Synthesis and Reactions of the Di-μ-hydrido Compound $[Mn_2H_2(CO)_4(Ph_2PCH_2PPh_2)_2]$

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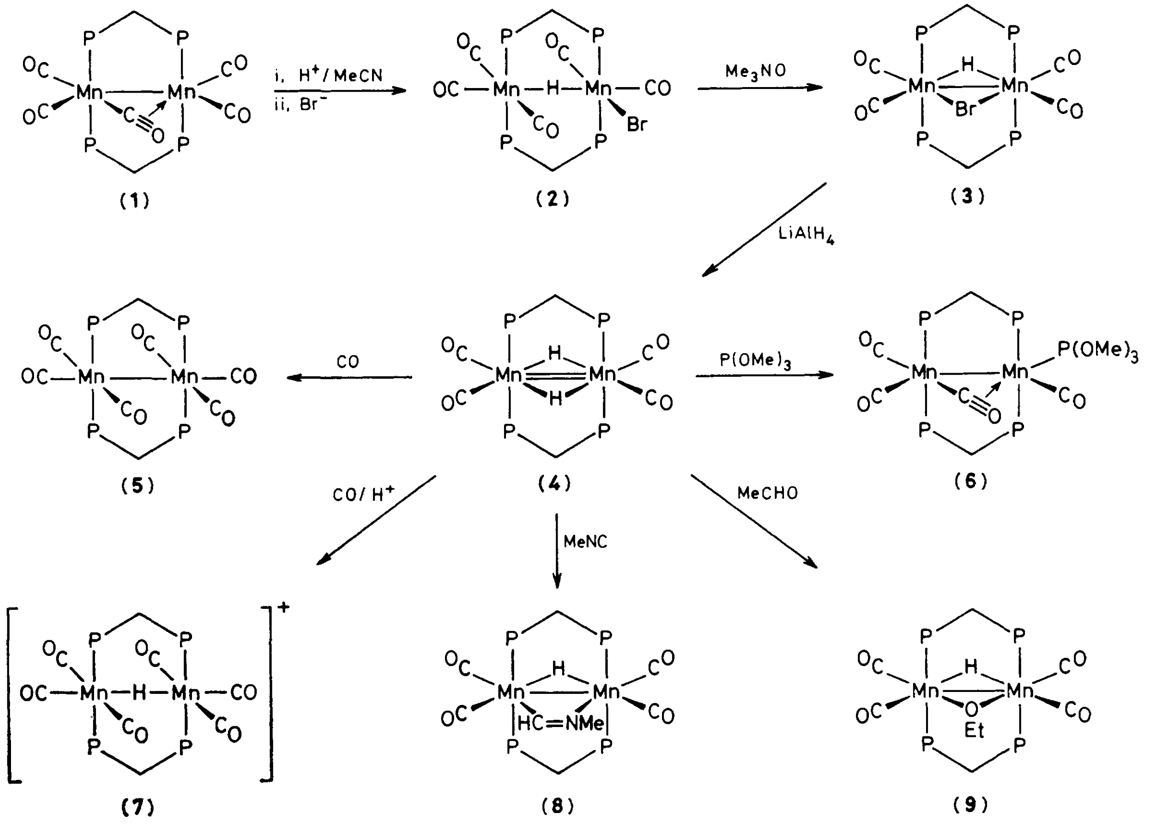
Decarbonylation of $[Mn_2HBr(CO)_5(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) using Me_3NO and treatment of the resultant tetracarbonyl derivative in tetrahydrofuran with $LiAlH_4$ gives deep purple crystals of the formally unsaturated compound $[Mn_2H_2(CO)_4(dppm)_2]$ which inserts MeCHO or MeNC to give μ-EtO or μ-MeN=CH complexes and reacts with certain other ligands such as CO or $P(OMe)_3$ with displacement of H_2.

The formally unsaturated compound $[Re_2H_2(CO)_8]$[1] readily breaks down to $[ReH(CO)_4(PPh_3)]$ on reaction with PPh_3 above −30 °C[2] whereas the use of the bridging diphosphine, $Ph_2PCH_2PPh_2$ (dppm), allows $[Re_2H_2(CO)_6(dppm)]$ to react



Scheme 1

with various reagents with retention of the dinuclear framework.[2–4] The apparently unknown $[Mn_2H_2(CO)_8]$ is expected to be even more readily bisected than its third-row analogue. We have now synthesised $[Mn_2H_2(CO)_4(dppm)_2]$ which undergoes insertion or H_2 elimination reactions without disrupting the $Mn_2(dppm)_2$ ring.

