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Selectivity in reductive elimination and organohalide transfer from methyl(aryl)benzylpalladium(IV) complexes of bidentate nitrogen donor ligands, PdBrMe(Ar)(CH2Ph)(L-2)

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Library and Cultural Collections University of Tasmania Private Bag 3 Hobart, TAS 7005 Australia E oa.repository@utas.edu.au Selectivity in reductive elimination from dialkyl(aryl)palladium(IV) complexes, and the observation of benzyl halide transfer from palladium(IV) to palladium(II). The X-ray structure of methyl(phenyl)(2,2'-bipyridyl)palladium(II)

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Abstract

The first arylpalladium(IV) complexes, [PdXMePhR(bpy)] (bpy = 2,2'-bipyridyl), have been isolated upon oxidative addition of methyl iodide or benzyl bromide to [PdMePh(bpy)]. These dialkyl(aryl)palladium(IV) complexes undergo reductive elimination in solution at *ca*. 0 °C: [PdBrMePh(CH₂Ph)(bpy)] decomposes quantitatively into [PdBr(CH₂Ph)(bpy)] and toluene whereas [PdIMe₂Ph(bpy)] gives ethane and toluene in 4 : 1 ratio together with the corresponding complexes [PdIR(bpy)] (R = Me or Ph). The reaction of methyl iodide with [PdMePh(tmeda)] at 0 °C yields ethane and [PdIPh(tmeda)] without detection of a palladium(IV) intermediate. No reaction of [PdMePh(tmeda)] with benzyl bromide was observed. The first demonstration that organic groups can be transferred from palladium(IV) to palladium(II) is reported. The molecular structure of [PdMePh(bpy)] in the solid state has been determined.

Recently we reported the first examples of arylpalladium(II) nitrogen donor complexes in which the aryl group is not part of either an intramolecularly coordinating group or a metallacyclic system, viz. [PdIPh(tmeda)] and [PdMePh(tmeda)] (1).¹ The remarkable stability of 1 and of its 2,2'-bipyridyl analogue [PdMePh(bpy)] (2) has enabled us to prepare novel arylpalladium(IV) complexes and to use these in a study of the selectivity of reductive elimination from dialkyl(aryl)palladium(IV) compounds. Moreover, we have observed the first example of alkyl halide transfer from palladium(IV) to palladium(II).

Yellow [PdMePh(bpy)] (2) was obtained from the reaction of [PdMePh(tmeda)] (1) with bpy in benzene and was recrystallized from acetone/pentane. The molecular structure² of 2 (figure 1) shows a square planar coordinated palladium with the methyl and phenyl group *cis* to each other and the phenyl group oriented approximately normal to the coordination plane (the angle between the least-squares planes of the phenyl ring [C11...C16] and of the coordination plane [C11, C17, N1, N2] is 78.68(19)^o). The bond lengths and bond angles have values similar to those observed earlier in related complexes.¹

 $\begin{array}{c} C3 \\ C4 \\ C5 \\ C1 \\ C5 \\ C1 \\ C11 \\ C16 \\ C12 \\ C12 \\ C13 \\ C13 \\ C12 \\ C13 \\ C13 \\ C14 \\ C12 \\ C13 \\ C13 \\ C13 \\ C14 \\ C12 \\ C13 \\ C13 \\ C14 \\ C14 \\ C12 \\ C13 \\ C13 \\ C14 \\ C12 \\ C13 \\ C13 \\ C14 \\ C12 \\ C13 \\ C13 \\ C13 \\ C14 \\ C12 \\ C13 \\$

Fig. 1. ORTEP drawing (50% probability level) of the molecular structure of [PdMePh(bpy)] (2). Selected bond lengths (Å) and angles (°): Pd-C17 2.020(5), Pd-C11 1.985(3), Pd-N1 2.117(3), Pd-N2 2.138(3), N1-Pd-N2 77.21(10), C11-Pd-C17 85.69(19), N1-Pd-C11-C12 98.7(3).

