and (upon workup) $Me–O_2CPh$ and $PhCO_2H$. We report here preliminary results indicating that the reaction of $PdMe_2(bpy)$ with diaroyl peroxides is a far more complex process than that expected by direct analogy with Eq. (1), and involves Pd(IV) intermediates, methyl group exchange reaction between Pd(II) and Pd(IV) centres, and the reaction of diaroyl peroxides with both dimethylpalladium(II) and monomethylpalladium(II) species.

$$\begin{aligned} Pd^{II}Me_2(bpy) + (PhSe)_2 &\rightarrow Pd^{IV}Me_2(SePh)_2(bpy) \\ &\rightarrow \sim 0.5\ Me–Me \\ &\quad + \sim 0.5\ Me–SePh \end{aligned} \qquad (1)$$

2. Results

When studied by ^1H NMR spectroscopy in acetone-d_6 at ambient temperature, $PdMe_2(L_2)$ (L_2 = bpy, tmeda) (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) were found to react cleanly with $(PhCO_2)_2$ to form inorganic products which were isolated and characterised by X-ray crystallography as square-planar coordination complexes containing unidentate benzoate groups,

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PII: S1387-7003(01)00296-9

$Pd(O_2CPh\text{–}O)_2(L_2\text{–}N,N')$ (Fig. 1). [1] For L_2 = bpy the benzoate groups are oriented on the same side of the PdN_2O_2 coordination plane, but for L_2 = tmeda the groups are on opposite sides in the same manner as reported for $Pd(O_2CMe\text{–}O)_2$(phen-N,N') (phen = 1,10-phenanthroline) [9].

When $(PhCO_2)_2$ was added to $PdMe_2$(bpy) at −70 °C, a slow reaction to form $PdMe_3(O_2CPh)$(bpy) and $PdMe(O_2CPh)$(bpy) occurred; on warming to −30 °C Me–Me and an increasing quantity of $PdMe(O_2CPh)$(bpy) were detected as $PdMe_2$(bpy) and $PdMe_3(O_2CPh)$(bpy) decreased, and at −10 °C Me–O_2CPh was detected together with $Pd(O_2CPh)_2$(bpy) as the sole palladium containing species were still present. No other products were detected, including in particular metallic palladium, methane or ethene. These observations are consistent with the sequence of reactions shown in Eqs. (2)–(5) to give the overall reaction as in Eq. (6).

(i) ∼−70 to ∼−30 °C:

$$Pd^{II}Me_2(bpy) + (PhCO_2)_2 \rightarrow \text{“}Pd^{IV}Me_2(O_2CPh)_2(bpy)\text{”} \quad (2)$$

$$Pd^{II}Me_2(bpy) + \text{“}Pd^{IV}Me_2(O_2CPh)_2(bpy)\text{”} \rightarrow Pd^{IV}Me_3(O_2CPh)(bpy) + Pd^{II}Me(O_2CPh)(bpy) \quad (3)$$

(ii) ∼−30 to ∼−10 °C:

$$Pd^{IV}Me_3(O_2CPh)(bpy) \rightarrow Pd^{II}Me(O_2CPh)(bpy) + Me\text{–}Me \quad (4)$$

(iii) >∼−10 °C:

$$2Pd^{II}Me(O_2CPh)(bpy) + 2(PhCO_2)_2 \rightarrow 2Pd^{II}(O_2CPh)_2(bpy) + 2Me\text{–}O_2CPh \quad (5)$$

(iv) Overall reaction:

$$2Pd^{II}Me_2(bpy) + 3(PhCO_2)_2 \rightarrow 2Pd^{II}(O_2CPh)_2(bpy) + Me\text{–}Me + 2Me\text{–}O_2CPh \quad (6)$$

