

MINIREVIEW

Photoactive *N*-heterocyclic carbene transition metal complexes in bond-forming photocatalysis: State-of-the-art and opportunities

Eve M. Poland  | Curtis C. Ho 

School of Natural Sciences—Chemistry,
University of Tasmania, Hobart,
Tasmania, Australia

Correspondence

Curtis C. Ho, School of Natural
Sciences—Chemistry, University of
Tasmania, Hobart 7001, Tasmania,
Australia.

Email: curtis.ho@utas.edu.au

Abstract

This Minireview presents and discusses recent developments in photoactive/photoluminescent *N*-heterocyclic carbene (NHC) transition metal complexes and their viability as catalysts in bond-forming photocatalysis. Specifically, we summarise key structural motifs adopted by photoactive NHC transition metal complexes and highlight some of their photophysical properties. Representative examples of their applications as catalysts in bond-forming photochemical reactions are also showcased presenting the state-of-the-art and future opportunities for this exciting class of NHC transition metal complexes.

KEYWORDS

NHC, carbene, photocatalysis, transition metal complexes

1 | INTRODUCTION

Since the isolation of the first free *N*-heterocyclic carbene (NHC) by Arduengo in 1991,^[1] NHCs have received consistent attention in academic research.^[2] They have demonstrated remarkable versatility with widespread applications in a range of fields including organocatalysis and organometallic catalysis, materials science and medicinal chemistry. In most cases, NHCs are heavily featured as innocent and non-innocent supporting ligands in a variety of metal complexes. Their implementation as versatile supporting ligands was exemplified most notably in synthetically valuable alkene metathesis and cross-coupling catalysis procedures, significant inventions that were recognised by the 2005 and 2010 Nobel Prizes in Chemistry, respectively.^[3]

The current environmental crisis has pushed a paradigm shift in chemical synthesis with significant efforts being made to enhance its economic and environmental

sustainability.^[4] Catalysis remains at the forefront of sustainable chemical synthesis in both academia and industry by effectively applying the principles of green chemistry.^[5] The past decade has seen the revival of photocatalysis^[6] and the closely related field of electrocatalysis,^[7] both of which have the potential to greatly enhance the sustainability of current catalytic processes through harnessing the energy of the sun.

An extensive review by Glaser and Wenger has recently surveyed the vast wealth of transition metal-based photoredox catalysts.^[8] In 2014, Visbala and Gimeno comprehensively reviewed photoactive/photoluminescent NHC metal complexes and their various applications.^[9] However, the recent decade has seen promising advances in the implementation of photoactive NHC transition metal complexes as catalysts in bond-forming photocatalysis. To the best of our knowledge, this aspect of NHC transition metal complexes has yet to be thoroughly reviewed.

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This Minireview details recently developed photoactive NHC transition metal complexes and highlights case study applications in bond-forming photocatalytic reactions. The first section of this review will highlight some key properties and the structural diversity found in photoactive NHC transition metal complexes. The second section showcases their application in bond-forming photocatalysis, especially processes mediated by visible light. The scope of this review is limited to photochemical reactions where the NHC transition metal complex functions as both photosensitiser and catalyst. As such, cooperative/synergistic dual component catalytic processes involving an exogenous photosensitiser and catalyst as two separate entities, though an intriguing field,^[10] will not be included in our discussions. Within the context of this review, NHCs include normal NHCs and abnormal NHCs (aNHCs or mesoionic carbenes) along with cyclic amino carbenes.

As the reader will discover, despite the rich coordination chemistry of NHC transition metal complexes, their implementation in chemical synthesis through photochemical processes is conspicuously less explored. This review hopes to draw attention to this field, which is ripe for harvest and invigorate research into the untapped potential of photoactive/photoluminescent NHC transition metal complexes for light-mediated chemical synthesis.

2 | REPRESENTATIVE PHOTOACTIVE NHC TRANSITION METAL COMPLEXES: STRUCTURAL DIVERSITY AND PROPERTIES

Harnessing solar energy for light-induced catalysis with transition metal complexes fundamentally relies on the ability of the transition metal complex to engage in single-electron transfer (SET) processes with organic molecules upon photoexcitation. As such, it is essential for transition metal-based photocatalysts to efficiently absorb photon energy attaining photocatalytically active excited states with lifetimes sufficiently long to engage in electron transfer processes with organic molecules. For comparison, the prototypical photoredox catalysts [Ru(bpy)₃]²⁺ and *fac*-[Ir(ppy)₃], have triplet metal-to-ligand charge-transfer (MLCT) lifetimes of 1100^[11] and 1900 ns,^[12] respectively, which is sufficiently long to engage in bimolecular SET reactions with a wide range of organic molecules.^[6a] As such, long-lived and high energy MLCT states are ideal properties for photoredox catalysts. An excellent review on the electronic structure of transition metal complexes and their implications for light harvesting by McCusker highlighted several key

strategies to extend photocatalytically active excited state lifetimes.^[13] These include employing ligands with strong σ -donor, π -acceptor and electron delocalisation capabilities, which facilitate the stabilisation of photocatalytically productive MLCT states and destabilisation of metal centre (MC) states. It comes with no surprise that NHCs have emerged as attractive ligands to enhance the photo-physical properties of their corresponding transition metal complexes due to their unique electron donating capabilities.

