Photochemically Generated Organometallic Radicals as Reducing Agents

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Irradiation of metal–metal bonded carbonyl dimers in the presence of appropriate ligands generates a class of intermediates which are powerful reducing agents; $Ru_3(CO)_{12}$, $CpMo(CO)_3Cl$ (Cp = cyclopentadienyl), and the ferricyanide ion were reduced in order to demonstrate the utility of these photogenerated reducing agents.

In a series of recent papers we and others have shown that the photochemical disproportionation reactions of metal–metal bonded carbonyl dimers proceed by a radical chain pathway.[1,2] A key step in the chain mechanism is the reduction of a dimer molecule by a photogenerated intermediate to generate a dimer radical anion, *e.g.* reaction (1). The exact nature of

$$Cp_2Mo_2(CO)_6 + R \rightarrow Cp_2Mo_2(CO)_6^- + R^+ \qquad (1)$$

Cp = Cyclopentadienyl
R = Photogenerated reducing agent

the reducing agent, R, in the reaction is still controversial† but the occurrence of reaction (1) in the disproportionation

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† Brown proposes (ref. 2) that the photogenerated intermediates are substituted 17-valence electron species, *e.g.* $Mn(CO)_3L_2$ in the disproportionation of $Mn_2(CO)_{10}$ or $CpMo(CO)_2L$ with $Cp_2Mo_2(CO)_6$, and we (ref. 1) believe the intermediates are 19-electron species, *e.g.* $Mn(CO)_3L_3$ or $CpMo(CO)_2L_2$. In both cases, the intermediates are formed following initial photochemical homolytic cleavage of the metal–metal bond.

process is agreed upon.[1,2] Typical reduction potentials for the metal carbonyl dimers are in the range −1.5 to −2.2 V.[3] Thus, the photogenerated reducing agents, R, are very powerful reductants and they should be capable of reducing substrates other than metal carbonyl dimers. In fact, we have found this to be the case. In this communication we report several reactions in which the species R reduce common organometallic and co-ordination complex substrates. In essence, we report here the discovery of a class of photogenerated reducing agents.

Our first test of the reducing ability of the intermediate R involved the reduction of $Ru_3(CO)_{12}$. Bruce, Matisons, and Nicholson reported that the phosphine substitution of $Ru_3(CO)_{12}$ is initiated by sodium diphenylketyl.[4] Their proposed mechanism involved the initial reduction of $Ru_3(CO)_{12}$ to form $Ru_3(CO)_{12}^-$, a species apparently highly susceptible to phosphine substitution. The formation of $Ru_3(CO)_{11}PR_3$ in a reaction system under conditions in which $Ru_3(CO)_{11}PR_3$ does not otherwise form would thus be indicative of the formation of $Ru_3(CO)_{12}^-$. When $Ru_3(CO)_{12}$ (4 mM), PMe_2Ph (4 mM), and $Cp_2Mo_2(CO)_6$ (1 mM) were irradiated ($\lambda > 525$ nm) in tetrahydrofuran (THF) solution, reaction (2), the product was $Ru_3(CO)_{11}PMe_2Ph$ [$\nu(C\equiv O)$ 2096, 2042, 2027, 2012, 1987sh cm^{-1}].[4]

$$Ru_3(CO)_{12} + PMe_2Ph \xrightarrow[Cp_2Mo_2(CO)_6]{h\nu} Ru_3(CO)_{11}PMe_2Ph \quad (2)$$

Control experiments showed that $Ru_3(CO)_{11}PMe_2Ph$ did not form in the absence of $Cp_2Mo_2(CO)_6$. In addition, control reactions showed that light was necessary for the reaction to occur. In accordance with the discussion above, the substitution of $Ru_3(CO)_{12}$ in this system is proposed to follow the pathway shown in Scheme 1. The PMe_2Ph substitution of $Ru_3(CO)_{12}$ could also be initiated by using the $Cp_2Fe_2(CO)_4$ complex instead of $Cp_2Mo_2(CO)_6$.

