Photochemically Initiated Electron Transfer Catalyzed Substitution Reactions of Metal Carbonyl Complexes

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Received October 24, 1984

In recent communications, we reported that photochemically generated 19-electron species were powerful reducing agents and could be used to reduce a variety of substrates [1]. In one of the more interesting applications of these photogenerated reducing agents, we demonstrated the electron transfer catalyzed (ETC) phosphine substitution of $Ru_3(CO)_{12}$*.

$$Ru_3(CO)_{12} + PMe_2Ph \xrightarrow[Cp_2Fe_2(CO)_4 \text{ or } Cp_2Mo_2(CO)_6]{h\nu} Ru_3(CO)_{12}PMe_2Ph + CO \qquad (1)$$

In this letter we present results that demonstrate the ETC substitution of other metal carbonyl complexes and that further illustrate the utility of using the 19-electron complexes as reducing agents.

As a logical extension of reaction (1) we carried out the ETC substitution of $Os_3(CO)_{12}$. Thus, irradiation** ($\lambda > 560$ nm) of a THF solution of $Os_3(CO)_{12}$ (3.0 mM) and PMe_2Ph (0.5 M) containing $Cp_2Fe_2(CO)_4$ (0.5 mM) led to the efficient formation of $Os_3(CO)_{11}PMe_2Ph$.

$$Os_3(CO)_{12} + PMe_2Ph \xrightarrow[Cp_2Fe_2(CO)_4]{h\nu\ \lambda > 560\ \text{nm}} Os_3(CO)_{11}PMe_2Ph + CO \qquad (2)$$

The product was identified by its infrared absorption spectrum (ν(C≡O) = 2106(m), 2050(s). 2031(s), 2016(vs), 1996(m), 1985(w)) [4]. It should be noted that whereas either $Cp_2Fe_2(CO)_4$ or $Cp_2Mo_2(CO)_6$ could be used to initiate reaction (1), only $Cp_2Fe_2(CO)_4$ can initiate reaction (2). Unpublished results from our laboratory have shown that the $Cp_2Fe_2(CO)_4/PR_3$ reducing system is more effective than the one employing the $Cp_2Mo_2(CO)_6$ dimer.

Similar irradiations ($\lambda > 560$ nm) of benzene solutions of $Fe(CO)_5$ with dppe led to $Fe(CO)_4$-dppe†.

$$Fe(CO)_5 + dppe \xrightarrow[Cp_2Fe_2(CO)_4]{h\nu} Fe(CO)_4(dppe\text{-}P) + CO \qquad (3)$$

dppe = 1,2-bis(diphenylphosphino)ethane

Once again, the products were identified by infrared spectroscopy (ν(C≡O) = 2051(s), 1974(m), 1939(vs)) [5]. Note that $Fe(CO)_4(dppe\text{-}P)$ is the only product of the reaction with dppe; no $Fe(CO)_3(dppe\text{-}P,P')$ is formed. Reaction (3) may thus prove to be a useful synthetic route to monodentate chelating ligand complexes of the type $Fe(CO)_4(L\ L)$ (where L L = bidentate ligand).

Attempts to effect the substitution of the $M(CO)_6$ (M = Cr, Mo, W) complexes by a method similar to that in reactions (1), (2) and (3) were unsuccessful. Also, we found that $Fe_3(CO)_{12}$ reacted thermally (in the dark) with the phosphines used in this study so the ETC substitution of this complex was not explored [6].

The mechanism of reactions (2) and (3) is probably analogous to the ETC pathway proposed for reaction (1) by Bruce *et al.* [1]. The pathway is shown in Scheme 1. In this scheme, the substitution

$$R + M(CO)_n \longrightarrow R^+ + M(CO)_n^- \qquad (4)$$

$$M(CO)_n^- + PR_3 \longrightarrow M(CO)_{n-1}(PR_3)^- + CO \qquad (5)$$

$$M(CO)_{n-1}(PR_3)^- + M(CO)_n \longrightarrow M(CO)_{n-1}(PR_3) + M(CO)_n^- \qquad (6)$$

Scheme 1.

cycle is initiated by reduction of the unsubstituted metal carbonyl complex (eqn. 4). The reduction labilizes the complex to substitution (eqn. 5). After the substitution, electron tranfer to an unsubstituted

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*The ETC substitution of $Ru_3(CO)_{12}$ was first reported by Bruce *et al.* [2]. ETC reactions have recently been reviewed [3a]. Note that ETC reactions may be induced by oxidation and/or reduction of the metal complex. For another example of a reduction induced ETC see [3b].

**All irradiations were carried out under anaerobic conditions using standard Schlenk techniques. A 200 watt high pressure Hg arc lamp was used for the irradiations. Corning Glass cut-off filters were used for wavelength selection.

†Note that neither $Fe(CO)_5$ nor $Os_3(CO)_{12}$ absorbs at the wavelengths used in these irradiations; only the $Cp_2Fe_2(CO)_4$ is absorbing light at these wavelengths. The reaction is thus not a photoreaction of the $Fe(CO)_5$ or $Os_3(CO)_{12}$ complexes.

0020-1693/85/$3.30

molecule occurs (eqn. 6) and the cycle is repeated. In the systems described in this letter, the reducing agent (*i.e.* the initiator) is a 19-electron species; we have demonstrated that such species form when solutions of $Cp_2Fe_2(CO)_4$ (or other metal carbonyl dimers) and phosphines are irradiated (Scheme 2)

$$Cp_2Fe_2(CO)_4 \xrightarrow{h\nu} 2CpFe(CO)_2 \qquad (7)$$

$$CpFe(CO)_2 \xrightarrow{PR_3} \underset{19}{CpFe(CO)_2PR_3} + \underset{19}{CpFe(CO)(PR_3)_2} \qquad (8)$$

Scheme 2.

[7]. Of course, only small amounts of $Cp_2Fe_2(CO)_4$ are needed to initiate the substitution reaction because the substitution pathway is a cycle. Consistent with the proposed pathway are the following results: 1) Only trace amounts of $Cp_2Fe_2(CO)_4$ are required to initiate the reaction. 2) Control experiments showed that the substitution products of reactions (2) and (3) did not form in the absence of $Cp_2Fe_2(CO)_4$. 3) Control experiments also showed that light was necessary for the reaction to occur.

The inability to substitute the $M(CO)_6$ complexes by the ETC pathway probably reflects the more negative reduction potentials of these complexes; eqn. 4 thus cannot occur. A comparison of the $E_{1/2}$ values for the various complexes is consistent with this proposal [8]: $Fe(CO)_5$, −1.68 V; $Ru_3(CO)_{12}$, −0.815 V; $Os_3(CO)_{12}$, −1.16 V; $Cr(CO)_6$, −2.7 V; $Mo(CO)_6$, −2.7 V; $W(CO)_6$, −2.6 V.

Finally, we note that the ETC substitution of $Fe(CO)_5$ may be nothing new. Shriver *et al.* [5] reported the substitution of this molecule catalyzed by iron carbonyl anions. An ETC pathway similar to that in Scheme I is probably applicable; the iron carbonyl anions may simply be acting as a reducing agent to initiate the chain.

Acknowledgements

We would like to thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for the support of this work.

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