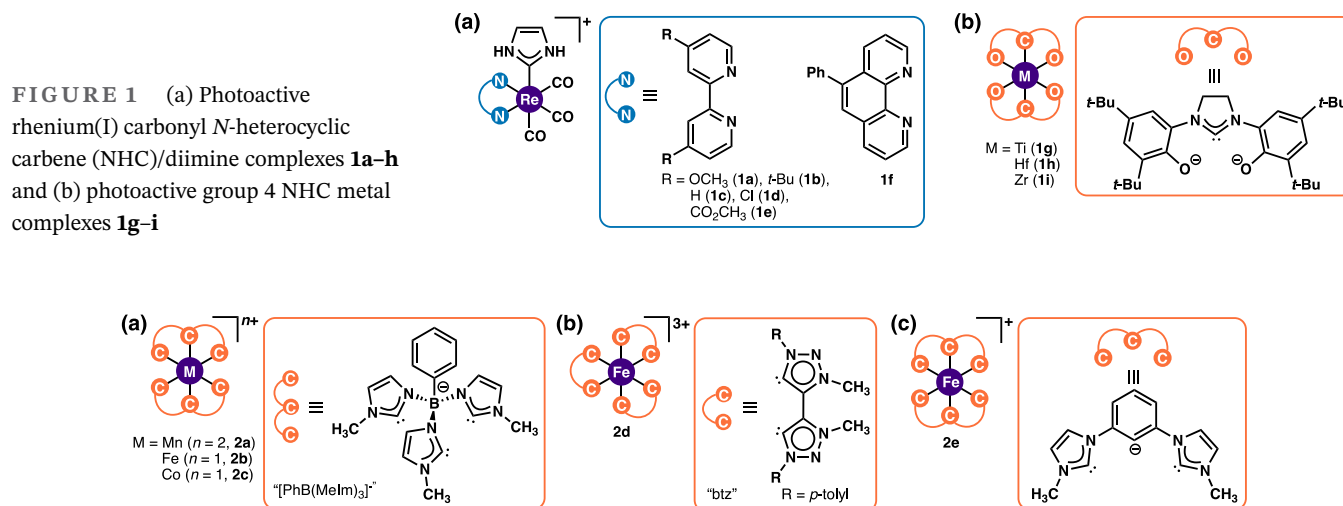
The exceptional σ -donor capacity of NHCs and their ease of systematic structural modification such as their inclusion in extended π -systems have imbued corresponding NHC transition metal complexes with promising photophysical and electrochemical properties that can be exploited for a range of applications. The first example of a photoactive carbene complex was reported in 1998 by Lai and co-workers.^[14] In the same year, they reported one of the earliest examples of photoactive NHC rhenium(I) carbonyl complexes containing a monodentate protic NHC supported by aromatic diimine ligands, **1a–f** (Figure 1a).^[15] All complexes featured absorption maxima in the ultraviolet (UV) region with the phenanthroline-ligated complex **1f** exhibiting the longest excited state lifetime at 2520 ns in CH₂Cl₂. These complexes also showed quasireversible oxidation steps in the +1.50 to +1.66 V range (vs. SCE). In 2014, Romaine and co-workers reported a series of NHC group 4 metal complexes **1g–i** bearing an OCO-pincer-type ligand with two pendant anionic phenolate donor groups.^[16] **1g–i** showed promising reversible redox behaviour with radical cations generated from oxidation thermally stable under argon (Figure 1b). The authors suggest that given the potential utility of these types of NHC metal complexes in catalysis,^[17] their work may open the way to novel redox-tuned group 4 NHC-based catalysts. Additionally, complexes **1h** and **1i** represent the first examples of emissive non-metallocene group 4 metal complexes.

Metal complexes supported by multidentate multi-NHC ligands are also known to be photoactive. For example, homoleptic complexes of manganese(IV), **2a**,^[18] iron(III), **2b**^[19] and cobalt(III), **2c**,^[20] featured the tripodal electron-donating tris(NHC)borate ligand [PhB(MeIm)₃][–] and displayed interesting luminescent properties (Figure 2a). Complex **2a** was the first molecular manganese(IV) compound for which luminescence has been reported whereas complex **2b** and **2c** exhibit long excited state lifetimes in the nanosecond to microsecond range. Iron(III) complex **2b** showed strong, visible light, room temperature photoluminescence with a 2.0 ns lifetime **2b** also capable of engaging in reductive and oxidative electron-transfer reactions shown through bimolecular quenching studies with methylviologen and

diphenylamine.^[19] Cobalt(III) complex **2c** displayed a weak but remarkably long-lived orange photoluminescence of ~ 1.0 μ s at 690 nm in CH₃CN at room temperature under UV irradiation. Related homoleptic iron(III) complexes **2d** (Figure 2b)^[21] and **2e** (Figure 2c)^[22] bearing a chelating 4,4'-bis(1,2,3-triazol-5-ylidene) (btz) ligands and a pincer-type phenylene-linked bis (NHC) ligands, respectively, also showed unusual luminescence behaviours upon UV excitation with 100 ps to ~ 4.0 ns excited state lifetimes.

In 2014, Liu and co-workers prepared the first example of a heteroleptic iron (II) complex bearing two btz ligands and one bipyridine (bpy) ligand, **3a** (Figure 3a).^[23] The authors performed extensive photophysical, electrochemical, spectroscopic and computational analysis of complex **3a** and revealed the btz ligand is both redox and photoredox active much like the prototypical bpy ligand. The exceptional donor capacity of the btz mesoionic carbene destabilises MC states and increases the energy gap between the photochemically valuable triplet MLCT state. This results in a longer-lived MLCT state of 13 ps compared with 130 fs for that of the homoleptic bipyridine complex [Fe(bpy)₃]²⁺. This is a significant increase when compared with the 9 ps MLCT lifetime of homoleptic pincer NHC iron(II) complex **3b** reported by the same group earlier (Figure 3b).^[24] These examples clearly indicate the possibility of utilising the MLCT states of NHC-ligated iron(II) complexes to replace expensive ruthenium(II) complexes in fields like photovoltaics and artificial photosynthesis. Additionally, employing NHC chemistry is indeed a viable strategy for improving the photophysical properties of photoactive metal complexes, in particular, iron photochemistry.^[25]

A large majority of photoactive NHC transition metal complexes have also mimicked the ligand motifs of [Ru(bpy)₃]²⁺ and *fac*-[Ir(ppy)₃] by incorporating NHC moieties into pyridyl ligand scaffolds. For example, Seung and co-workers prepared homoleptic NHC ruthenium(II) complexes **4a–b** (Figure 4a), which are NHC analogues of [Ru(bpy)₃]²⁺ and [Ru(terpy)₂]²⁺.^[26] **4a** exhibited promising photoluminescence properties with a long MLCT lifetime of 820 ns in CH₃CN and 3100 ns in water when excited with 354 nm light at room temperature. Both complexes have absorption maxima in the UV region (368 nm for **4a** and 382 nm for **4b**). The lifetime of this chromophore in water is particularly important for light harvesting applications such as artificial photosynthesis.^[27] However, their short wavelength and high energy absorption maxima may hinder visible-light-mediated photoredox reactions. Albrecht and co-workers prepared a series of related heteroleptic mixed bpy/NHC ruthenium(II) complexes where the NHC contains a pendant pyridyl donor group (Figure 4b, **4c–f**).^[28] All complexes showed strong absorption in the high UV range (<300 nm) and a less strong band in the visible region with an absorption maxima in the 410–470 nm range when irradiated in CH₃CN with 355 nm light. All complexes are emissive at room temperature, with emission maxima in the range of 610–620 nm. Complexes **4d–e** with the sterically most demanding *N*-substituents showed the longest-lived lifetimes at 334 and 33 ns, respectively. The authors proposed that the larger *N*-substituents may be important in extending excited state lifetimes of these complexes. Interestingly, benzimidazole-derived NHC complex **4f** had the shortest lifetime at 50 ns.