Another test for the formation of a photogenerated reducing agent involved the reduction of $CpMo(CO)_3Cl$. Dessy and King[5] showed that electrochemical reduction of $CpMo(CO)_3Cl$ led to $CpMo(CO)_3^-$. We found that irradiation ($\lambda > 525$ nm) of $CpMo(CO)_3Cl$ (10 mM) with $Cp_2Fe_2(CO)_4$ (10 mM) and dppe (100 mM) [dppe = 1,2-bis(diphenylphosphino)ethane] in THF, reaction (3), led to the efficient formation of $CpMo(CO)_3^-$ [$\nu(C\equiv O)$ 1894 and 1770 cm^{-1}][6] and $CpFe(CO)dppe^+$ [$\nu(C\equiv O)$ 1979 cm^{-1}].[7] Control experiments showed that no $CpMo(CO)_3^-$ formed in the absence of dppe. The dppe is necessary, of course, to form the reducing agent, R.[†] Control experiments also showed that light was necessary for reaction (3) to occur.

$$2\ CpMo(CO)_3Cl + Cp_2Fe_2(CO)_4 + 2\ dppe \xrightarrow{h\nu} 2\ CpMo(CO)_3^- + 2\ CpFe(CO)dppe^+ \quad (3)$$

$$Cp_2Mo_2(CO)_6 \xrightarrow[PMe_2Ph]{h\nu} R$$

$$R + Ru_3(CO)_{12} \longrightarrow R^+ + Ru_3(CO)_{12}^-$$

$$Ru_3(CO)_{12}^- \xrightarrow{PMe_2Ph} Ru_3(CO)_{11}PMe_2Ph$$

Scheme 1. The final step is a substitution according to the chain mechanism in ref. 5.

Further evidence that the photogenerated reducing agents are potent reductants comes from experiments which show that these complexes can be used to reduce the dimers of other metals. For example, irradiation ($\lambda > 525$ nm) of $Mn_2(CO)_{10}$ (10 mM) with dppe (100 mM) in the presence of $Cp_2Fe_2(CO)_4$ (10 mM) in THF solution proceeds according to equation (4).

$$Mn_2(CO)_{10} + Cp_2Fe_2(CO)_4 + dppe \xrightarrow{h\nu} 2\ Mn(CO)_5^- + 2\ CpFe(CO)dppe^+ \quad (4)$$

We[1b] and others[2] have shown that phosphines will not disproportionate $Mn_2(CO)_{10}$ and thus the $Mn(CO)_5^-$ forming in reaction (4) must be formed in the reduction of $Mn_2(CO)_{10}$ by the photogenerated reducing agent. In a related system we found that the reaction shown in equation (5) occurred in THF. In this case the photogenerated reducing agent is acting to reduce $Cp_2Mo_2(CO)_6$. Note that dien by itself will not photochemically disproportionate $Cp_2Mo_2(CO)_6$ under these conditions.

$$Mn_2(CO)_{10} + dien + Cp_2Mo_2(CO)_6 \xrightarrow{h\nu} 2\ Mn(CO)_3(dien)^+ + 2\ CpMo(CO)_3^- \quad (5)$$

dien = Diethylenetriamine

We have also found that the photogenerated reducing agents will reduce co-ordination complexes. To demonstrate this use we irradiated ($\lambda > 525$ nm) an MeCN solution of $Cp_2Mo_2(CO)_6$ (10 mM), PMe_2Ph (100 mM), and $K_3Fe(CN)_6$ (25 mM). The reaction proceeded as in equation (6). The products were identified by i.r. spectroscopy [$CpMo(CO)_2(PMe_2Ph)_2^+$, $\nu(C\equiv O)$ 1961, 1884 cm^{-1}; $Fe(CN)_6^{4-}$, $\nu(C\equiv N)$ 2045 cm^{-1}].

$$Cp_2Mo_2(CO)_6 + 2\ Fe(CN)_6^{3-} \xrightarrow[PMe_2Ph]{h\nu} 2\ CpMo(CO)_2(PMe_2Ph)_2^+ + 2\ Fe(CN)_6^{4-} \quad (6)$$

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