¹H NMR studies of the reactions of MeI and PhCH₂Br with 1 and 2 were conducted by adding an excess of the alkyl halide to a solution of each complex in $(CD_3)_2CO$ at -60 °C, followed by warming until reaction occurred. Reaction of 1 with MeI at 0 °C gives [PdIPh(tmeda)] and ethane only, without a detectable palladium(IV) intermediate (equation 1).

$$PdMePh(tmeda) + MeI \longrightarrow PdIPh(tmeda) + MeMe (1)$$
1

However, 2 reacts at 0 °C to give spectra consistent with the formation of two isomeric forms of [PdIMe₂Ph(bpy)] (3) (figure 2). The isomers are unstable at 0 °C and undergo reductive elimination to



Fig. 2. Isomers of $[PdIMe_2Ph(bpy)]$ (3), present in ca. 1 : 1 ratio in CDCl₃.

form ethane (80%), toluene (20%), and $[PdIR(bpy)]^{3,4}$ (equation 2) and were not observed in pure form under these conditions. The selectivity in reductive elimination from $[PdIMe_2Ph(bpy)]$ (equation 2), and

$$PdMePh(bpy) + MeI \longrightarrow PdIMe_2Ph(bpy) \longrightarrow$$

$$2 \qquad 3$$

$$\longrightarrow 0.8[PdIPh(bpy) + MeMe] \qquad (2)$$

$$0.2[PdIMe(bpy) + MePh]$$

presumably also from [PdIMe₂Ph(tmeda)] (equation 1), is consistent with the reported preference for ethane elimination from a range of Pd^{IV}XMe₂R complexes where R \neq ary1, e.g. [PdBrMe₂(CH₂Ph)(L₂)].^{5,6a} Surprisingly, benzyl bromide does not react with 1 even at 50 °C (the decomposition temperature of the latter complex in acetone) although 2 readily forms [PdBrMePh(CH₂Ph)(bpy)] (4) (equation 3) at 0 °C. Complex 4 undergoes a relatively slow reductive elimination at 0 °C, with exclusive coupling of phenyl and methyl groups (equation 3).⁴

$$\begin{array}{c} PdMePh(bpy) + PhCH_2Br \longrightarrow PdBrMe(CH_2Ph)Ph(bpy) \\ 2 & 4 \\ \longrightarrow PdBr(CH_2Ph)(bpy) + MePh \end{array} \tag{3}$$

The inability of PhCH₂Br to react with 1 may be ascribed to steric effects. Such effects have been found to be very important in S_N^2 reactions of platinum(II) complexes, *e.g.* [PtMe₂(phen)] reacts *ca.* 1,000 times slower with EtI than with MeI.⁷ Although the two dimethylamino groups in [PdMePh(tmeda)] are in the nucleophile instead of in the electrophile, their size may well be a dominant factor in determining the relative reactivities of 1 and 2. In addition, the dimethylamino groups appear to encourage dissociation of iodide from [PdIMe₃(tmeda)],⁸ and halide dissociation is implicated as the first step in reductive eliminations from Pd^{IV}Me₃ complexes.^{6b,8}

The palladium(IV) complexes [PdIMe₂Ph(bpy)] (3) and [PdBrMePh(CH₂Ph)(bpy)] (4) were isolated as white solids on reaction of [PdMePh(bpy)] with excess alkyl halide at 0 °C in acetone, followed by addition of pentane (4) or cooling to -60 °C and addition of pentane (3).¹⁰ In the ¹H spectrum (CDCl₃) of 3 the presence of two isomers is indicated by three wellresolved bpy-H6 resonances at 9.10 ppm (d, 2H, 3b), 8.98 ppm (d, 1H, 3a) and 8.76 ppm (d, 1H, 3a). We believe that the H6 resonance of 3a next to the phenyl group lies at high field owing to the proximity of this H6 to the phenyl ring which is forced to lie approximately normal to the bpy plane (cf. figure 1). The relative intensities of the H6 resonances indicate that the isomers 3a and 3b occur in ca. 1 : 1 ratio. This result is consistent with the three methyl signals found at 2.31 (3b), 2.30 (3a) and 1.70 (3a) ppm with intensity ratio 2:1:1 corresponding to three Pd^{IV}-bound methyls in different environments. A comparison with spectra of $PdIMe_2R(bpy)$ (R = Me,^{9b} CH₂CH=CH₂¹¹) indicates that the two low-field resonances correspond to methyl groups trans to bpy and the upfield resonance to a methyl group trans to iodine.

