

Di-manganese carbonyl compounds containing bis(dicyclohexylphosphino)methane (dcpm) ligation

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Abstract

The reaction of $[\text{Mn}_2(\text{CO})_{10}]$ with bis(dicyclohexylphosphino)methane (dcpm) in refluxing cyclohexane yields the simple substitution products $[\text{Mn}_2(\text{dcpm})(\text{CO})_8]$ (**1**) and $[\text{Mn}_2(\text{dcpm})_2(\text{CO})_6]$ (**2**). The solid state structures of **1** and **2** show the dcpm ligands to be bridging the di-manganese core with a pseudo-octahedral coordination about each Mn metal center. The ^{13}C NMR spectra of **1** and **2** show the carbonyl ligands to be non-fluxional on the NMR time scale at 30 °C. Attempts to thermally induce decarbonylation of **2** at 174 °C in refluxing n-decane failed. However, photolysis of **2** in benzene was found to efficiently produce the complex $[\text{Mn}_2(\text{dcpm})_2(\text{CO})_5]$ (**3**) shown to contain a semi-bridging carbonyl ligand both in solution $\nu(\text{M}-\text{CO}) = 1637 \text{ cm}^{-1}$, and in the solid state (X-ray diffraction). The Mn–Mn distance of 2.928(2) Å in **3** is shorter than the values of 2.976(2) and 3.025(2) Å found for **1** and **2**, respectively. Crystal data at 293 K for $\text{Mn}_2\text{P}_2\text{O}_8\text{C}_{33}\text{H}_{46}$ (**1**): $a = 13.097(1)$, $b = 11.6635(9)$, $c = 23.501(2)$ Å, $\beta = 101.035(7)^\circ$, $Z = 4$ in space group $P2_1/n$; for $\text{Mn}_2\text{P}_4\text{O}_8\text{C}_{68}\text{H}_{120}$ (**2**· $2\text{C}_6\text{H}_{14}$) at 293 K: $a = 20.714(5)$, $b = 15.856(2)$, $c = 20.910(5)$ Å, $\beta = 94.34(2)^\circ$, $Z = 4$ in space group $C2/c$; for $\text{Mn}_2\text{P}_4\text{O}_5\text{C}_{53}\text{H}_{92}$ (**3**) at 293 K: $a = 11.0309(9)$, $b = 12.319(2)$, $c = 21.518(2)$ Å, $\alpha = 83.361(9)$, $\beta = 76.293(7)$, $\gamma = 85.646(9)^\circ$, $Z = 2$ in space group $P1$.

Keywords: Crystal structures; Manganese complexes; Carbonyl complexes; Bidentate ligand complexes; Dinuclear complexes

1. Introduction

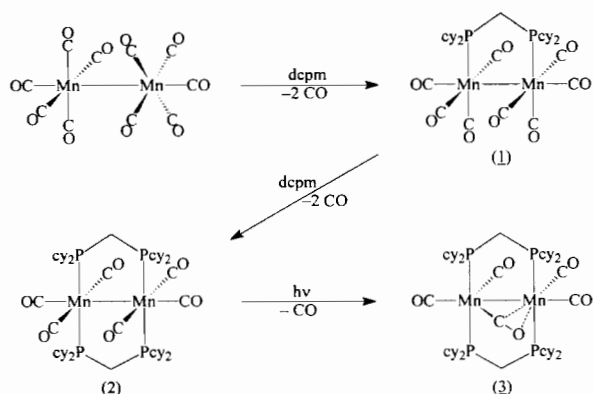
The use of binucleating phosphine ligands (exemplified by dppm: $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) has played a pivotal role in the explosive development of the chemistry of bimetallic complexes [1–3]. Furthermore, considerable attention has recently been focused on the use of bi- and tridentate phosphine ligands containing bulky (typically electron-donating) substituents at phosphorus [4–6]. During our studies of the chemistry of early d-block metal aryloxide compounds [7] we discovered a process for the catalytic hydrogenation of arylphosphine ligands into their saturated counterparts [8]. This process makes available gram quantities of mono-, bi- and polydentate phosphine ligands containing cyclohexyl substituents directly from their commercially available aryl counterparts. We wish to report here on the reactivity of one of these ligands, $[(c\text{-C}_6\text{H}_{11})_2\text{PCH}_2\text{P}(c\text{-C}_6\text{H}_{11})_2]$, dcpm [9,10], with dimanganese decacarbonyl.