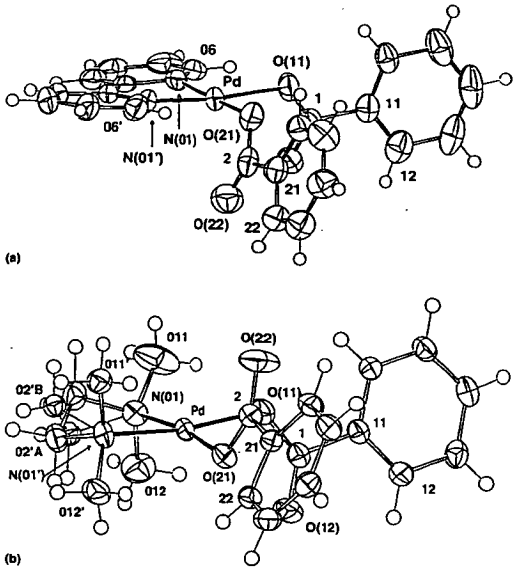

Fig. 1. Projections of molecules of $Pd(O_2CPh)_2(L_2)$ (L_2 = bpy, tmeda) illustrating the square planar coordination geometry with unidentate carboxylate groups, showing 50% thermal ellipsoids for the non-hydrogen atoms, hydrogen atoms having an arbitrary radius of 0.1 Å. (a) $Pd(O_2CPh)_2$(bpy). Selected bond lengths (Å) and angles (°), Pd–O(11) 2.006(3), Pd–O(21) 1.991(4), Pd–N(01) 2.022(4), Pd–N(01′) 2.010(4), Pd···O(12) 3.106(4), Pd···O(22) 3.057(5) Å, O(11)–Pd–O(21) 87.3(1), O(11)–Pd–N(01) 96.9(1), O(11)–Pd–N(01′) 172.8(2), O(21)–Pd–N(01) 175.6(1), O(21)–Pd–N(01′) 95.0(2), N(01)–Pd–N(01′) 80.7(2), Pd–O(11)–C(1) 120.8(3), Pd–O(21)–C(2) 119.1(3) (°). (b) $Pd(O_2CPh)_2$(tmeda), showing disorder in the tmeda ligand. Selected bond lengths (Å) and angles (°), Pd–O(11) 2.018(1), Pd–O(21) 2.020(1), Pd–N(01) 2.048(1), Pd–N(01′) 2.052(1), Pd···O(12) 3.165(1), Pd···O(22) 3.122(1) Å, O(11)–Pd–O(21) 93.75(5), O(11)–Pd–N(01) 91.65(5), O(11)–Pd–N(02) 171.82(6), O(21)–Pd–N(01) 172.34(5), O(21)–Pd–N(01′) 89.39(5), N(01)–Pd–N(01′) 85.99(6), Pd–O(11)–C(1) 122.2(1), Pd–O(21)–C(2) 120.7(1)°.

Thus, for combined Eqs. (2) and (3) in (i), when the reagents are mixed in 2:1 ratio and the reaction is allowed to go to completion at −70 °C, the only species detected in solution are the products of Eq. (3) in 1:1 ratio, where undetected “$PdMe_2(O_2CPh)_2$(bpy)” is assumed to undergo the rapid exchange reaction of Eq. (2). Exchange reactions similar to this are commonly observed in Pd(IV) chemistry [10,11]; they occur at low temperature, and proceed in a direction that gives the most stable Pd(IV) species.

To model Eq. (4), the previously reported complex $PdMe_3I$(bpy) [12] was reacted with $Ag[O_2CPh]$ at −70 °C in an NMR tube in a procedure similar to that re-

[1] Structure determinations: Full spheres of multi-scan absorption corrected CCD area-detector diffractometer data (Bruker AXS instrument; monochromatic MoKα) radiation, $\lambda = 0.71073$ Å, T ca. 153 K yielded N_t (total) reflections, merging to N unique (R_{int} quoted), $N_0[F > 4\sigma(F)]$ used in full-matrix least-squares refinement [anisotropic thermal parameters for non-hydrogen atoms, $(x,y,z,U_{iso})_H$ constrained]. $Pd(O_2CPh)_2$(bpy): $C_{24}H_{18}N_2O_4Pd$, M = 504.84, Monoclinic, space group $P2_1/c$, a = 8.647(1), b = 13.428(2), c = 17.477(2) Å, β = 96.975(3)°, V = 2014.2(2) Å^3, $D_c(Z=4)$ = 1.664 g cm^{-3}, N_t = 25727 ($2\theta_{max}$ = 58°), N = 5355 (R_{int} = 0.037), N_0 = 3985 ‘observed’ (R = 0.051, R_w = 0.060). $Pd(O_2CPh)_2$(tmeda): $C_{20}H_{26}N_2O_4Pd$, M = 464.86, Monoclinic, space group $P2_1/n$, a = 11.7882(8), b = 14.5363(9), c = 11.8319(8) Å, β = 98.072(2)°, V = 2007.4(2) Å^3, $D_c(Z=4)$ = 1.538 g cm^{-3}, N_t = 41400 ($2\theta_{max}$ = 75°), N = 10524 (R_{int} = 0.029), N_0 = 7757 (R = 0.032, R_w = 0.037). The methylene groups of tmeda are disordered over two sites with populations 0.771(6) and 1–0.771(6).

ported for the synthesis of $PdMe_2(CH_2Ph)(O_2CPh)$(bpy) [13], to give a ^1H NMR spectrum indicating the presence of $PdMe_3(O_2CPh)$(bpy). [2] This complex was found to be stable up to ~−30 °C, at which temperature it underwent reductive elimination of ethane and formation of $PdMe(O_2CPh)$(bpy). When combined reactions 2–4 in (i) and (ii) were studied by mixing reagents in 2:1 ratio, and the reaction allowed to go to completion at −30 °C, the only species remaining were $PdMe(O_2CPh)$(bpy) and Me–Me.