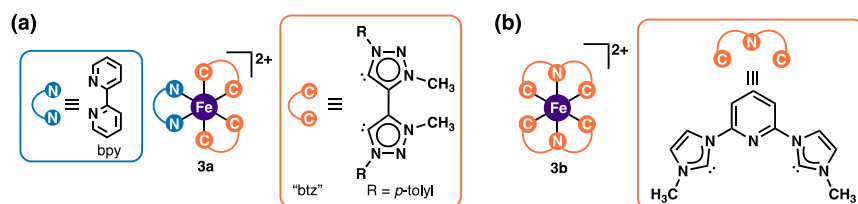


FIGURE 3 Examples of heteroleptic chelating bis(mesoionic carbene) bipyridine iron(II) complex **3a** (a) and homoleptic pincer *N*-heterocyclic carbene (NHC) iron(II) complex **3b** (b)

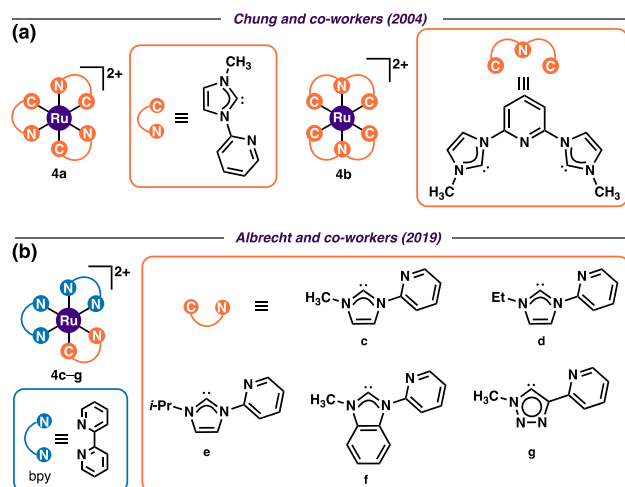


FIGURE 4 Examples of pyridyl-*N*-heterocyclic carbene (NHC) ruthenium(II) complexes: (a) homoleptic complexes **4a–b** and (b) heteroleptic complexes **4c–f**

As mentioned earlier, the inclusion of mesoionic carbene moieties into ligand scaffolds has a positive effect on prolonging MLCT excited state lifetimes. Brown and co-workers prepared a series of heteroleptic bis(tridentate) mesoionic carbene ruthenium(II) complexes bearing a substituted terpyridine (terpy) ligand, **5a–d** (Figure 5).^[29] These exhibited microsecond excited-state lifetimes at room temperature in CH₃CN. The most significant of which being **5d** having an excited state lifetime of 7.9 μs. **5a–d** had absorption maxima in the 463–472 nm range. Although no applications for these complexes have been determined thus far, the prolonged excited-state lifetimes show promise for light-mediated applications.

More recently, monodentate cyclic (aryl/alkyl) (amino)carbenes (CAAC), monoaminocarbenes (MAC) and diamidocarbenes (DAC) have entered the field of chromophoric ligands.^[30] The ability for CAAC-type ligands to enhance the photophysical properties of transition metal complexes is primarily due to their superior π -accepting and σ -donating properties compared to normal NHC ligands. For example, linear copper(I) complexes **6a–e** showed relatively low energy absorption maxima between 250 and 550 nm in THF (Figure 6).^[31] The Steffen and Thompson research groups have pioneered advancements in this field since 2017. In

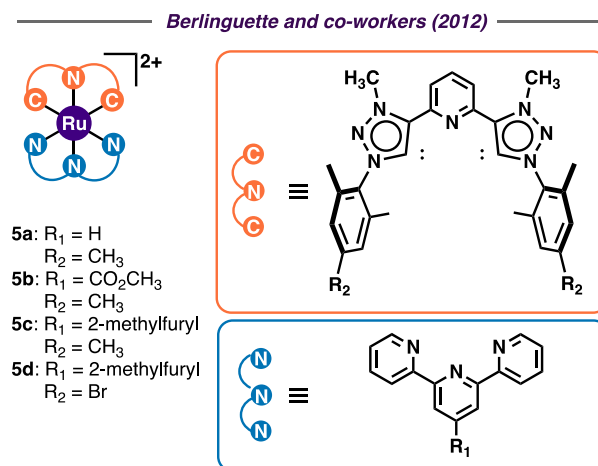


FIGURE 5 Examples of heteroleptic bis(tridentate) mesoionic carbene/terpy ruthenium(II) complexes

particular, complex **6d** showed photoluminescence efficiencies >99% and microsecond lifetimes, which led to an efficient blue-emitting organic light-emitting diode (OLED).^[32]

Liske and co-workers also prepared a series of linear NHC copper(I) pyridine complexes **7a–b** (Figure 7).^[31a,d] Complex **7a** showed very intense blue-to-blue green photoluminescence with remarkable quantum yields of up to 87% and microsecond lifetimes when in the form of powders, neat films and dilute doped films of poly(methyl methacrylate) (PMMA; 1–10%). More interestingly, the authors report these linear carbene copper(I) complexes exhibit mechanochromic luminescence displaying enhanced emission intensity when single crystals were ground. The related linear NHC copper(I) complex **7b** bearing an extremely bulky *N*-triphenylmethyl substituent showed intense blue to orange luminescence when doped in 10% PMMA films and in the solid state with microsecond lifetimes.

3 | APPLICATIONS OF NHC TRANSITION METAL COMPLEXES IN BOND-FORMING PHOTOCATALYSIS

As Visbal and Gimeno's 2014 review extensively described the properties and applications of photoactive

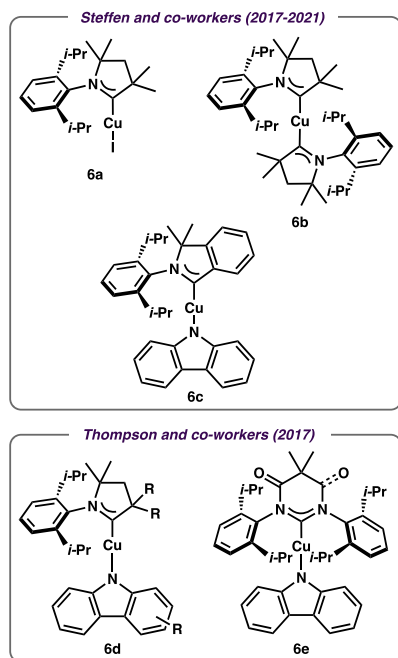


FIGURE 6 Examples of photoluminescent linear cyclic (aryl/alkyl)(amino)carbenes (CAAC), monoaminocarbenes (MAC) and diamidocarbenes (DAC) copper(I) complexes **6a–e**

NHC metal complexes as luminophores in OLEDs such as flat panel displays and solid-state lighting sources,^[9] this section will highlight the application of photoactive NHC transition metal complexes in photocatalytic bond-forming reactions, which are summarised in Table 1.