2. Results and discussion

The thermal reaction of $\text{Mn}_2(\text{CO})_{10}$ with the ligands $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) [11] and $\text{Me}_2\text{PCH}_2\text{PMe}_2$ (dmpm) [12,13] has been extensively studied. The formation of $[\text{Mn}_2(\text{dppm})_2(\text{CO})_6]$ and its facile thermal decarbonylation to $[\text{Mn}_2(\text{dppm})_2(\text{CO})_5]$ containing a semi-bridging carbonyl ligand was an important development in organometallic chemistry [11]. In the case of the reaction of $\text{Mn}_2(\text{CO})_{10}$ with dmpm, two substitutional isomers of stoichiometry $[\text{Mn}_2(\text{dmpm})_2(\text{CO})_6]$ have been identified [12,13]. In this case it was observed that decarbonylation to the pentacarbonyl could only be achieved photochemically.

The reaction of dcpm with $\text{Mn}_2(\text{CO})_{10}$ in refluxing cyclohexane leads to the simple substitution products $[\text{Mn}_2(\text{dcpm})(\text{CO})_8]$ (**1**) and $[\text{Mn}_2(\text{dcpm})_2(\text{CO})_6]$ (**2**) (Scheme 1). Both yellow **1** and orange **2** were recrystallized from chloroform/hexane mixtures. The thermal stability of the hexacarbonyl **2** was found to be high. Refluxing an n-decane solution of **2** was not found to

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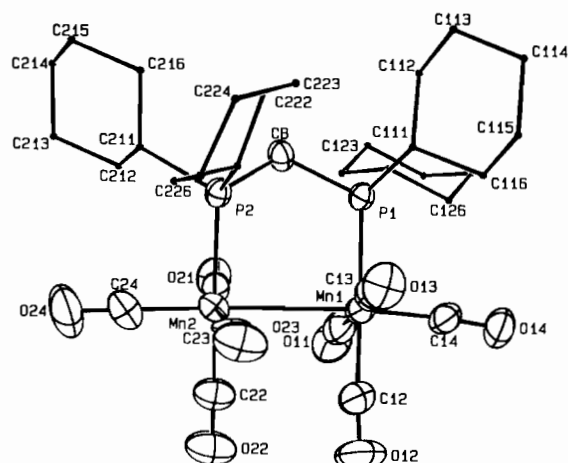
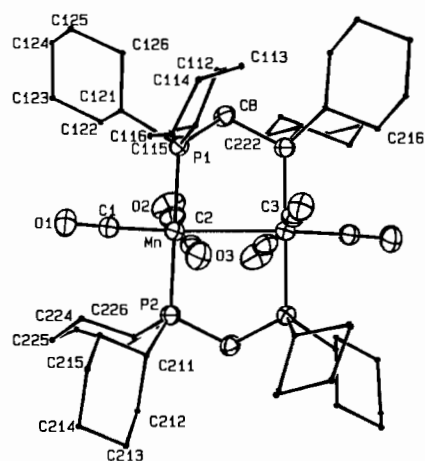
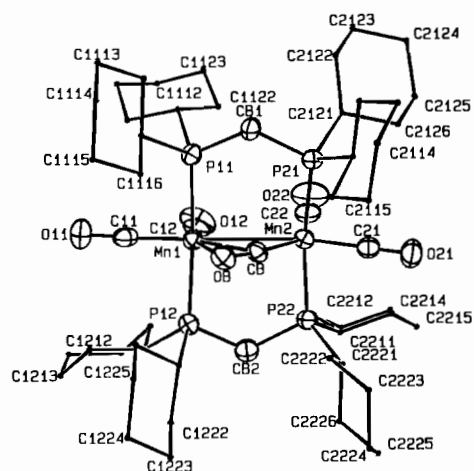
Scheme 1.

lead to decarbonylation. The facile thermal decarbonylation of $[\text{Mn}_2(\text{dppm})_2(\text{CO})_6]$ [11] compared to $[\text{Mn}_2(\text{dmpm})_2(\text{CO})_6]$ [12,13] can be rationalized in terms of steric arguments. However, the lack of thermal decarbonylation of **2** which contains bulkier substituents at phosphorus, negates this steric argument. The photolysis of benzene solutions of **2** generates the pentacarbonyl compound **3** in high yield (Scheme 1).