The ¹H NMR spectrum (CDCl₃) of 4 shows unique PdMe, PdPh, and PdCH₂Ph environments, and two pyridine-ring environments. The PdMe resonance, at 2.39 ppm, occurs downfield from that of the methyl groups in [PdBrMe₂(CH₂Ph)(bpy)] (1.98 ppm). Because the latter complex has both methyl groups trans to bpy,^{5b} and resonances for PdMe groups trans to a halogen are generally upfield from those trans to nitrogen donors, ^{8,9} it is reasonable to assume that compound 4 has either structure 4a or 4b (figure 3).



Fig.3. Possible isomers of [PdBrMe(CH₂Ph)Ph(bpy)] (4).

Since $[PdMe_2(bpy)]$ forms more stable palladium(IV) compounds than does [PdMePh(bpy)], the reactivity of $[PdMe_2(bpy)]$ toward $[PdBrMePh(CH_2Ph)(bpy)]$ (4) was investigated. ¹H NMR studies in $(CD_3)_2CO$ at 0 °C showed selective benzyl-transfer as in equation 4.

 $PdBrMe(CH_2Ph)Ph(bpy) + PdMe_2(bpy) \longrightarrow$

$$\longrightarrow$$
 PdMePh(bpy) + PdBrMe₂(CH₂Ph)(bpy) (4)

This reaction probably follows the same mechanism as was proposed by Canty and Puddephatt for the alkyl halide transfer from PdBrMe₂(CH₂Ph)(phen)] to [PtMe₂(phen)].^{6a} The isolation of arylpalladium(IV) complexes indicates that organopalladium(IV) chemistry now extends beyond the initially reported alkyl and benzyl complexes. The observation of selectivity in reductive elimination (equations 1-3) and in the transfer of groups from palladium(IV) to palladium(II) (equation 4) may be important in the further development of this new oxidation state in organic synthesis and catalysis.

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References and notes.

- ¹W. de Graaf, J. van Wegen, J. Boersma, A.L. Spek and G. van Koten, Recl. Trav. Chim. Pays-Bas 108, 275 (1989).
- ² Crystal data for 2: $C_{17}H_{16}N_2Pd$: Space group P2₁/n, cell dimensions a = 8.570(1) Å, b = 19.486(1) Å, c = 9.449(1) Å, $\beta = 111.36(1)^{\circ}$. X-ray data were collected at room temperature on an Enraf-Nonius CAD-4 T diffractometer [MoK α monochromator, $\lambda = 0.71073$ Å, rotating anode, $\Theta_{max} = 27.5^{\circ}$] for a plate-shaped crystal [0.03 x 0.40 x 0.68 mm] glued on top of a glass fiber. A total of 7392 reflections were scanned, corrected for L_p and merged into a unique set of 2750 reflections [$R_{av} = 0.027$] with $I > 2.5 \sigma(I)$. The structure was solved with Patterson techniques [SHELXS-86] and refined on F to R = 0.033 [$W_R = 0.043$] with SHELX-76. Refined and derived parameters have been deposited with the Cambridge Crystallographic Data Center.
- ³ The new complex [PdIPh(bpy)] was obtained in 70% yield by oxidative addition of iodobenzene to bis(dibenzylideneacetone)palladium(0) in benzene in the presence of bpy, in the same manner as reported for [PdIPh(tmeda)].¹