4 | BOND-FORMING REACTIONS

In 2012, To and co-workers reported one of the first examples of a NHC transition metal complex facilitating bond-forming reactions through photoredox catalysis through the oxidative transformation of secondary and tertiary amines by monodentate NHC gold(III) complex supported by a bis-cyclometalated dinaphthalene-2-yl-pyridine ligand (Scheme 1).^[33] The authors demonstrated that the incorporation of the NHC ligand led to increased luminescence efficiency of the gold(III) complexes **8a–b**.^[33] Both complexes absorbed in the visible region (~ 400 nm) in CH_2Cl_2 with emissive intraligand excited state lifetimes of 282 (for **8a**) and 506 μs (for **8b**). These long-lived triplet excited states could be harnessed to catalyse oxidative functionalisation of secondary and tertiary benzylic amines. In the presence of O_2 , complex **8a** was shown to catalyse the oxidation of secondary amines to imines under >385 nm light irradiation (Scheme 1a). A variety of functional groups could be tolerated efficiently producing the corresponding imines in excellent

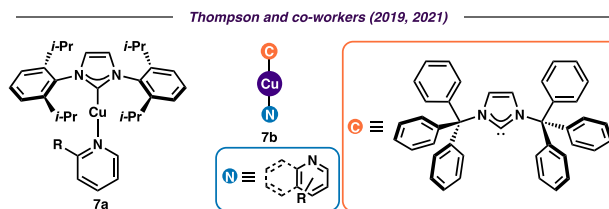


FIGURE 7 Examples of linear NHC copper(I) pyridine-type complexes **7a–b**

yields. The authors proposed that singlet O_2 generated from the photo-excited triplet state of **8a** is the active oxidant in this reaction. **8a** was also shown to catalyse the oxidative cyanation of tertiary amines such as *N*-aryltetrahydroisoquinolines under UV irradiation (Scheme 1b). Photo-excited **8a** generates singlet O_2 that reacts with the $\alpha\text{-C-H}$ of the *N*-aryltetrahydroisoquinoline molecule to give an unstable iminium intermediate. This rapidly reacts with nucleophile NaCN to give the corresponding α -cyanated product. This reaction is tolerable to a variety of R-substituents on the *N*-aryl group.

In 2016, Yang and co-workers prepared an extensive array of chelating bis(NHC) iridium(III) complexes bearing cyclometalated C/N ligands and screened them in several visible-light-induced reductive cyclisations of aryl and alkyl bromides to form indolines and pyrrolidines, respectively (Scheme 2).^[37] All complexes absorbed in the visible region and displayed microsecond emission lifetimes. Complexes **9a–c** showed to be the most active photocatalysts producing cyclised products in good to excellent yields. Interestingly for the reductive cyclisation of aromatic bromides, these NHC iridium(III) photocatalysts outperformed prototypical photoredox catalysts $[\text{Ru}(\text{bpy})_3]^{2+}$ and *fac*- $[\text{Ir}(\text{ppy})_3]$. The authors proposed a radical mechanism as evidenced by total reaction inhibition in the presence of radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). They suggest the photocatalytic reaction could be initiated from the oxidative quenching of the photo-excited catalyst with the aryl/alkyl halides. This results in carbon-halogen bond cleavage to give an alkyl radical in the case of sp^3 carbons or a radical anion intermediate for sp^2 carbons. Subsequent reactions of these radical intermediates with C(sp^2)-H bonds afford C–C bond formation and furnish the cyclised product.

A series of structurally related NHC iridium(III) complexes **10(ppy)a–h** and **10(ppz)a–b** supported by cyclometalated ppy and ppz ligands were prepared by Lam and co-workers (Scheme 3).^[36] This series of complexes featured a unique pyridinium-derived NHC ligand. The authors obtained detailed photophysical data for

TABLE 1 Summary of bond-forming reactions catalysed by photoactive NHC transition metal complexes

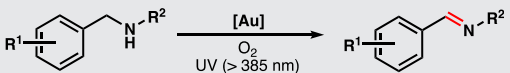
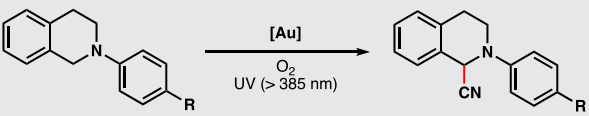
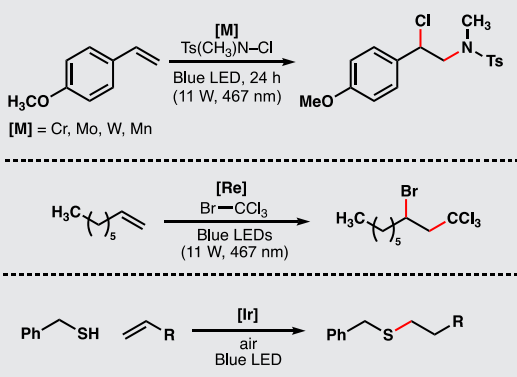
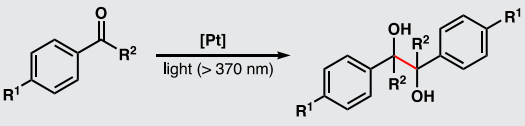
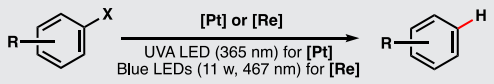
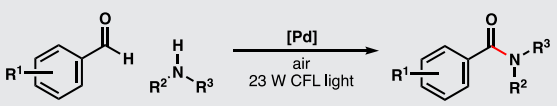
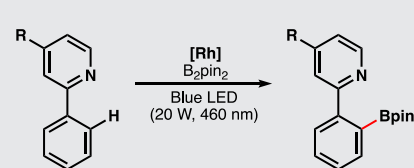
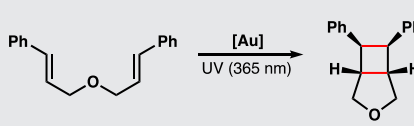
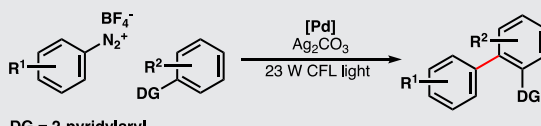
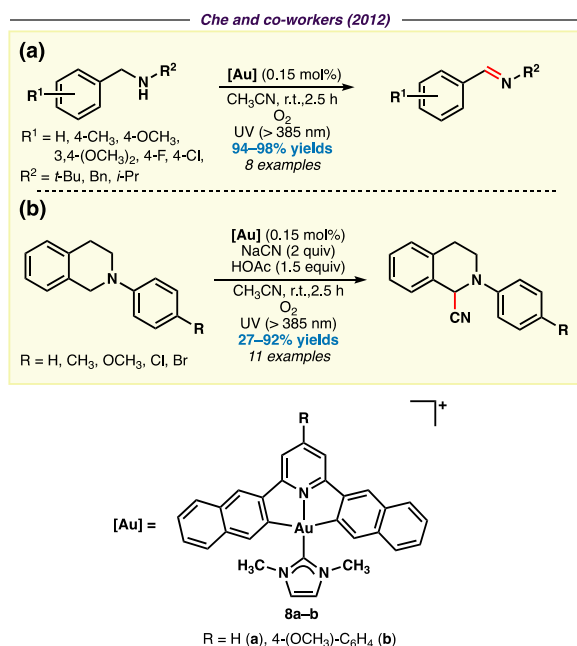
Reaction Type	Reference
Oxidation of secondary amines to imines	To et al. ^[33]
	
Oxidative α -cyanation of tertiary amines	To et al. ^[33]
	
Atom transfer radical addition	Previous studies ^[34–37]
	
Reductive Coupling of aromatic carbonyls	Li et al. ^[38]
	
Reductive hydrodehalogenation	Casson et al. and Li et al. ^[35,38]
	