A more convincing rationale for the lack of facile decarbonylation of the dmpm and dcpm hexacarbonyl compounds recognizes that the presence of more basic, electron-donating phosphine ligation will lead to an increase in manganese to carbonyl π -backbonding, leading to an increase in Mn–CO bond strength. A comparison of the IR spectra of these complexes clearly show this increased backbonding (vide infra). It is interesting to note that the use of the non-symmetrical ligand $[(c\text{-C}_6\text{H}_{11})_2\text{PCH}_2\text{PPh}_2]$ was found to lead directly to the pentacarbonyl product upon reaction with $\text{Mn}_2(\text{CO})_{10}$ in refluxing decane [14].

2.1. Structural studies

The three complexes **1**, **2** and **3** were subjected to single crystal X-ray diffraction analysis. An ORTEP view of each compound is shown in Figs. 1–3 while selected bond distances and angles are collected in Tables 1–3. The molecular structures of **1** and **2** are not unusual, with the coordination geometry about each manganese atom being close to octahedral. In both complexes the dcpm ligands bridge the metal–metal bond, the two ligands in **2** being mutually *trans*: $\text{P}(1)\text{--Mn--P}(2) = 179.46(7)^\circ$. Both **1** and **2** contain two carbonyl ligands that are *trans* to the metal–metal bond. In both these structures the carbonyl ligands that are perpendicular to the Mn–Mn axis are distorted slightly towards the center of the molecule: Mn–Mn–CO angles of $83\text{--}88^\circ$. A projection down the Mn–Mn axis of compounds **1** and **2** shows a ground state structure in which there is a 20° rotation from a fully eclipsed conformation.

Fig. 1. ORTEP view of $[\text{Mn}_2(\text{dcpm})(\text{CO})_6]$ (**1**).Fig. 2. ORTEP view of $[\text{Mn}_2(\text{dcpm})_2(\text{CO})_6]$ (**2**).Fig. 3. ORTEP view of $[\text{Mn}_2(\text{dcpm})_2(\text{CO})_5]$ (**3**).

The molecular structure of the pentacarbonyl **3** is worthy of special discussion. It can be seen (Fig. 3, Table 3) that the two dcpm ligands in **3** are mutually *trans*: $\text{P}(11)\text{--Mn}(1)\text{--P}(12) = 173.2(1)^\circ$ and $\text{P}(21)\text{--Mn}(2)\text{--P}(22) = 173.2(1)^\circ$.

Table 1
Selected bond distances (Å) and angles (°) for $[\text{Mn}_2(\text{CO})_8(\text{dcpm})]$ (1)

Mn(1)–Mn(2)	2.976(2)		
Mn(1)–P(1)	2.338(2)	Mn(2)–P(2)	2.321(2)
Mn(1)–C(11)	1.822(9)	Mn(2)–C(21)	1.830(8)
Mn(1)–C(12)	1.813(8)	Mn(2)–C(22)	1.809(9)
Mn(1)–C(13)	1.823(8)	Mn(2)–C(23)	1.844(8)
Mn(1)–C(14)	1.780(8)	Mn(2)–C(24)	1.764(9)
C(11)–O(11)	1.152(8)	C(21)–O(21)	1.142(7)
C(12)–O(12)	1.145(8)	C(22)–O(22)	1.135(8)
C(13)–O(13)	1.148(8)	C(23)–O(23)	1.140(7)
C(14)–O(14)	1.160(8)	C(24)–O(24)	1.160(9)
Mn(2)–Mn(1)–P(1)	91.09(5)	Mn(1)–Mn(2)–P(2)	89.96(6)
–C(11)	86.1(2)	–C(21)	83.2(2)
–C(12)	86.5(2)	–C(22)	87.5(3)
–C(13)	86.8(2)	–C(23)	84.8(2)
–C(14)	175.1(2)		
P(1)–Mn(1)–C(11)	94.1(3)	C(11)–Mn(1)–C(12)	89.3(4)
–C(12)	175.7(3)	–C(13)	172.6(3)
–C(13)	88.2(2)	–C(14)	92.0(3)
–C(14)	93.6(2)	C(12)–Mn(1)–C(13)	88.1(3)
C(13)–Mn(1)–C(14)	94.9(3)	–C(14)	88.9(3)
P(2)–Mn(2)–C(21)	88.2(2)	C(21)–Mn(2)–C(22)	89.2(3)
–C(22)	176.6(3)	–C(23)	167.9(3)
–C(23)	90.4(2)	–C(24)	97.3(3)
–C(24)	92.5(3)	C(22)–Mn(2)–C(23)	91.6(3)
C(23)–Mn(2)–C(24)	94.8(3)	–C(24)	90.0(4)

