Proton-induced Ligand Uptake by $[Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2]$ to give Hydrogen-bridged Dimanganese Complexes

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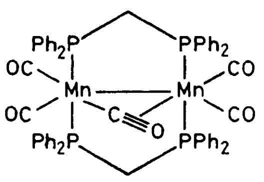
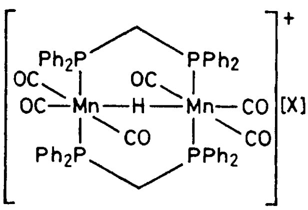
Summary $[Mn_2(CO)_5(dpm)_2]$ (dpm = $Ph_2PCH_2PPh_2$) does not react with nucleophiles but reacts readily with acids absorbing CO to give $[Mn_2(\mu\text{-}H)(CO)_6(dpm)_2]^+$ which with $LiBHEt_3$ regenerates $[Mn_2(CO)_5(dpm)_2]$; if other anionic or neutral ligands are present, these may be co-ordinated on protonation instead of CO.

WHEN first reported in 1975, $[Mn_2(CO)_5(dpm)_2]$ (dpm = $Ph_2PCH_2PPh_2$) (**1**) aroused much interest because of the novel 4e-donor bridging CO which was the first of its type.[1] Since then the only reported reactions of (**1**) have been the reversible uptake of CO[2] or CNR,[3] and despite tentative suggestions that the 4e-donor bridging mode might activate CO towards nucleophilic attack, no example of this has been reported.

In investigating the chemistry of (**1**), we have found that it reacts neither with nucleophiles ($LiBHEt_3$, LiMe, *etc.*) nor with H_2 (50 atm). For example, a solution of (**1**) in tetrahydrofuran (THF) does not react with $LiBHEt_3$ (10 mol per mol of Mn_2) even after three days at room temperature. Turning our attention to electrophiles we found that complex (**1**) reacts readily with fluoroboric, trifluoroacetic, or fluorosulphonic acids to give the new compounds $[Mn_2H(CO)_6(dpm)_2]^+[X]^-$ (**2**) where X = BF_4, $(CF_3CO_2)_2H$, or FSO_3. For example, a red-orange suspension of (**1**) in CH_2Cl_2 reacts with 8 mol. equiv. of CF_3CO_2H to give an orange solution after 5 h at 20 °C. After removal of solvent and the excess of acid *in vacuo*, orange needles of (**2**) [X = $(CF_3CO_2)_2H$] were caused to precipitate from $CHCl_3$–Et_2O at −20 °C. Unable adequately to identify (**2**) spectroscopically, we attempted to obtain single crystals for *X*-ray structural analysis but found that crystals of (**2**) [X = $(CF_3CO_2)_2H$] readily broke down to a powder with loss of solvent of crystallisation. However, suitable crystals of (**2**) (X = BPh_4) were prepared from the reaction of (**2**) [X = $(CF_3CO_2)_2H$] in methanol with $NaBPh_4$ and by recrystallisation of the precipitate from CH_2Cl_2–heptane. Although the structure determination is still incomplete,[4] diffraction data have established the formulation and overall structure shown when taken with spectroscopic data [^1H n.m.r. ($CDCl_3$): δ 7·50 (m, 40H, PPh), 6·85 (m, 20H, BPh), 3·95 (t, J_{PH} 9 Hz, 4H, PCH_2P), and −26·18 (quintet, J_{PH} 15·2 Hz, MnHMn); ^{31}P n.m.r. (−40 °C): δ 58·9 p.p.m., downfield from H_3PO_4 as external reference; ν(CO) (CH_2Cl_2): 2034w, 1978s, 1956m(sh), and 1948m(sh) cm^{-1}]. The symmetrical quintet for hydride in the ^1H n.m.r. spectrum confirms that it is bridging. Although the parent carbonyl cation $[Mn_2H(CO)_{10}]^+$ appears to be unknown, the isoelectronic complex $[Cr_2H(CO)_{10}]^-$ (and its Mo and W analogues) have been well studied.[5]


(1)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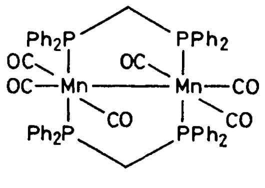
(3)

Protonation of (**1**) under an atmosphere of CO is *ca.* 10 times more rapid than under nitrogen, giving (**2**) in higher yield with the absorption of CO (1·02 mol per mol of Mn_2). Compound (**1**) reacts very slowly with CO to give $[Mn_2(CO)_6(dmp)_2]$ (**3**) and (**3**) is protonated very slowly to give (**2**) so that (**2**) cannot be formed in this reaction *via* (**3**). We believe that an initial protonation of (**1**) leads to a highly reactive intermediate which either is co-ordinatively unsaturated or contains co-ordinated solvent. This then adds CO, abstracted from other complex molecules in the absence of a CO atmosphere. An extension of the Mn–Mn bond on protonation [compare Mn–Mn distances 2·93 Å in (**1**) with 3·2 Å in (**2**) (X = BPh_4)] would make the 4e-donor bridging mode as in (**1**) unfavourable and render the intermediate unsaturated.

Protonation of (**1**) in the presence of other 2e-donor ligands such as Y^- (Y = Br or CN) or L (L = $4\text{-}MeC_6H_4NC$ or MeCN) gives complexes of type $[Mn_2HY(CO)_5(dpm)_2]$ or $[Mn_2HL(CO)_5(dpm)_2]^+$, all containing bridging hydrides which give ^1H n.m.r. quintets.

Unlike complex (**1**), complex (**2**) reacts readily with $LiBHEt_3$ in THF at 0 °C to regenerate (**1**). Significantly, this cannot be a simple deprotonation to give (**3**) since we have shown that (**3**) does not decarbonylate under these reaction conditions. Rather, we propose that nucleophilic attack is at CO to give $[Mn_2H(CHO)(CO)_5(dpm)_2]$ which rapidly decomposes to (**1**). Also of interest is the reaction of (**2**) with H_2 (50 atm) at 100 °C to give colourless or pale yellow products not containing any metal carbonyl.

We thank the S.R.C. and I.C.I. Petrochemicals Division for support (C.A.S.E. award to H. C. A.).

(*Received*, 11*th May* 1981; *Com.* 551.)

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