C–N coupling (through photocatalytic superoxide generation)	Hsu et al. ^[39]
	

TABLE 1 (Continued)

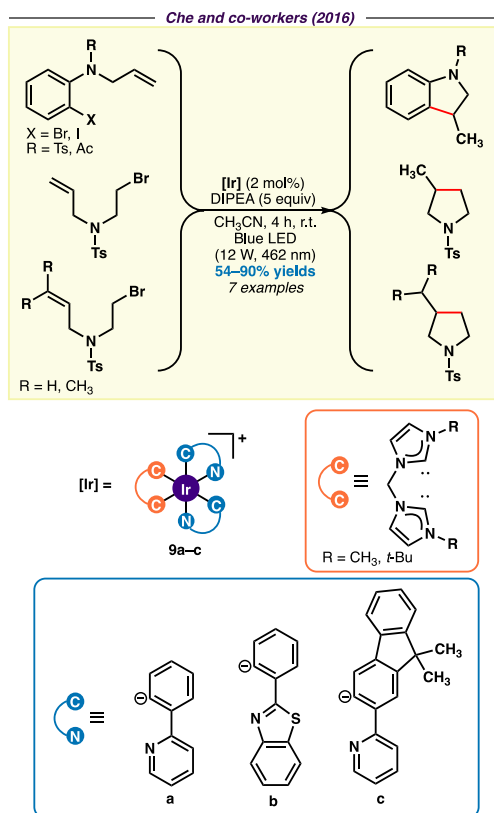
Reaction Type	Reference
C–H borylation	Thongpaen et al. ^[40]
	
Cycloaddition (through photocatalytic energy transfer)	Tzouras et al. ^[30]
	
Csp ² –Csp ² coupling	Hsu et al. ^[39]
	



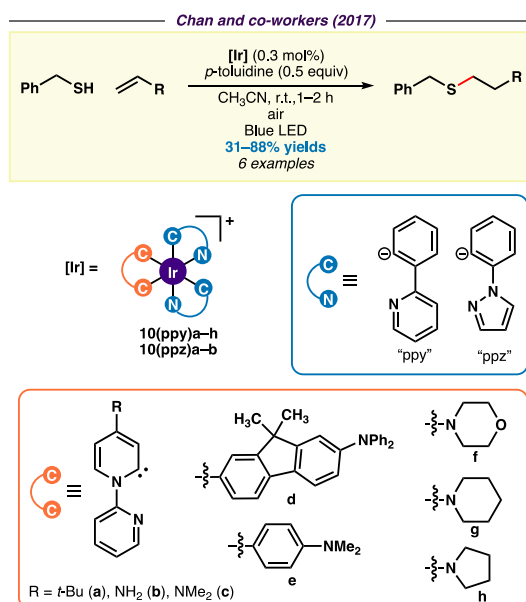
SCHEME 1 (a) Oxidation of secondary amines to imines and (b) oxidative cyanation of tertiary amines through photo-induced singlet oxygen generation by *N*-heterocyclic carbene (NHC) gold(III) catalyst **8a–b**

these complexes showing emission maxima that range from 516 to 682 nm with lifetimes of up to 3.0 μ s. In particular, electrochemical data obtained by cyclic voltammetry of complex **10(ppy)a** showed to be a strong photooxidant with an excited-state redox potential of +0.71 V (vs. Fc/Fc⁺). Thus, a visible-light-driven thiol–ene reaction was chosen to demonstrate the oxidising nature of the excited state of **10(ppy)a**. This complex efficiently catalysed the radical addition of benzylmercaptan to a range of alkenes including cyclohexene, methyl acrylate and phenylacetylene in 79–81% yields. The reaction is also compatible with internal/terminal alkenes possessing other functionalities. In these reactions, the photo-excited **10(ppy)a** produces the thiyl radical through reductive quenching mediated by *p*-toluidine. The thiyl radical then adds to the alkene substrate, which abstracts a proton from another thiol molecule thus continuing the catalytic cycle.^[41]

The same group in 2018 prepared an air-stable blue phosphorescent tetradentate NHC platinum(II) complex **11** was shown to be stable in solution upon continuous irradiation in degassed DMF using a UV lamp (12 W, 365 nm) for 96 h.^[38] **11** absorbs strongly in the UVA

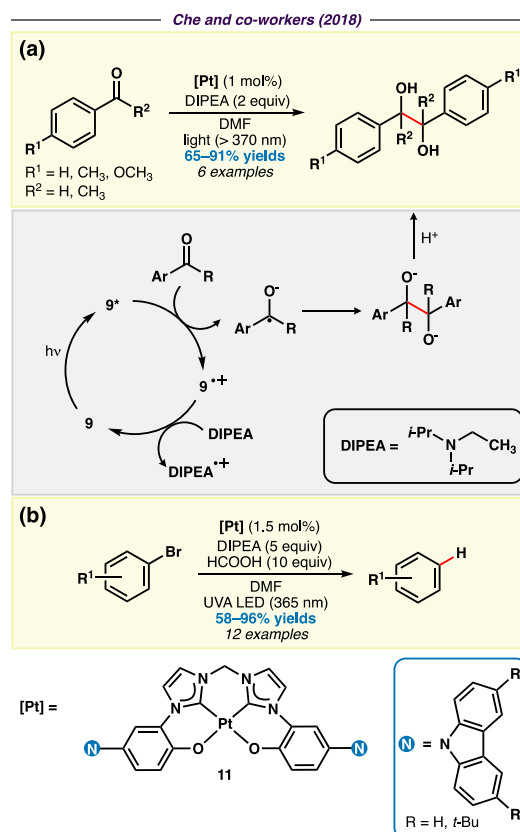


SCHEME 2 Reductive cyclisation of aromatic and alkyl bromides catalysed by iridium(III) visible-light photoredox catalysts **9a–c**



SCHEME 3 Visible-light-catalysed radical thiol-ene addition employing photocatalyst **10(ppya)** and related photoactive *N*-heterocyclic carbene (NHC) iridium(III) complexes **10(ppya)–h** and **10(ppz)a–b**

region (315–400 nm) and displays a long-lived emission lifetime of 6.7 μ s. Electrochemical studies by cyclic voltammetry revealed that **11** shows a reversible oxidation wave at 0.35 V (vs. Fc/Fc⁺), which is likely attributed to the carbazoyl moieties. The authors also found that the excited state redox potential is estimated to be –2.63 V (vs. Fc/Fc⁺), revealing that the excited state reducing power is comparable with those of the most powerful tungsten(0),^[42] molybdenum(0)^[43] and organic dye photo-reductants.^[44] As such, the high photostability, strong absorption, long emission lifetime and increased redox reversibility of **11** lend it to be a promising, strong photo-reductant. This was indeed demonstrated through light-induced reductive coupling of aromatic carbonyls (Scheme 4a). When benchmarked against known cyclometalated 2-phenylpyridyl-ligated platinum(II) photocatalysts and *fac*-[Ir(ppy)₃], **11** proved to be superior in this transformation. Photocatalyst **11** was also capable of efficient reductive hydrodebromination of aryl bromides (Scheme 4b). The authors propose that the light-induced reductive coupling proceeds via an outer-sphere electron transfer mechanism from photoexcited **11** to