Table 2
Selected bond distances (Å) and angles (°) for $[\text{Mn}_2(\text{CO})_6(\text{dcpm})_2]$ (2)

Mn–Mn	3.025(2)		
Mn–P(1)	2.297(2)	Mn–P(2)	2.295(2)
Mn–C(1)	1.761(7)	Mn–C(2)	1.823(7)
Mn–C(3)	1.800(6)		
Mn–Mn–P(1)	88.47(5)	Mn–Mn–P(2)	91.30(6)
Mn–Mn–C(1)	176.7(2)	Mn–Mn–C(2)	83.5(2)
Mn–Mn–C(3)	84.3(2)	Mn–C(1)–O(1)	177.0(5)
Mn–C(2)–O(2)	174.1(6)	Mn–C(3)–O(3)	174.6(5)
P(1)–Mn–P(2)	179.46(7)	P(2)–Mn–C(1)	92.0(2)
–C(1)	88.2(2)	–C(2)	92.6(2)
–C(2)	87.9(2)	–C(3)	88.1(2)
–C(3)	91.4(2)		

$\text{P}(22) = 169.6(1)^\circ$. The five carbonyl ligands are arranged in a plane approximately perpendicular to the two P–Mn–P axes with all P–Mn–C (carbonyl) angles close to 90° (Table 4). In Fig. 4 is shown a representation of the $[\text{Mn}_2(\text{CO})_5]$ core of the molecule along with selected bond distances and angles for both **3** and $[\text{Mn}_2(\text{CO})_5(\text{dppm})_2]$. It can be seen that the majority of the structural parameters are identical within experimental error, the only significant difference concerns the semi-bridging carbonyl ligand [19]. The Mn(2)–C(B) distance of 1.788(9) Å in **3** is shorter than the value of 1.93(3) Å reported for $[\text{Mn}_2(\text{CO})_5(\text{dppm})_2]$ while

Table 3
Selected bond distances (Å) and angles (°) for $[\text{Mn}_2(\text{CO})_5(\text{dcpm})_2]$ (3)

Mn(1)–Mn(2)	2.928(2)		
Mn(1)–P(11)	2.308(3)	Mn(2)–P(21)	2.277(3)
Mn(1)–P(12)	2.296(3)	Mn(2)–P(22)	2.273(3)
Mn(1)–C(B)	2.074(9)	Mn(2)–C(B)	1.788(9)
Mn(1)–C(11)	1.78(1)	Mn(2)–C(21)	1.761(1)
Mn(1)–C(12)	1.739(9)	Mn(2)–C(22)	1.81(1)
C(B)–O(B)	1.199(9)		
Mn(2)–Mn(1)–P(11)	90.33(9)	Mn(1)–Mn(2)–P(21)	94.53(9)
–P(12)	93.14(9)	–P(22)	92.48(9)
–C(B)	37.2(2)	–C(B)	44.5(3)
–C(11)	176.0(3)	–C(21)	160.2(3)
–C(12)	86.3(3)	–C(22)	96.2(3)
P(11)–Mn(1)–P(12)	173.2(1)	P(21)–Mn(2)–P(22)	169.6(1)
–C(B)	90.4(3)	–C(B)	86.8(3)
–C(11)	86.3(3)	–C(21)	85.4(3)
–C(12)	94.4(3)	–C(22)	90.9(3)
C(B)–Mn(1)–C(11)	140.5(4)	C(B)–Mn(2)–C(21)	115.9(4)
–C(12)	123.4(4)	–C(22)	140.1(4)
P(12)–Mn(1)–C(B)	88.9(3)	P(22)–Mn(2)–C(B)	92.9(3)
–C(11)	90.0(3)	–C(22)	96.0(3)
–C(12)	91.6(3)		

