

## Synthesis and Reactions of the Di- $\mu$ -hydrido Compound $[\text{Mn}_2\text{H}_2(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]$

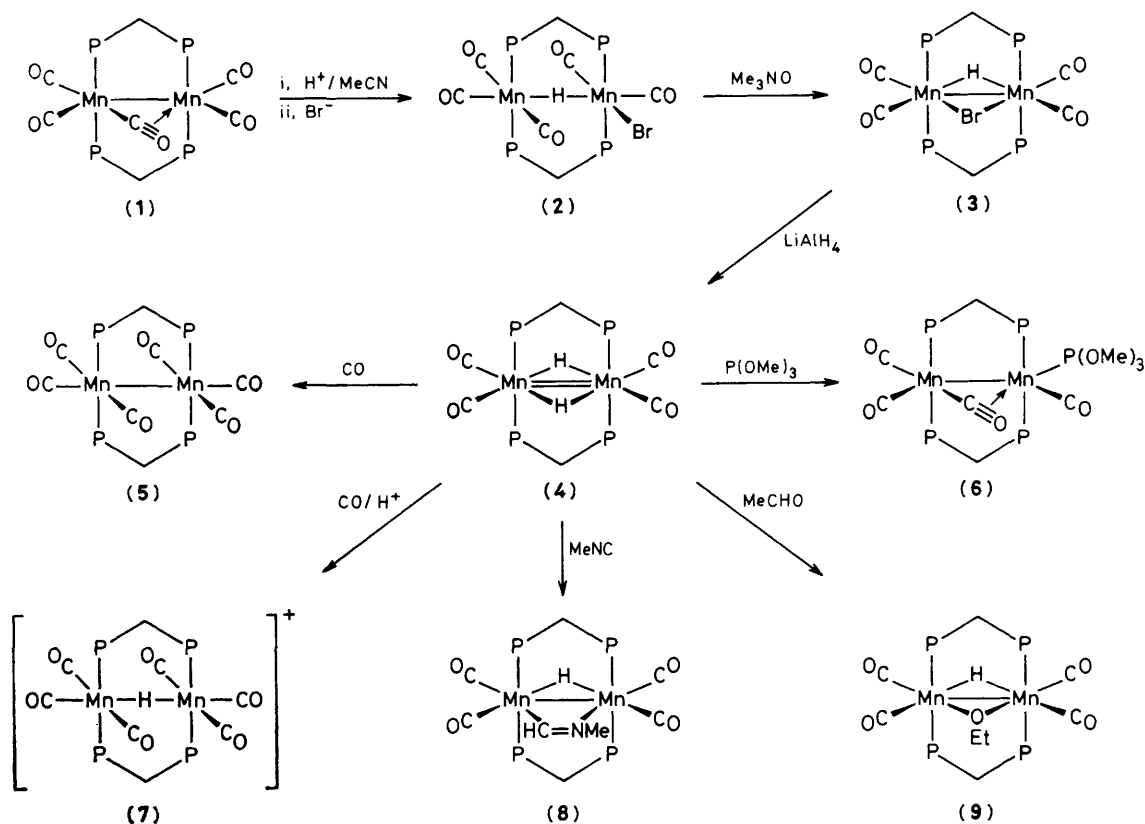
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Decarbonylation of  $[\text{Mn}_2\text{HBr}(\text{CO})_5(\text{dppm})_2]$  ( $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) using  $\text{Me}_3\text{NO}$  and treatment of the resultant tetracarbonyl derivative in tetrahydrofuran with  $\text{LiAlH}_4$  gives deep purple crystals of the formally unsaturated compound  $[\text{Mn}_2\text{H}_2(\text{CO})_4(\text{dppm})_2]$  which inserts  $\text{MeCHO}$  or  $\text{MeNC}$  to give  $\mu\text{-EtO}$  or  $\mu\text{-MeN=CH}$  complexes and reacts with certain other ligands such as  $\text{CO}$  or  $\text{P(OMe)}_3$  with displacement of  $\text{H}_2$ .

The formally unsaturated compound  $[\text{Re}_2\text{H}_2(\text{CO})_8]^+$  readily breaks down to  $[\text{ReH}(\text{CO})_4(\text{PPh}_3)]$  on reaction with  $\text{PPh}_3$

above  $-30^\circ\text{C}^2$  whereas the use of the bridging diphosphine,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  ( $\text{dppm}$ ), allows  $[\text{Re}_2\text{H}_2(\text{CO})_6(\text{dppm})]$  to react



Scheme 1

with various reagents with retention of the dinuclear framework.<sup>2-4</sup> The apparently unknown  $[\text{Mn}_2\text{H}_2(\text{CO})_8]$  is expected to be even more readily bisected than its third-row analogue. We have now synthesised  $[\text{Mn}_2\text{H}_2(\text{CO})_4(\text{dppm})_2]$  which undergoes insertion or  $\text{H}_2$  elimination reactions without disrupting the  $\text{Mn}_2(\text{dppm})_2$  ring.