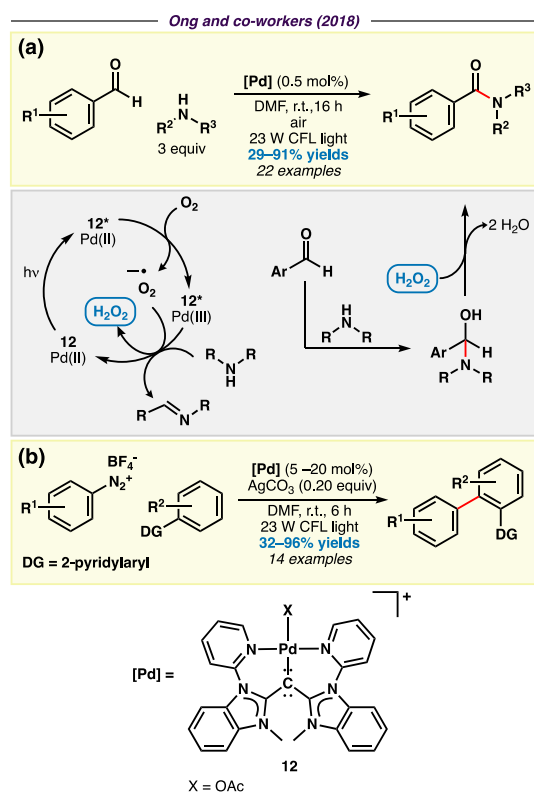
SCHEME 4 (a) Reductive coupling of aromatic carbonyls and (b) reductive hydrodebromination of aryl bromides by square planar tetradentate bis(NHC) platinum(II) photoredox catalyst **9** under ultraviolet (UV) irradiation

aromatic carbonyls producing a radical anion. This undergoes radical-radical coupling and furnishes the final diol product upon protonation. Reductive quenching with DIPEA regenerates the ground state photocatalyst **11**. Hydrodebromination is thought to follow a similar outer-sphere electron transfer mechanism with DIPEA serving as both the sacrificial reductant to regenerate the catalyst and proton source.

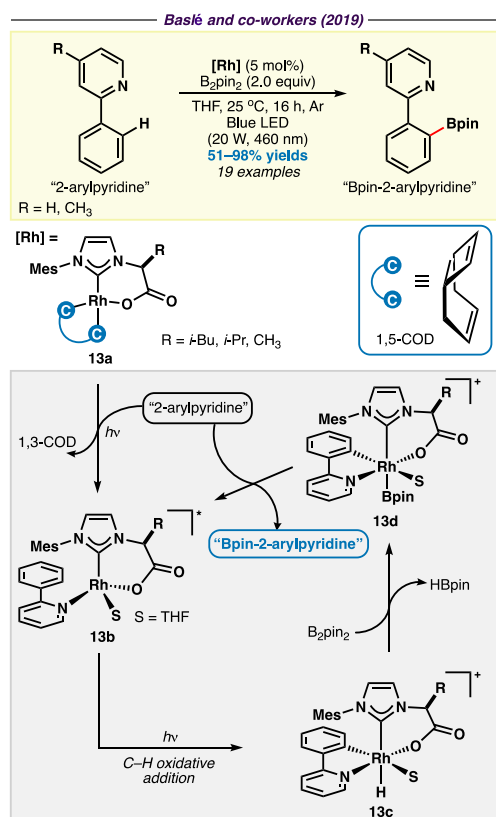
Though not an NHC transition metal complex, Hsu and co-workers developed palladium(II) photocatalyst **12** featuring an electronically related carbodicarbene ligand (Scheme 5).^[39] **12** displayed very interesting reactivity in facilitating both conventional $2e^-$ cross-coupling reactions and $1e^-$ photoredox processes. **12** absorbs strongly in the visible region (499 nm) and shows a reversible redox couple for Pd(III)/Pd(II) at 0.87 V (vs. the saturated calomel electrode, SCE). Photoredox catalyst **12** was shown to catalyse visible-light-mediated C–N coupling between aromatic aldehydes and secondary amines with moderate to excellent yields (Scheme 5A). This light-mediated C–N coupling procedure was amenable to a range of electron withdrawing and donating groups at the *meta*- and *para*-positions of the aromatic aldehyde along with secondary amines varying in ring size

including pyrrolidine, piperidine and azepane. Acyclic amines such as dibenzylamine and diallylamine were also screened resulting in yields of 76% and 29%, respectively. Notably, this light-mediated C–N cross-coupling protocol requires the presence of oxygen and hence must be performed in air. The authors propose that upon photoexcitation of **12**, its excited state **12**^{*} reacts favourably with O₂ through an oxidative quenching process followed by proton transfer from amines to generate H₂O₂. This acts as an in situ photogenerated oxidant. Acetal or aminal formation from the addition of the secondary amine to the aromatic aldehyde is then oxidised by H₂O₂, furnishing aldehyde product. **10** also catalyses visible-light-mediated C–H arylations of aryl substrates containing *ortho*-directing groups with aryl diazonium salts. The substrate scope for both aryl diazonium salts and aryl substrates bearing an *ortho*-directing group was broad (Scheme 5b). The authors reasoned that photoexcited **12**^{*} is able to react with aryl diazonium salts to generate an aryl radical which couples with **12** then participates in conventional C–C cross-coupling processes. Where electron-rich substrates were employed, an increase in photocatalyst loading up to 20 mol% was required to achieve higher conversions. Finally, the authors demonstrated **12** was capable of facilitating one-pot tandem conventional Suzuki–Miyaura cross-couplings followed by photoredox C–N coupling without the need for an exogenous photosensitiser.

In 2019, Thongpaen and co-workers developed chelating NHC rhodium(I) complex **13a** and explored its photocatalytic activity in regioselective aromatic C–H borylations directed by a pyridine group using B₂pin₂ [bis(pinacolato) diboron] as the borylating agent (Scheme 6).^[40] UV–vis spectra of **13a** showed strong absorbance in the visible light region suitable for excitation with blue LEDs. **13a** proved to be active in the visible-light-mediated C–H borylation of 2-arylpyridine-based substrates. The chelating binding mode of NHC ligand in **13a** showed to be instrumental in providing photocatalytic activity as [(IMes)Rh(COD)Cl] (IMes = 1,3-Bis(2,4,6-trimethylphenyl)imidazoline-2-ylidene, COD = 1,5-cyclooctadiene), and [Rh(COD)Cl]₂ afforded <5% of the desired borylated product. When compared with electron rich substrates, a slight decrease of reactivity was observed with electron deficient molecules. The authors proposed C–H borylation begins with the photodissociation and isomerisation of 1,5-cyclooctadiene to 1,3-cyclooctadiene^[45] from **13a** followed by *N*-coordination of the 2-arylpyridine substrate producing **13b**. Visible-light-induced C–H oxidative addition generates rhodium(III) hydride **13c**. This then undergoes dehydroboration with B₂pin₂ affording rhodium(III) boryl complex **13d**. Reductive elimination from this furnishes the *ortho*-borylated product and regenerates the



