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Addition of Small Molecules to $Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2$ Including the Isolation of a Diazomethane Adduct

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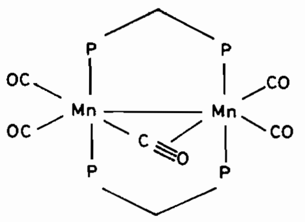
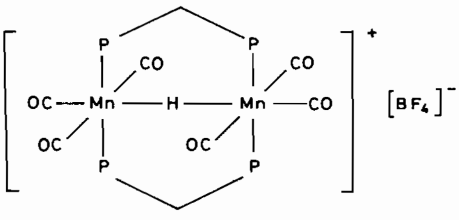
The unusual, 4-electron donor, η^2-μ_2 bonding mode of the bridging carbonyl ligand found in $[Mn_2(CO)_5(dppm)_2]$ (**1**) is attracting interest as a possible means of activating carbon monoxide [1]†. This is exemplified by a recent observation of the proton induced carbonylation of (**1**) to afford $[Mn_2(CO)_6H(dppm)_2]^+$ (**2**) and its subsequent decarbonylation reactions [2]. We wish to report that in general, addition of small molecules to (**1**) leads to displacement of the carbonyl oxygen atom from the manganese coordination sphere, resulting in adducts containing only normal, 2-electron donor carbonyl ligands. Relevant spectroscopic data (IR and ^{31}P NMR) are listed in Table I.



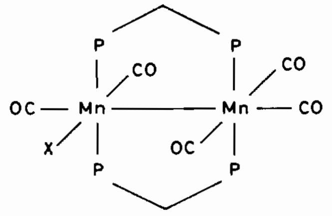
(1)



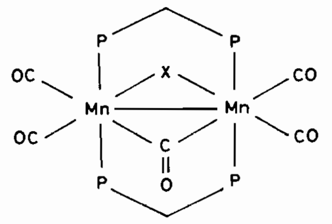
(2)

Treatment of (**1**) in dichloromethane with SO_2 rapidly gives an orange–red solution. Addition of diethyl ether affords bright orange crystals of $[Mn_2(CO)_5(SO_2)(dppm)_2]$ (**3**) [75% yield; ν(SO) = 1144 and 1015 cm^{-1}, $\delta(SO_2)$ = 575 cm^{-1}].*,** The addition of SO_2 is reversible; heating a chloroform solution of (**3**) at reflux for several hours quantitatively regenerates (**1**). Addition of benzenediazonium fluoroborate to (**1**) in CH_2Cl_2 yields red–black crystals of $[Mn_2(CO)_5(N_2C_6H_5)(dppm)_2][BF_4]$ (**4**) [71%; ν(NN) = 1519 cm^{-1}] on addition of Et_2O and cooling to –5 °C. Similarly, a purple crystalline adduct $[Mn_2(CO)_5(CS_2)(dppm)_2]$ (**5**) [38%; ν(CS) = 1018 cm^{-1}] is obtained from carbon disulphide and (**1**) in boiling CH_2Cl_2. Certain structural assignments can be made on the basis of the spectral data. Some rather low values of ν(CO) for terminal carbonyl ligands are found in other $Mn_2(dppm)_2$ complexes, making definite assignment of ν(CO) to bridging carbonyls here somewhat tenuous [1a, b].

There are numerous examples of bridging SO_2 ligands, in particular the complexes $[M_2Cl_2(\mu\text{-}SO_2)(dppm)_2]$ (M = Pd, Pt) have very similar ν(SO) and $\delta(SO_2)$ to (**3**). In contrast, only a restricted number of bridging CS_2 [6] and ArN_2^+ [7] complexes are known. The feasible alternative structures of (**3**), (**4**) and (**5**) are **a**, ones containing only terminal ligands or **b**, ones with an η^1-μ_2 bridging carbonyl

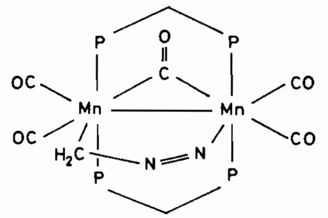


(a)



(b)

X = SO_2 (3), $N_2C_6H_5^+$ (4), CS_2 (5),
N_2CH_2 (6), $N_2C(CO_2Et)_2$ (7), $N_2C_5Cl_4$ (8),
$N_2CH_3^+$ (9), BF_3 (10), H^- (11).



(6c)

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† Abbreviations: dppm = methylenebis(diphenylphosphine). $N_2C_5Cl_4$ = 1,2,3,4-tetrachloro-5-diazo-1,3-cyclopentadiene.

*Infra-red spectra as Nujol Mulls.