- ⁴ The complexes [PdIMe(L₂)],^{9a,5a} [PdIPh(tmeda)],¹ [PdBr(CH₂Ph)(bpy)] and [PdBrMe₂(CH₂Ph)(bpy)]^{5b} have been reported earlier. Spectra of solutions of ethane, methane, toluene, ethylbenzene, benzene, diphenylmethane, and biphenyl were obtained to assist with interpretation of NMR spectra.
- ⁵ (a) W. de Graaf, J. Boersma and G. van Koten, Organometallics 9, 1479 (1990). (b) P.K. Byers, A.J. Canty, B.W. Skelton, P.R. Traill, A.A. Watson and A.H. White, ibid. 9, 3080 (1990).
- ⁶ (a)K.-T. Aye, A.J. Canty, M. Crespo, R.J. Puddephatt, J.D. Scott and A.A. Watson, Organometallics 8, 1518 (1989). (b) P.K. Byers, A.J. Canty, M. Crespo, R.J. Puddephatt and J.D. Scott, ibid. 7, 1363 (1988).
- ⁷ P.K. Monaghan and R.J. Puddephatt, J. Chem. Soc., Dalton Trans., 595 (1988).
- ⁸ W. de Graaf, J. Boersma, W.J.J. Smeets, A.L. Spek and G. van Koten, Organometallics 8, 2907 (1989).
- 9 (a) P.K. Byers, A.J. Canty, B.W. Skelton and A.H. White, J. Chem. Soc., Chem. Commun., 1722 (1986). (b) P.K. Byers, A.J. Canty, B.W. Skelton and A.H. White, Organometallics 9, 826 (1990). (c) A.J. Canty, P.R. Traill, B.W. Skelton and A.H. White, J. Organomet. Chem. 402, C33 (1991).
- ¹⁰ **2**: ¹H NMR (300 MHz, CD₃COCD₃): δ 0.38 (s, 3H, PdMe); 6.83 (t, ³J = 7.3 Hz, ⁴J = 1.4 Hz, 1H, p-PhH); 6.96 (t, ³J = 7.3 Hz, ⁴J = 1.4 Hz, 2H, m-PhH); 7.47 (d, ³J = 7.8 Hz, ⁴J = 1.4 Hz, 2H, o-PhH); 7.56 (m, 1H, bpy); 7.77 (m, 1H, bpy); 8.21 (m, 3H, bpy); 8.54 (m, 2H, bpy); 8.81 (d, ³J = 4.5 Hz, 1H, bpy).

3: ¹H NMR (300 MHz, CDCl₃): δ 1.70, 2.30, 2.31 (s, Pd*Me*); 6.77 (m, 2H, Ph); 6.85 (m, 3H, Ph); 7.16 (m, 3H, Ph); 7.46 (m, 1H, bpy); 7.65 (m, 3H, bpy); 7.80 (s, v br, 2H, Ph); 8.11 (m, 8H, bpy); 8.76 (d, ³J = 4.9 Hz, 1H, bpy); 8.98 (d, ³J = 4.9 Hz, 1H, bpy); 9.10 (d, ³J = 4.8 Hz, 2H, bpy).

4: ¹H NMR (300 MHz, CDCl₃): δ 2.39 (s, 3H, PdMe); 3.79 (AB, 2H, -CH₂-); 6.43 (s, br, 2H, o-Ar); 6.61 (t, ³J = 7.6 Hz, 2H, m-Ar); 6.79 (t, ³J = 7.4 Hz, 1H, p-Ar); 7.25 (m, 7H, CDCl₃ + bpy + Ar); 7.45 (m, 1H, bpy); 7.86 (m, 6H, bpy); 8.06 (d, 7.9 Hz, 1H, bpy); 8.38 (d, ³J = 5.0 Hz, 1H, bpy); 8.73 (d, ³J = 4.9 Hz, 1H, bpy).

¹¹ P.K. Byers, A.J. Canty, P.R. Traill and A.A. Watson, J. Organomet. Chem. **390**, 399 (1990).