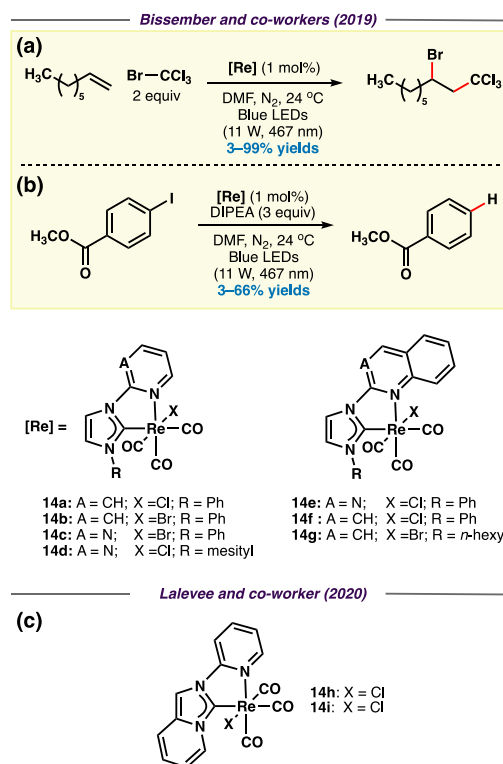
SCHEME 5 (a) C–N coupling of aromatic aldehydes with secondary amines and (b) C–H arylations with aryl diazonium salts mediated by square planar carbodicarbene-ligated palladium(II) visible-light photoredox catalyst **12**



SCHEME 6 Pyridine-directed C–H borylation by chelating NHC rhodium(I) photoredox catalyst **13**

rhodium(I) photocatalyst **13b**. Attempts to isolate hydride intermediate **13c** through stoichiometric photo-induced C–H oxidative addition reactions were unsuccessful presumably due to its pronounced instability; however, ¹H nuclear magnetic resonance (NMR) spectroscopic studies showed a doublet at δ_{H} –21.7 ppm with a coupling constant of J_{RhH} = 36.9 Hz indicative of the presence of a rhodium-bound hydride ligand.

The photophysical and photochemical properties of NHC rhenium(I) carbonyl complexes have been established by Casson and co-workers paving the path for their applications in photoredox catalysis.^[35] In 2019, Nicholls and co-workers evaluated the photocatalytic activities of a series of chelating *N*-pyridyl substituted NHC rhenium(I) carbonyl complexes **14a–g** in both oxidative and reductive functionalisations of organic molecules.^[46] Though generally these did not perform favourably in oxidative transformations such as Povarov-type reactions, **14a–g** showed excellent activity in reductive processes such as atom-transfer radical-addition (ATRA) and hydrodehalogenation reactions (Scheme 7a, b, respectively). This represents one of the first examples of visible-light-mediated ATRA catalysed by a photoactive NHC transition metal complex. The



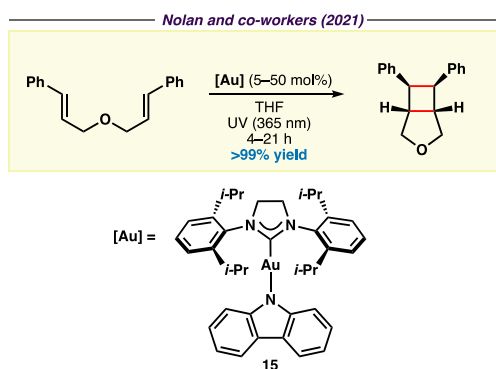
SCHEME 7 Atom-transfer radical-addition (ATRA) (a) and hydrodehalogenation (b) reactions catalysed by chelating *N*-pyridyl substituted NHC rhenium(I) carbonyl visible-light photoredox catalysts **14a–g** and benzannulated NHC rhenium(I) carbonyl complexes **14h–i** (c) for photoredox catalytic systems in light-promoted polymerisation reactions

mechanism for this transformation is akin to that discussed earlier for reductive cyclisation of aryl and alkyl bromides (vide supra). In short, carbon–halogen bond within the transfer agent BrCCl₃ is photochemically reduced by photocatalyst **14** affording a putative radical species that then adds to the olefin substrates. All photocatalysts except **14e** promoted ATRA reactions in excellent yields. This notable exception suggests that complex **14e** is a poorly reducing catalyst. In the hydrodehalogenation of methyl 2-iodobenzoate catalyst, **14g** provided the best yields at 74% after 24 h of irradiation. In comparison, [Ru(bpy)₃]²⁺ provided only a very low yield. This suggests that species **14g** (or derivatives thereof) will likely serve as the most useful system for establishing the reductive photoredox functionalisation of substrates in the future.

In 2020, Chen and co-workers reported the application of NHC rhenium(I) carbonyl complexes structurally similar to **14a–g** visible-light-promoted polymerisation reactions involving polyethyleneglycol (PEG)-acrylate monomers (Scheme 5c, **14h–i**).^[47] The authors report excellent radical polymerisation profiles, and final conversions are obtained under soft irradiations (LED lamp,

405 nm) by using **14h–i** with iodonium salts and amines as photoinitiating systems. The polymerisation efficiency of chloride complex **14h** was higher than that of **14i**.

The photoredox chemistry presented thus far relies on the ability of the photoexcited catalysts to engage in electron transfer with organic molecules. A second, fundamental pathway for the decay of photoexcited states, however, is energy transfer, which is arguably not as well developed as photoredox catalysis.^[48] To date, the most common and active energy transfer photocatalysts are based on [Ru(bpy)₃]²⁺ and [Ir(ppy)₃] derivatives. Energy transfer photocatalysis beyond ruthenium and iridium-based catalysts is relatively new. Wu and co-workers were the first to show that heteroleptic phenanthroline-ligated copper(I) photocatalysts are also able to facilitate energy transfer processes such as [2 + 2] photodimerisation of chalcones and alkene *E/Z*-isomerisations with yields comparable with iridium-based photocatalysts,^[49] because there have been two other reports showing the viability of heteroleptic phenanthroline copper(I) complexes as energy transfer catalysts.^[50] In 2021, Tzouras and co-workers reported the first example of a linear NHC gold(I) carbazolyl complex, **15**, capable of the UV-induced photocatalytic [2 + 2]-cycloaddition of (*E,E'*)-dicinnamyl ether through energy transfer (Scheme 8).^[30] **15** is stable under photolytic conditions and emits solely via phosphorescence in THF at 430 nm with exceptionally long lifetimes of 266 μ s. **15** exhibits remarkable efficiency for this transformation with relatively low catalyst loadings (5 mol%) and short reaction times (4 h). As this particular example was a proof-of-concept study, the authors did not provide detailed mechanistic discussions. Photoactive NHC coinage metal complexes structurally similar to **15** featuring a variety of carbene ligands (vide supra) are well known; however, their primary applications are predominantly in blue OLED and related emissive materials. The authors conclude that this proof-of-