To model Eq. (5), $PdMe(O_2CPh)$(bpy) [3] was synthesised by the reaction of PdMeI(bpy) with $Ag[O_2CPh]$, and it was found to be unreactive toward $(PhCO_2)_2$ in acetone-d_6 until the temperature was increased to −10 °C, at which temperature it underwent the reaction of Eq. (5).

Thus, to model the reactions of (Eqs. (2)–(5)) in (i)–(iii), summarised as Eq. (6) in (iv), the reaction was performed with the reagents in stoichiometry 2:3, resulting in the detection of the products of Eq. (6) and with all reagents consumed. Identical results for the overall reaction were obtained for the reactions of $PdMe_2$(bpy) with $(ArCO_2)_2$ (Ar = p-$CF_3C_6H_4$, p-$NO_2C_6H_4$) and of $PdMe_2$(tmeda) with $(PhCO_2)_2$.

3. Discussion

The results reported here show that carbon–oxygen coupling in the reaction of $PdMe_2$(bpy) with diaroyl peroxides occurs at a *mono*methylpalladium centre rather than at a *di*methylpalladium centre, and thus the C–O coupling may involve oxidation of MePd(II) to a MePd(IV) intermediate in a similar manner to that proposed in recent studies using other reagents as oxidants for monoorganopalladium(II) reactants [1–7]. The processes involving oxidation of $PdMe_2$(bpy) to give an undetected Pd(IV) species, assumed to be "$PdMe_2(O_2CAr)_2$(bpy)", subsequent exchange reactions between Pd(II) and Pd(IV) centres, reductive elimination of ethane from a characterised Pd(IV)intermediate, and reaction of diaroyl peroxide with the monomethylpalladium(II) species thus formed, illustrate the complexity of reactivity that is possible in organopalladium(IV) chemistry and the caution needed in assigning reaction pathways from deceptively simple reactions. In particular, C–O coupling does not occur from the Pd(IV) complex detected spectroscopically, $PdMe_3(O_2CPh)$(bpy).

This work is currently being extended to include a range of ancillary ligands at palladium(II), the inclusion of more complicated systems such as (alkyl)(aryl)palladium(II) reagents to probe selectivity in carbon oxygen bond formation, and studies of reactions similar to that of Eq. (1) as model "simple" systems in which a reagent acts as an oxidising agent for palladium(II) to facilitate carbon heteroatom coupling.

4. Supplementary material

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (Deposition nos. 161792 and 161793). Copies of the information can be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Australian Research Council for financial support.

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[2] ^1H NMR data for $PdMe_3(O_2CPh)$(bpy) in acetone-d_6 at −70 °C (400 MHz): δ9.04 (d, 2H, H6-bpy, ^3J = 4.7 Hz); 8.62 (d, 2H, H3-bpy, ^3J = 7.8 Hz); 8.23 ('t', 2H, H4-bpy); 7.81 ('t', 2H, H5-bpy); 7.67 (d, 2H, H2, 6-Ph, ^3J = 7.6 Hz); 7.21 (t, 1H, H4-Ph, ^3J = 6.8 Hz); 7.13 ('t', 2H, H3, 5-Ph); 1.69 (s, 6H, $PdCH_3$); 0.61 (s, 3H, $PdCH_3$).

[3] $PdMe(O_2CPh)$(bpy). ^1H NMR in acetone-d_6 (400 MHz): δ 8.60 (d(br), 1H, H6-bpy, ^3J = 5.5 Hz); 8.55 (d(br), 1H, H3-bpy, ^3J = 8.2 Hz); 8.49 (d(br), 1H, H3-bpy, ^3J = 8.2 Hz); 8.36 (d(br), 1H, H6-bpy, ^3J = 5.4 Hz); 8.21 (m, 1H, H4-bpy); 8.10 (m, 3H, H4-bpy and H2.6-Ph); 7.65 (m, 1H, H5-bpy); 7.56 (m, 1H, H5-bpy); 7.48–7.37 (m, 3H, H3,4,5-Ph); 0.87 (s, 3H, $PdCH_3$).