Photochemistry of a Novel Asymmetrical Diphosphine-bridged Binuclear Manganese(0) Complex: *mer,fac*-$Mn_2(CO)_6(Me_2PCH_2PMe_2)_2$

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The first example of a *cis,trans* bis(dmpm) [dmpm = bis(dimethylphosphino)methane] diphosphine-bridged complex, *mer,fac*-$Mn_2(CO)_6(Me_2PCH_2PMe_2)_2$, (**1**), is readily oxidized by one electron to give an unusual binuclear cation, (**3**), $E^\circ[(\mathbf{3})/(\mathbf{1})] \sim -0.5$ V *vs.* saturated calomel electrode (SCE), and is also a potent photoreductant, $-1.35 \leqslant E^\circ[(\mathbf{3})/(\mathbf{1}^*)] \leqslant -1.87$ V *vs.* SCE.

Diphosphine-bridged dimanganese complexes of bis(diphenylphosphino)methane (dppm) have been actively studied for ten years.[1] Recently, dimanganese complexes bridged by bis(dimethylphosphino)methane (dmpm) have been described.[2] However, the photochemistry of diphosphine-bridged dimanganese complexes is essentially nonexistent. We now report the synthesis and photochemistry of a novel, asymmetrical diphosphine-bridged complex, *mer,fac*-$Mn_2(CO)_6(dmpm)_2$, (**1**).

The synthesis of (**1**) and its chemical and photochemical reactions are summarized in Scheme 1. The reaction of dmpm with $Mn_2(CO)_{10}$ gives a mixture of two isomers. One isomer is the symmetrical *mer,mer*-$Mn_2(CO)_6(dmpm)_2$, (**2**), recently reported by King.[2a] The other isomer is the asymmetrical complex (**1**).

Complex (**1**) can be separated from (**2**) by Soxhlet extraction and was characterized by elemental analysis[†] and i.r. and n.m.r. spectroscopy {i.r. [in tetrahydrofuran (THF)], ν(CO) 2020(vw), 1940(m), 1890(s), 1860(s) cm^{-1}; ^1H n.m.r. (200 MHz; CD_2Cl_2), δ 3.25 (m, 2H, CH_2), 1.73 [d, ^2J(PMe) 4 Hz, 6H, 2Me], 1.58 [d, ^2J(PMe) 8 Hz, 3H, Me], and 1.47 [d, ^2J(PMe) 8 Hz, 3H, Me]; $^{31}P\{^1H\}$n.m.r. (81 MHz; CD_3CN–MeCN) AA′BB′ centred at δ ~ 6.5}. On the basis of these spectroscopic data we propose the structure shown for (**1**) in Scheme 1. The *cis,trans*-diphosphine configuration, although unusual, has precedent. The complexes $[Rh_2(CO)Cl_2\{P(OPh)_2N(Et)P(OPh)_2\}_2]$,[3] $[Pt_2Me_3(dppm)_2]^+$,[4] $[Rh_2(CO)_3(dppm)_2]$,[5] and $[Ni_2(CNMe)_4(dppm)_2]^{2+}$ [6] all have a *cis,trans* configuration for the bridging ligand.

Complex (**1**) is easily oxidized by one electron to give *in situ* an unusual binuclear radical cation [*mer,fac*-$Mn_2(CO)_6(dmpm)_2]^{\cdot +}$, (**3**). The cyclic voltammogram of (**1**) shows only an irreversible oxidation which onsets at ~ −0.20 V *vs.* SCE. However, by using one-electron oxidants of known E°, the redox potential of (**1**) with respect to (**3**), $E^\circ[(\mathbf{3})/(\mathbf{1})]$, has been estimated to be between −0.5 and −0.6 V *vs.* SCE. The e.s.r. spectrum of (**3**) in THF exhibits a six line pattern with g ~2.005 and a_{Mn} = 91 G (1 G = 10^{-4} T). Only a broad featureless e.s.r. resonance is observed when the solvent is changed to CH_2Cl_2 or MeCN. Complex (**3**) can be reduced back to (**1**) with $Co(C_5H_5)_2$. The six line e.s.r. spectrum

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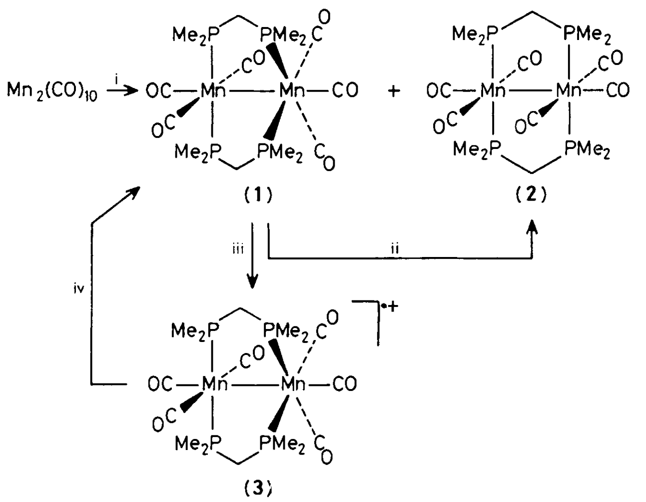
[†] Satisfactory elemental analyses (C,H) were obtained.



Scheme 1. *Reagents:* i, dmpm in toluene (110 °C, 4—6 h); ii, refluxing THF (66 °C) or toluene (110 °C) or photolysis in THF (5 °C); iii, $[Fe(C_5H_5)_2]^+$ in THF or photolysis in MeCN in presence of redox substrates: $1,4\text{-}(NO_2)_2C_6H_4$, $PhNO_2$, maleic anhydride, $Ru(bipy)_3{}^{2+}$; iv, $Co(C_5H_5)_2$ in THF.

suggests a localization of the unpaired electron on one of the two Mn ($I = 5/2$) metal centres. Whether the unpaired electron is on the meridionally or facially co-ordinated Mn, is not known at this time. However, a theoretical analysis,[7] following the principle of ligand additivity,[8] suggests that both (**1**) and (**3**) will have dπ HOMOs largely localized on the *mer*-Mn centre.

Complex (**1**) is also highly photosensitive. Broad band (λ >290 nm) photolysis of (**1**) in THF converts (**1**) into the symmetrical isomer (**2**). In MeCN, (**1**) is a potent one-electron photoreductant. Photolysis of solutions containing (**1**) and a one-electron accepting substrate, *i.e.* S = 1,4-dinitrobenzene, maleic anhydride, nitrobenzene, or $[Ru(bipy)_3]Cl_2$ (bipy = 2,2′-bipyridine), results in formation of (**3**) and the corresponding reduced radical of the substrate, $S^{\bullet -}$. The excited state redox potential of (**1**) has been estimated to be $-1.35 \leqslant E^\circ[(\mathbf{3})/(\mathbf{1}^*)] \leqslant -1.87$ V *vs.* SCE. The photochemical reactivity of the asymmetrical excited state, $[mer,fac\text{-}Mn_2(CO)_6(dmpm)_2]^*$, is under investigation.

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