Photoassisted C–C Coupling *via* Electron Transfer to Benzylic Halides by a Bis(di-imine) Copper(I) Complex

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Owing to its special topography $Cu(dap)_2^+$ [dap = 2,9 bis(*p*-anisyl)-1,10-phenanthroline] displays photophysical properties which allow its use as an efficient redox photocatalyst in reductive coupling of *p*-$NO_2C_6H_4CH_2Br$.

Until now, the use of inorganic redox photocatalysts in organic synthesis has been mainly restricted to $Ru(bipy)_3^{2+}$ (bipy = 2,2′-bipyridine).[1–4] In particular, it was recently shown that $Ru^I(bipy)_3^+$ can be photogenerated in the presence of an electron donor and used as an electron transfer agent to benzyl bromide.[5]

Although copper(I) complexes have been shown to display interesting metal-to-ligand charge transfer (MLCT) excited states,[6] the use of di-imine Cu^I complexes in preparative photochemistry has been limited,[7] owing to the short lifetime of their excited states. It has been shown that the use of rigid and encaging ligands leads to copper(I) complexes with relatively long-lived MLCT excited states, even in polar media,[8] and photochemical reduction of water by such complexes has been demonstrated.[9] We now report that the complex $Cu(dap)_2^+$[10] [dap = 2,9-bis(*p*-anisyl)-1,10-phenanthroline] can be used as a redox photocatalyst for converting nitrobenzyl halides $ArCH_2Br$ into their bibenzylic coupling products under anaerobic conditions whereas, in the presence of oxygen, nitrobenzaldehyde is obtained almost quantitatively.

Photochemical and photoelectrochemical experiments have been carried out with $Cu(dap)_2^+$. In a typical photochemical experiment, 15 μmol of $Cu(dap)_2^+$, 944 μmol of *p*-nitrobenzyl bromide, and 1700 μmol of triethylamine, used as an electron donor D, in strictly deaerated CH_2Cl_2, were irradiated (λ >350 nm) for 25 h. After work-up, 220 μmol of bis-(*p*-nitro)bibenzyl (47%) were obtained.† The turnover number on $Cu(dap)_2^+$ was 30, clearly indicating the catalytic nature of the process. At the end of the experiment, solution analysis show that the starting complex is entirely unchanged (>95%) and is thus efficiently recycled in the photocatalytic process. The reactions in Scheme 1 account for the observed process. Photophysical measurements show that the MLCT excited state $^*Cu(dap)_2^+$ is efficiently quenched by substituted benzyl bromides $XC_6H_4CH_2Br$. The bimolecular rate constants k_Q [equation (2)] obtained from Stern–Volmer plots are in good agreement with the electrochemical properties of the corresponding benzylic halides, as shown in Table 1: the less negative the reduction peak potential E_p of $ArCH_2Br$, the more efficient the quenching of $^*Cu(dap)_2^+$.

It is noteworthy that $^*Cu(dap)_2^+$ is a strong reductant, able to transfer an electron onto a weak electron acceptor like a benzyl bromide derivative. The redox potential of the $Cu^{II}/^*Cu^I$ couple, calculated from the excited-state energy

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† Small amounts of starting material are recovered in addition to unidentified products, probably originating from the thermal reaction between the benzyl bromide derivative and the amine electron donor. Blank experiments carried out without copper(I) complex show that u.v. light irradiation leads to noticeable transformation of the substrate. However, when a cut-off filter (400 nm) is used no photochemical reaction takes place without the inorganic photocatalyst.

Table 1. Quenching of $Cu(dap)_2^+$ emission by benzylic bromides $XC_6H_4CH_2Br$.[a]

X	p-NO_2	o-NO_2	m-NO_2	H
E_p	-0.86[b]	-0.91[b]	-1.08[b]	-1.22[c]
k_Q[d]	6.3×10^8	3.7×10^8	1.2×10^8	5×10^6

[a] Emission measurements taken at 25 °C in CH_2Cl_2. $Cu(dap)_2^+$ has an emission spectrum centred around 670 nm. Excitation wavelength: $\lambda_{exc.}$ 470 nm. The acceptor concentration was in the range: $[ArCH_2Br] = 5 \times 10^{-3}$ to 10^{-1} M. [b] V *vs.* saturated calomel electrode (s.c.e.) in MeCN, (see J. G. Lawless, D. E. Bartak and M. D. Hawley, *J. Am. Chem. Soc.*, 1969, **91**, 7121). [c] $E_{1/2}$, V *vs.* s.c.e. in dimethylformamide: F. H. Covitz, *J. Am. Chem. Soc.*, 1967, **89**, 5403. [d] Rate constants in $dm^3\ mol^{-1}\ s^{-1}$; the values are obtained assumming an excited state lifetime of 270 ns for $^*Cu(dap)_2^+$ (D. R. McMillin, personal communication).