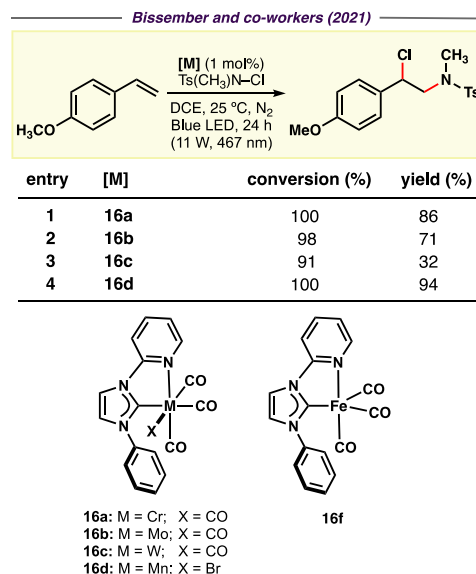


SCHEME 8 Photocatalytic [2 + 2]-cycloaddition of (*E,E'*)-dicinnamyl ether mediated by linear *N*-heterocyclic carbene (NHC) gold(I) carbazolyl energy transfer catalyst **15**

concept reaction may provide a new perspective on the implementation of complexes similar to **15** in energy transfer processes.

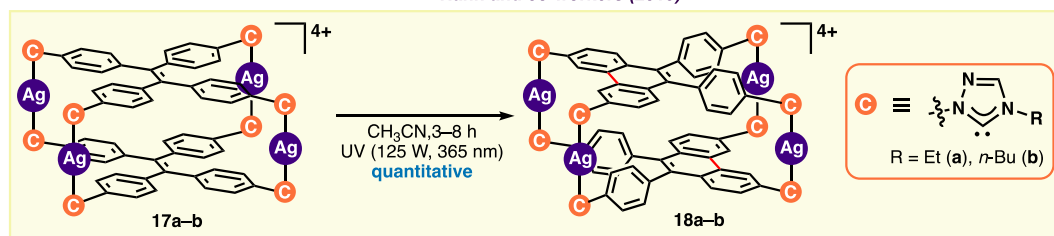
More recently, Tang and co-workers prepared a series of structurally-related NHC chromium, molybdenum, tungsten, manganese and iron carbonyl complexes (Scheme 9, **16a–f**).^[34] Complexes **16a–d** were investigated for their capacity to facilitate a range of photoinduced reactions via the reductive or oxidative functionalisation of organic molecules. Complex **16f** was not screened due its air and moisture sensitivity. **16a, 16b** and **16d** were shown to efficiently facilitate ATRA processes, however performed very poorly in reductive decarboxylation reactions (3–5% yields). These complexes were not active in photoinduced oxidative functionalisation reactions. **16a–d** could not promote photoinduced energy transfer processes such as *E/Z*-isomerisation of alkenes either. More interestingly, photophysical studies revealed decarbonylation occurs when these complexes are exposed to UV light in CH₃CN, with the CO ligand being replaced with a labile CH₃CN molecule. Considering this photolability, these types of catalysts may potentially allow for the development of photo-induced reactions involving less conventional inner-sphere electron transfer pathways.

Though not strictly in the field of homogeneous bond-forming catalysis, in investigating metallo-supramolecular assemblies with terphenylethylene (TPE) bridged tetrakis (NHC) silver complexes for applications in aggregation-induced emission (Scheme 10, **17a–b**),



SCHEME 9 Photoinduced atom-transfer radical-addition (ATRA) reaction catalysed by chelating *N*-heterocyclic carbene (NHC) chromium, molybdenum, tungsten and manganese carbonyl complexes **16a–d** and iron carbonyl complex **16f**

Hanh and co-workers (2019)



SCHEME 10 Csp^2 - Csp^2 bond formation through oxidative photocyclisation of metallo-supramolecular terphenylethylene (TPE)-bridged tetrakis (*N*-heterocyclic carbene [NHC]) silver complexes **17a-b** to form complexes **18a-b**

Sinha and co-workers discovered **17**-type assemblies undergo light-induced supramolecule-to-supramolecule structural transformation by an oxidative photocyclisation involving phenyl groups of the TPE core.^[51] It is worth noting that this photo-induced dehydrogenative coupling only occurs in the NHC-ligated silver complexes and the free triazolium precursor does not exhibit the same reactivity. The authors note that this structural transformation results in a significant change of the luminescence properties of the resulting supramolecular assemblies. As such, the photo-induced C-C coupling can be monitored by the fluorescence emission spectra of complexes **17a-b**. Green fluorescence at 510 nm in CH_3CN weakens and continually decreases after prolonged times of irradiation until being fully quenched for forming complexes **18a-b**.

5 | CONCLUSIONS AND OUTLOOK

Photoactive/photoluminescent NHC transition metal complexes represent a growing field within contemporary coordination chemistry. Since the first report of a photoluminescent NHC transition metal complex in 1998, this class of NHC transition metal complexes has predominantly been employed in photoactive and emissive materials with some medical applications such as photosensitisers in photodynamic therapy. As exemplified in the foregoing sections, the structural diversity of photoactive NHC transition metal complexes is vastly extensive, and strategies to tune NHC ligands and their corresponding metal complexes to enhance favourable photophysical properties such as strong visible-light absorption and long-lived photocatalytically active MLCT states are becoming clearer.

In general, strongly electron-donating mesoionic carbenes and cyclic amino carbenes have been shown to prolong excited state lifetimes when compared with their normal NHC congeners. Whereas, the effect of mixed NHC/polypyridyl heteroleptic ligand systems versus homoleptic NHC-ligation on metal complex photophysics

is highly dependent on the metal and its oxidation state. A combination of NHCs and the established photoactivity of polypyridyl ligands has led to the generation of another class of photoactive transition metal complexes where the NHC ligand contains a pendant pyridyl group and binds to the metal in a multi-dentate fashion. This not only simplifies synthetic procedures accessing these types of NHC transition metal complexes but also attributes them with enhanced stability in solution and during photochemical processes.

With the renaissance of visible-light photocatalysis, applications of photoactive NHC transition metal complexes in photo-induced bond-forming photoredox and energy transfer processes remains in its infancy. However, as represented in the sections above, their potential as photocatalysts in bond-forming reactions is evident and promising, especially for reductive functionalisation of organic molecules via radical pathways. Hence, given the wealth of known photoactive NHC transition metal complexes and detailed reports of their photophysical and photochemical properties in the current literature, we tentatively predict that the implementation of this class of NHC transition metal complexes in photocatalysis for chemical synthesis will only flourish in the years to come.

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DATA AVAILABILITY STATEMENT

Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

ORCID

Eve M. Poland <https://orcid.org/0000-0002-7287-7640>

Curtis C. Ho <https://orcid.org/0000-0002-7555-0635>

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