**Satisfactory elemental analyses were obtained for all complexes except where stated otherwise.

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TABLE I. Infra-red and ^{31}P NMR Spectral Data.

Compound		ν(CO) cm^{-1}	δ_P[a]
$Mn_2(CO)_5(dppm)_2$	**(1)**	1940(m), 1902(vs), 1868(s), 1832(m), 1648(m)[b,c]	69.45(s)[c]
$Mn_2(CO)_5(SO_2)(dppm)_2$	**(3)**	2025(s), 1967(s), 1926(s), 1889(s), 1848(m)[d]	64.82(s)
$[Mn_2(CO)_5(N_2Ph)(dppm)_2][BF_4]$	**(4)**	1972(s), 1921(s,sh), 1904(s), 1861(s)[d]	53.01(s)
$Mn_2(CO)_5(CS_2)(dppm)_2$	**(5)**	1946(s), 1914(s), 1887(m), 1863(s)[d]	61.79(s)
$Mn_2(CO)_5(CH_2N_2)(dppm)_2$	**(6)**	1945(m,sh), 1919(s), 1872(s), 1810(m)[c]	57.63(m)[e]
		1960(s), 1948(m,sh), 1920(vs), 1870(m,sh), 1857(s), 1815(m)[d]	
$Mn_2(CO)_5[N_2C(CO_2Et)_2](dppm)_2$	**(7)**	1937(vs), 1867(s), 1850(m,sh), 1800(m), 1676(m)[c]	57.15(m)[e]
$Mn_2(CO)_5(N_2C_5Cl_4)(dppm)_2$	**(8)**	1957(s), 1931(s), 1896(s), 1856(m)[c]	f
$[Mn_2(CO)_5(N_2CH_3)(dppm)_2][BF_4]$	**(9)**	1979(s), 1959(vs), 1911(s), 1876(m)[c]	56.64(m)[e]
$Mn_2(CO)_5(BF_3)(dppm)_2$	**(10)**	2028(m), 1950(vs,br), 1926(s), 1785(s)[c]	55.49(s)
$[Mn_2(CO)_6H(dppm)_2][BF_4]$	**(2)**	2034(w), 1979(s), 1955(s,sh), 1947(m,sh)[c]	59.05(s)
$Li[Mn(CO)_5H(dppm)_2]$	**(11)**	1907(m), 1866(vs), 1831(m), 1773(m), 1599(w)[g]	72.81(s)[g]

[a] ^{31}P-{^{1}H} spectra in ppm downfield from 85% H_3PO_4. [b] Ref. 1(a). [c] In CH_2Cl_2. [d] Nujol mull. [e] Centre of AA'BB' multiplet. [f] Not measured. [g] In THF.

together with either S-bound SO_2, bridging CS_2 or bridging $N_2C_6H_5^+$ ligands.

Surprisingly, diazomethane in ether reacts with a CH_2Cl_2 solution of **(1)**, *without* the liberation of dinitrogen, affording orange–red, air-stable crystals of $[Mn_2(CO)_5(CH_2N_2)(dppm)_2]$ **(6)** [88%; ν(CNN) = 1605 cm^{-1}; ^{1}H NMR in CD_2Cl_2 δ = 4.78 ppm (S, CH_2N_2)]. This appears to be the first example of simple coordination of diazomethane to a transition metal. There is a complex reported, with composition $[Mn_2(CO)_{10}(CH_2N_2)]$, but this is known to contain a carbonyl group incorporated with the coordinated CH_2N_2 moiety [8]. Of the possible bonding modes of CH_2N_2 in **(6)**, symmetric arrangements such as **(6b)** are analogous to those found in $[Cp_2Mo_2(CO)_4(\mu\text{-}N_2CPh_2)]$ [9] and $[Cp_3Co_3(\mu\text{-}CO)(\mu\text{-}N_2CPh_2)]$ [10]. Observation of non-equivalent phosphorus environments in the ^{31}P NMR spectrum excludes such a structure. A 1,3-dipolar addition of CH_2N_2 across the metal–metal bond in **(1)** would yield **(6c)**. Although common in organic chemistry, such transition metal adducts of diazo compounds have never been isolated, but are considered possible intermediates in the elimination of dinitrogen to form bridging methylene complexes [9, 11]. The absence of any observable P–H coupling between the CH_2N_2 protons and the dppm ligands makes **(6c)** an unlikely configuration. Moreover, **(6)** is thermally stable, showing little tendency to decompose below 200 °C. At present **(6a)**, involving a $Mn{-}N{=}N{=}CH_2$ unit, is the favoured structure. There are numerous examples of *substituted* diazoalkanes bonding in this manner to mononuclear systems [12].