The compound $[Mn_2(CO)_5(dppm)_2]$ (**1**),[5,6] reacts with HBF_4 with uptake of donor molecules L to give $[Mn_2H(CO)_5L(dppm)_2][BF_4]$ and the product has been isolated where L = MeCN, for example.[7,8] The MeCN ligand may be replaced by anions, such as cyanide[8] or bromide (Scheme 1). Addition of an excess of KBr to the acetonitrile cation in methanol at room temperature gives compound (**2**) as orange-red crystals (87%).† A large excess of Me_3NO reacts with compound (**2**) in refluxing dichloromethane–methanol mixtures (40 h) to give the decarbonylation product (**3**) as yellow-orange crystals (62%).† Metathetical replacement of bromide by hydride results from treating the tetrahydrofuran solution of (**3**) with a large excess of $LiAlH_4$. The resultant green solution (murky with suspended $LiAlH_4$) is hydrolysed slowly in moist air, and filtered through Celite to give a deep purple solution giving $[Mn_2H_2(CO)_4(dppm)_2]$ (**4**), as dark purple thermally and air-stable crystals (80—90%). The single or double metal–metal bonds shown for compounds in Scheme 1 are those formally required to give an 18 electron configuration,‡ although in practice the bonding will be through the bridging ligands. The structure of (**4**) is based on spectroscopic evidence† and a single-crystal *X*-ray study.[9] The double hydride bridged compound (**4**) is directly comparable with $[Os_3H_2(CO)_{10}]$[10] and $[Os_2H_2(CO)_2(\eta\text{-}C_5Me_5)_2]$[11] as well as $[Re_2H_2(CO)_8]$,[1] which are also formally unsaturated, and is a rare example of a first row metal compound of this type.

Compound (**4**) is much more crowded than $[Re_2H_2(CO)_6(dppm)]$ and is generally less reactive, not forming detectable amounts of adduct with 2 electron donors (no immediate reaction at room temperature in neat PMe_2Ph or with this phosphine in refluxing toluene), although the reactions shown in Scheme 1 probably do occur by direct preliminary additions. Likewise carbon monoxide at atmospheric pressure does not form an adduct while at 20 atm it displaces H_2. Trimethyl phosphite similarly displaces H_2 in refluxing toluene but only one ligand is added. Compound (**6**), $[Mn_2(CO)_4\{P(OMe)_3\}(dppm)_2]\cdot CH_2Cl_2$ may be crystallised (85% yield) from CH_2Cl_2–pentane mixtures as the first simple substitution derivative of compound (**1**).† The μ-CO

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† Key spectroscopic data for new compounds. Compound (**2**): ν(CO) (CH_2Cl_2), 2 037w, 1 955s, 1 926s, 1 856m cm^{-1}; ^1H n.m.r. ($CDCl_3$), δ −21.09 (quintet, J_{PH} 19.3 Hz, Mn*H*Mn). Compound (**3**): ν(CO) (CH_2Cl_2), 1 942m, 1 926vs, 1 904m, 1 861vs cm^{-1}; ^1H n.m.r. ($CDCl_3$), δ −12.75 (quintet, J_{PH} 17.6 Hz, Mn*H*Mn). Compound (**4**): ν(CO) (CH_2Cl_2), 1 939w, 1 920s, 1 855vs cm^{-1}; ^1H n.m.r. ($CDCl_3$), δ −15.40 (quintet, J_{PH} 18.7 Hz, Mn*H*Mn), 3.66 (quintet, J_{PH} 3.7 Hz, PCH_2P), 7.1—7.8 (Ph); ^{31}P n.m.r., δ 70.1 p.p.m. (s). Compound (**6**): ν(CO) (CH_2Cl_2), 1 911vs, 1 842vs, 1 824s(sh), 1 623m cm^{-1}; ^1H n.m.r. ($CDCl_3$), δ 3.26 (d, J_{PH} 10.0 Hz, OCH_3), 4.05 and 3.72 (m, PCH_2P), 6.7—7.8 (Ph); ^{31}P n.m.r. δ 74.42 and 58.55 (m, dppm) and 24.51 [m, $P(OMe)_3$]. Compound (**8**): ν(CO) (CH_2Cl_2), 1 932s, 1 914vs, 1 847s cm^{-1}, ν(CN) (Nujol) 1 530w cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ −17.90 (quintet, J_{PH} 16.4 Hz, Mn*H*Mn), 3.02 (s, N*Me*), 10.89 (s, *H*C=N). Compound (**9**): ν(CO) (CH_2Cl_2), 1 914m, 1 924vs, 1 861s, 1 844m cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ −10.87 (quintet, J_{PH} 12.5 Hz, Mn*H*Mn), 1.13 (t, J_{HH} 6.5 Hz, OCH_2CH_3), 3.70 (quartet, J_{PH} 6.5 Hz, OCH_2CH_3), 2.79 and 3.24 (m, PCH_2P).

‡ Compounds (**2**) and (**7**) require single manganese–manganese bonds on this basis. The Mn–H–Mn groups as in $[M_2H(CO)_{10}]^-$ (M = Cr, Mo, or W) may be bent rather than as shown.

ligand is characterised as a 4 electron donor by ν(CO) at 1623 cm^{-1} [1645 cm^{-1} for compound (**1**)], but we are not sure of the co-ordination site of the phosphite. The uptake of only one $P(OMe)_3$ illustrates the crowding in these $Mn_2(dppm)_2$ complexes. Protonation of compound (**4**) with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 gives compound (**7**),[7] with a higher yield (94%) under a CO atmosphere. Compound (**5**) is not an intermediate in this reaction since it is only very slowly protonated.

Although (**4**) reacts with various unsaturated molecules, alkynes, diazomethane *etc.*, we have so far only properly characterised the products (**8**) and (**9**) from MeNC and MeCHO respectively (Scheme 1).†

The dppm ligands firmly hold the two Mn atoms together and allow a hydride and organic chemistry to be developed corresponding to that normally associated with second and third row metals although the eight phenyl groups hinder the incorporation of bulky ligands.

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