The compound  $[\text{Mn}_2(\text{CO})_5(\text{dppm})_2]$  (1),<sup>5,6</sup> reacts with  $\text{HBF}_4$  with uptake of donor molecules L to give  $[\text{Mn}_2\text{H}(\text{CO})_5\text{L}(\text{dppm})_2][\text{BF}_4]$  and the product has been isolated where  $\text{L} = \text{MeCN}$ , for example.<sup>7,8</sup> The MeCN ligand may be replaced by anions, such as cyanide<sup>8</sup> 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%).<sup>†</sup> A large excess of  $\text{Me}_3\text{NO}$  reacts with compound (2) in refluxing dichloromethane-methanol mixtures (40 h) to give the decarbonylation product (3) as yellow-orange crystals

(62%).<sup>†</sup> Metathetical replacement of bromide by hydride results from treating the tetrahydrofuran solution of (3) with a large excess of  $\text{LiAlH}_4$ . The resultant green solution (murky with suspended  $\text{LiAlH}_4$ ) is hydrolysed slowly in moist air, and filtered through Celite to give a deep purple solution giving  $[\text{Mn}_2\text{H}_2(\text{CO})_4(\text{dppm})_2]$  (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,<sup>‡</sup> although in practice the bonding will be through the bridging ligands. The structure of (4) is based on spectroscopic evidence<sup>†</sup> and a single-crystal X-ray study.<sup>9</sup> The double hydride bridged compound (4) is directly comparable with  $[\text{Os}_2\text{H}_2(\text{CO})_{10}]$ <sup>10</sup> and  $[\text{Os}_2\text{H}_2(\text{CO})_8(\eta\text{-C}_5\text{Me}_5)_2]$ <sup>11</sup> as well as  $[\text{Re}_2\text{H}_2(\text{CO})_8]$ ,<sup>1</sup> 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  $[\text{Re}_2\text{H}_2(\text{CO})_6(\text{dppm})]$  and is generally less reactive, not forming detectable amounts of adduct with 2 electron donors (no immediate reaction at room temperature in neat  $\text{PMe}_2\text{Ph}$  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  $\text{H}_2$ . Trimethyl phosphite similarly displaces  $\text{H}_2$  in refluxing toluene but only one ligand is added. Compound (6),  $[\text{Mn}_2(\text{CO})_4\{\text{P(OMe)}_3\}(\text{dppm})_2]\text{-CH}_2\text{Cl}_2$  may be crystallised (85% yield) from  $\text{CH}_2\text{Cl}_2$ -pentane mixtures as the first simple substitution derivative of compound (1).<sup>†</sup> The  $\mu\text{-CO}$

<sup>†</sup> Key spectroscopic data for new compounds. Compound (2):  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ), 2037w, 1955s, 1926s, 1856m  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ),  $\delta$  -21.09 (quintet,  $J_{\text{FH}}$  19.3 Hz,  $\text{MnHMn}$ ). Compound (3):  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ), 1942m, 1926vs, 1904m, 1861vs  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ),  $\delta$  -12.75 (quintet,  $J_{\text{FH}}$  17.6 Hz,  $\text{MnHMn}$ ). Compound (4):  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ), 1939w, 1920s, 1855vs  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ),  $\delta$  -15.40 (quintet,  $J_{\text{FH}}$  18.7 Hz,  $\text{MnHMn}$ ), 3.66 (quintet,  $J_{\text{FH}}$  3.7 Hz,  $\text{PCH}_2\text{P}$ ), 7.1–7.8 (Ph);  $^{31}\text{P}$  n.m.r.,  $\delta$  70.1 p.p.m. (s). Compound (6):  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ), 1911vs, 1842vs, 1824s(sh), 1623m  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ),  $\delta$  3.26 (d,  $J_{\text{FH}}$  10.0 Hz,  $\text{OCH}_3$ ), 4.05 and 3.72 (m,  $\text{PCH}_2\text{P}$ ), 6.7–7.8 (Ph);  $^{31}\text{P}$  n.m.r.,  $\delta$  74.42 and 58.55 (m, dppm) and 24.51 [m,  $\text{P(OMe)}_3$ ]. Compound (8):  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ), 1932s, 1914vs, 1847s  $\text{cm}^{-1}$ ,  $\nu(\text{CN})$  (Nujol) 1530w  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  -17.90 (quintet,  $J_{\text{FH}}$  16.4 Hz,  $\text{MnHMn}$ ), 3.02 (s,  $\text{NMe}$ ), 10.89 (s,  $\text{HC=N}$ ). Compound (9):  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ), 1914m, 1924vs, 1861s, 1844m  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  -10.87 (quintet,  $J_{\text{FH}}$  12.5 Hz,  $\text{MnHMn}$ ), 1.13 (t,  $J_{\text{HH}}$  6.5 Hz,  $\text{OCH}_2\text{CH}_3$ ), 3.70 (quartet,  $J_{\text{FH}}$  6.5 Hz,  $\text{OCH}_2\text{CH}_3$ ), 2.79 and 3.24 (m,  $\text{PCH}_2\text{P}$ ).

<sup>‡</sup> Compounds (2) and (7) require single manganese-manganese bonds on this basis. The  $\text{Mn-H-Mn}$  groups as in  $[\text{M}_2\text{H}(\text{CO})_{10}]^-$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$ ) may be bent rather than as shown.

ligand is characterised as a 4 electron donor by  $\nu(\text{CO})$  at  $1623\text{ cm}^{-1}$  [ $1645\text{ cm}^{-1}$  for compound (1)], but we are not sure of the co-ordination site of the phosphite. The uptake of only one  $\text{P}(\text{OMe})_3$  illustrates the crowding in these  $\text{Mn}_2\text{-(dppm)}_2$  complexes. Protonation of compound (4) with  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$  gives compound (7),<sup>7</sup> 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).<sup>†</sup>

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.

We thank the S.E.R.C. and I.C.I. (Petrochemicals and Polymers Division) for support.

Received, 6th May 1983; Com. 574

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