Although the relatively electron-rich, N_2CPh_2 and N_2CMePh, fail to react with **(1)** under mild conditions, both the activated diazoalkanes, $N_2C(CO_2Et)_2$ and $N_2C_5Cl_4$†, afford the red–brown crystalline complexes $[Mn_2(CO)_5\{N_2C(CO_2Et)_2\}(dppm)_2]$ **(7)** and $[Mn_2(CO)_5(N_2C_5Cl_4)(dppm)_2]$ **(8)** respectively, together with other products. These complexes appear structurally similar to the parent **(6)**, and readily protonate to give deeply coloured salts. Thus, treating a CH_2Cl_2 solution of **(6)** with an excess of aqueous HBF_4 immediately affords, purple $[Mn_2(CO)_5(N_2CH_3)(dppm)_2][BF_4]$ **(9)** [80%; δ(NN) = 1762 cm^{-1}]. This reaction is readily reversed; merely shaking a CH_2Cl_2 solution of **(9)** with water quickly regenerates **(6)**.

The Lewis acid, boron trifluoride, also reacts with **(1)** in solution. Thus, titration of **(1)** in CH_2Cl_2 with $BF_3 \cdot Et_2O$ to form a deep–red, 1:1 adduct can be followed either by changes in ν(CO) in the infrared spectrum or by ^{31}P NMR spectroscopy.

The adduct $[Mn_2(CO)_5(BF_3)(dppm)_2]$ **(10)**, which is stable for only a few hours in solution, has a ν(CO) at 1785 cm^{-1}, suggesting the presence of either a normal 2-electron bridging carbonyl ligand or a $Mn{-}C{=}O{-} \rightarrow BF_3$ interaction. Attempts to isolate **(10)** lead to decomposition, from which the orange crystalline $[Mn_2(CO)_6H(dppm)_2][BF_4]$ **(2)** [15%; ^{1}H NMR in CH_2Cl_2, δ = –26.3 ppm (quintet, $^2H_{PH}$ = 15 Hz, Mn–*H*–Mn)] is isolated. The latter complex is best prepared by direct reaction of aqueous HBF_4 with **(1)** under a CO atmosphere, and was recently independently reported by

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† See footnote L.H. column p. L141.

Aspinall and Deeming [2]. The nature of other Lewis acid adducts of (**1**) as well as the cationic products from the oxidation of (**1**) are subjects of current study.

In contrast to the reactivity of (**1**) with electrophiles as outlined above, it is surprising that electron-donor ligands generally fail to coordinate. Thus, boiling with neat trimethyl phosphine, acetonitrile or pyridine leaves (**1**) unchanged, although reaction with CO or isonitriles has been reported to yield $[Mn_2(CO)_5L(dppm)_2]$(L = CO, MeNC, $PhCH_2NC$, p-MeC_6H_4NC) [1, 3]. While treatment with $LiBEt_3H$ has no effect[†], (**1**) completely reacts with two equivalents of $LiAlH_4$ in tetrahydrofuran (monitored by IR spectroscopy) to produce a brown solution. On cooling to −10 °C, very air-sensitive, brown crystals of $[Li(THF)_x][Mn_2(CO)_5H(dppm)_2]$ (**11**) [^1H NMR in THF, $\delta = -9.29$ pppm (quintet, $^2J_{PH} = 17.6$ Hz, Mn–*H*–Mn)] are deposited [13]. Presumably the second equivalent of $LiAlH_4$ promotes hydride transfer by acting as an acceptor for AlH_3 [14]. From the particularly low ν(CO) found in the IR spectrum and from the ^1H NMR spectrum which shows coupling of the hydride resonance to four equivalent phosphorus nuclei, it seems that (**11**) has the bridging structure **b**, similar to that found for the hydride complex $[Rh_2(\mu\text{-}Cl)(\mu\text{-}H)(dppm)_2][BPh_4]$ [15].

The reactivity of (**1**) towards small molecules shows similarities to that of other bridging dppm systems, such as $[M_2Cl_2(dppm)_2]$ (M = Pd, Pt) and $[Rh_2(CO)_2(\mu\text{-}Cl)(dppm)_2]^+$ [4, 6a, 15, 16]. However, it is concluded that coordination of a carbonyl ligand in the η^2-μ_2 mode to relatively electron-rich manganese atoms does not confer any markedly increased activity upon either the carbon or oxygen atoms. This may be contrasted to the fixation of the carbonyl ligands of electropositive metals such as aluminium or zirconium [17]. Work is underway to elucidate the crystal structures of several of the above complexes and to develop further the chemistry of (**1**).

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[†] See footnote L. H. column p. L141.