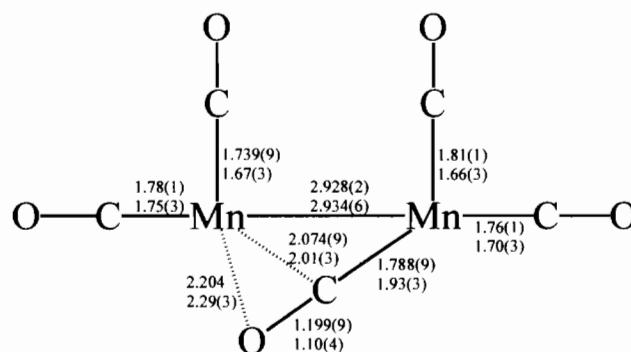


Fig. 4. Structural parameters for the carbonyl ligands in $[\text{Mn}_2(\text{L-L})_2(\text{CO})_5]$; L-L = dcpm, upper values and dpmm lower values.

Table 4
Mn–Mn bond lengths for selected dimanganese carbonyl compounds

Compound	$d(\text{Mn}–\text{Mn})$ (Å)	Reference
$[\text{Mn}_2(\text{CO})_{10}]$	2.904(1)	[15]
$[\text{Mn}_2(\text{dcpm})(\text{CO})_8]$ (1)	2.976(2)	this work
$[\text{Mn}_2(\text{dcpm})_2(\text{CO})_6]$ (2)	3.025(2)	this work
$[\text{Mn}_2(\text{dppm})_2(\text{CO})_6]$	3.010(3)	[22]
$[\text{Mn}_2(\text{dcpm})_2(\text{CO})_5]$ (3)	2.928(2)	this work
$[\text{Mn}_2(\text{dppm})_2(\text{CO})_5]$	2.934(6)	[11]
$[\text{Mn}_2(\text{PMe}_2\text{Ph})(\text{CO})_9]$	2.904	[16]
$[\text{Mn}_2(\text{PMePh}_2)_2(\text{CO})_8]$	2.90	[17]
$[\text{Mn}_2(\text{PEt}_3)_2(\text{CO})_8]$	2.913(4)	[18]

the Mn(2)–O(B) distance of 2.204(9) Å in **3** is slightly shorter than the distance of 2.29(3) Å reported for the dpmm analogue.

Table 5
Carbonyl stretching frequencies for selected dimanganese carbonyl compounds

Compound	$\bar{\nu}(\text{CO})$ (cm^{-1})	Reference
$[\text{Mn}_2(\text{dcpm})(\text{CO})_8]$ (1)	2048(s), 1981(s), 1955(s), 1934(m), 1907(m)	^a
$[\text{Mn}_2(\text{dmpm})(\text{CO})_8]$	2054(m), 1984(s), 1961(s), 1937(m), 1912(m)	[12]
$[\text{Mn}_2(\text{dppm})(\text{CO})_8]$	2060(s), 2000(m), 1997(s), 1952(m), 1925(s)	[11]
$[\text{Mn}_2(\text{dcpm})_2(\text{CO})_6]$ (2)	1896(s), 1882(vs), 1837(m)	^a
$[\text{Mn}_2(\text{dmpm})_2(\text{CO})_6]$	1980(m), 1906(s), 1894(s), 1850(m)	[12]
$[\text{Mn}_2(\text{dppm})_2(\text{CO})_6]$	1987(vw), 1923(sh), 1912(s), 1866(m)	[11]
$[\text{Mn}_2(\text{dcpm})_2(\text{CO})_5]$ (3)	1917(m), 1875(s), 1837(m), 1810(m), 1637(m)	^a
$[\text{Mn}_2(\text{dmpm})_2(\text{CO})_5]$	1930(m), 1895(s), 1852(s), 1827(m), 1640(m)	[12]
$[\text{Mn}_2(\text{dppm})_2(\text{CO})_5]$	1940(m), 1902(s), 1862(s), 1832(m), 1648(m)	[11]

^aThis work; IR spectra recorded in CH_2Cl_2 solution.