$$Cu(dap)_2^+ \xrightarrow{h\nu} {}^*Cu(dap)_2^+ \qquad (1)$$

$$^*Cu(dap)_2^+ + ArCH_2Br \xrightarrow{k_Q} Cu(dap)_2^{2+} + ArCH_2^{\bullet} + Br^- \qquad (2)$$

$$2\ ArCH_2^{\bullet} \rightarrow ArCH_2\text{–}CH_2Ar \qquad (3)$$

$$^*Cu(dap)_2^+ + ArCH_2^{\bullet} \rightarrow Cu(dap)_2^{2+} + ArCH_2^- \qquad (4)$$

$$ArCH_2^- + ArCH_2Br \rightarrow ArCH_2\text{–}CH_2Ar + Br^- \qquad (5)$$

$$Cu(dap)_2^{2+} + D \rightarrow Cu(dap)_2^+ + D^+ \qquad (6)$$

$$D^+ \rightarrow D_{oxidized} \qquad (7)$$

$$Ar = XC_6H_4;\ X = o\text{-}, m\text{-}, p\text{-}NO_2, H$$

Scheme 1

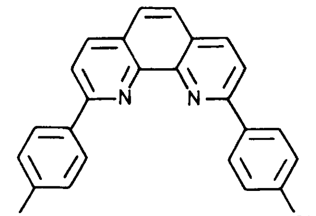
level (2.05 eV)[10] and the redox potential of the Cu^{II}/Cu^{I} couple [+0.62 V *vs.* saturated calomel electrode (s.c.e.) in MeCN] is −1.43 V [for comparison $E^0 = -0.82$ V *vs.* normal hydrogen electrode for $Ru(bipy)_3^{3+}/{}^*Ru(bipy)_3^{2+}$ in H_2O[11]]. The experimental value estimated from the data in Table 1 is also markedly negative, although slightly less than the calculated one.

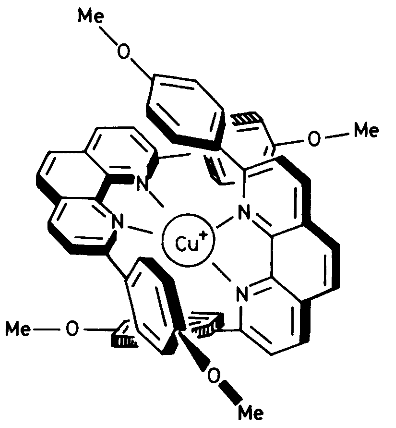
Equation (3) corresponds to a classical radical coupling. At the present stage, it is difficult to exclude that the bibenzylic product is also formed *via* nucleophilic attack on p-$NO_2C_6H_4CH_2Br$ by p-$NO_2C_6H_4CH_2^-$, the latter being obtained *via* dielectronic reduction of the bromide [equations (4) and (5)].

If oxygen is present, the course of the photochemical reaction is drastically modified. Using the same experimental conditions as those described above, but operating in air, a 95% yield of p-nitrobenzaldehyde is obtained, making the procedure preparative. Although mechanistic considerations are only speculative, it is likely that the radical formed by equation (2) rapidly reacts with O_2, subsequently leading to p-$NO_2C_6H_4CHO$ in a multistep reaction.

The only function of the electron donor D is to regenerate the photocatalyst [equation (6)]. In the absence of D, $Cu(dap)_2^{2+}$ is photogenerated from its cuprous precursor, either in deaerated solution or in the presence of air. The electron acceptor acts thus as an irreversibly consumed oxidant.

The regeneration of $Cu(dap)_2^+$ can also be carried out electrochemically, equation (8). Under light illumination, the photoelectrochemical cell based on $Cu(dap)_2^+/p$-$NO_2C_6H_4CH_2Br$, O_2/Pt is operative at a potential much less negative than that required in the dark, as shown in Figure 1. For comparison purposes, photocurrent measurements have also been carried out with other photosensitizers.


dap


$Cu(dap)_2^+$

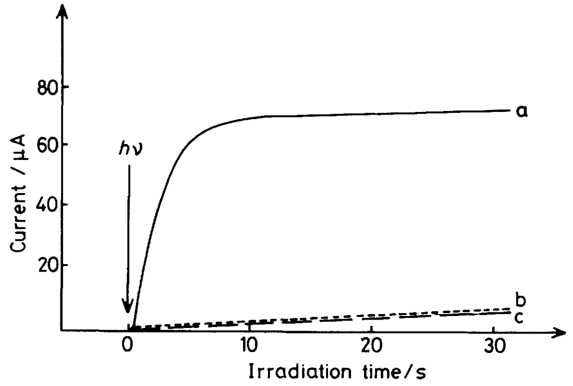


Figure 1. Photochemical oxidation of: (a) $Cu(dap)_2^+$, (b) $Cu(dmp)_2^+$, and (c) $Ru(bipy)_3^{2+}$. The concentration of generated oxidized species is monitored by measuring the current intensity of reduction of the oxidized species on a rotating platinum electrode (1500 r.p.m.), at a potential of 0 V. The MeCN solution (20 ml) is 5.5×10^{-3} M in p-$NO_2C_6H_4CH_2Br$, 2.5×10^{-4} M in copper(I) or ruthenium(II) complex; supporting electrolyte: $NEt_4^+ClO_4^-$ (0.1 M); room temperature; light source: halogen lamp (150 W).

$$Cu(dap)_2^{2+} + e^- \xrightarrow{i} Cu(dap)_2^+ \qquad (8)$$

i, Pt cathode at fixed potential of 0 V.

It is remarkable that $Cu(dap)_2^+$ is by far the most efficient photosensitizer. This is due to the combination of its redox properties and its excited state lifetime: the reducing power of

${}^*Cu(dap)_2^+$ is almost 0.5 V more pronounced than that of ${}^*Ru(bipy)_3^{2+}$, the latter being unable to transfer an electron to p-$NO_2C_6H_4CH_2Br$. ${}^*Cu(dap)_2^+$ has a lifetime long enough to react with the benzyl bromide derivative whereas ${}^*Cu(dmp)_2^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) is rapidly deactivated by non-operative processes.

In conclusion, the special topography of $Cu(dap)_2^+$, consisting of two entwined dap subunits fitting together, is responsible for its unusual photophysical properties allowing photochemical transformation of benzylic bromide derivatives.

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