The other structural feature of note for complexes **1**, **2** and **3** concerns the manganese–manganese bond distances. These are collected in Table 4 along with the Mn–Mn distances for some related dimanganese carbonyl compounds. It can be seen that successive substitution of dcpm into the coordination sphere of $\text{Mn}_2(\text{CO})_{10}$ leads to an elongation of the Mn–Mn distance in **1** and **2**. However, the metal–metal bond contracts from 3.025(2) Å in the hexacarbonyl **2** to 2.928(2) Å in the pentacarbonyl **3**.

2.2. Spectroscopic studies

The IR bands attributable to the carbonyl ligands of **1**, **2** and **3** are listed in Table 5 along with those reported for the dppm and dmpm analogues. It can be seen that the vibrational frequencies of the dcpm complexes obtained in this study are consistently lower than those reported for the dmpm complexes implying a greater basicity for the cyclohexyl ligand over its methyl counterpart. This is not surprising given the known higher basicity of $\text{P}(c\text{-C}_6\text{H}_{11})_3$ over PMe_3 [20]. The semi-bridging carbonyl ligand in **3** is observed in the solution IR spectrum at 1637 cm^{-1} , a slightly lower frequency than the 1640 cm^{-1} reported for $[\text{Mn}_2(\text{dmpm})_2(\text{CO})_5]$ and significantly lower than the 1648 cm^{-1} value reported for $[\text{Mn}_2(\text{dppm})_2(\text{CO})_5]$.

The lack of facile inversion about the phosphorus atoms in the parent dcpm ligand results in all eleven protons and six carbon atoms of the cyclohexyl ring being non-equivalent. Hence the aliphatic region of the ^1H and ^{13}C NMR spectra of derivatives of dcpm tend to be of little use. However, the ^{31}P NMR spectra and the carbonyl region of the ^{13}C NMR spectra of complexes **1**, **2** and **3** are highly informative. The equivalence of the phosphorus atoms within **1** and **2** are evidenced by a single ^{31}P resonance. In the pentacarbonyl **3** a well-resolved AA'BB' pattern is observed in the ^{31}P NMR spectrum at 25 °C. A similar AA'BB' pattern is observed in the room temperature ^{31}P NMR spectrum of both $[\text{Mn}_2(\text{dppm})_2(\text{CO})_5]$ and $[\text{Mn}_2(\text{dppm})_2(\text{CO})_5]$.

The significance of the lack of exchange of inequivalent phosphorus atoms in $[\text{Mn}_2(\text{dppm})_2(\text{CO})_5]$ was first recognized by Caulton et al. [11d]. A subsequent study utilizing ^{13}C enriched material showed that the molecule exhibits a highly specific, localized fluxionality of the carbonyl ligands. This process involves a concerted wagging motion leading to exchange of the semi-bridging carbonyl ligand with one of the terminal sites. This generates a virtual mirror plane for the molecule along the Mn–Mn axis but does not lead to exchange of the non-equivalent metal atoms. The ^{13}C NMR spectrum of the carbonyl region of $[\text{Mn}_2(\text{dcpm})_2(\text{CO})_5]$ (**3**) at 25 °C shows a sharp triplet at $\delta 229.0\text{ ppm}$ ($J=30.1\text{ Hz}$) and two broad features centered at $\delta 222.8$ and 230.1 ppm . This pattern is similar to that reported by Caulton and Marsella [11c] for the dppm complex and implies that a similar fluxional process is occurring. It is interesting to note that the ^{13}C NMR spectrum of $[\text{Mn}_2(\text{dcpm})_2(\text{CO})_6]$ (**2**) shows two well resolved triplets at $\delta 231.7$ and 242.1 ppm in the ratio of 2:4 consistent with a static structure. This contrasts with the facile,

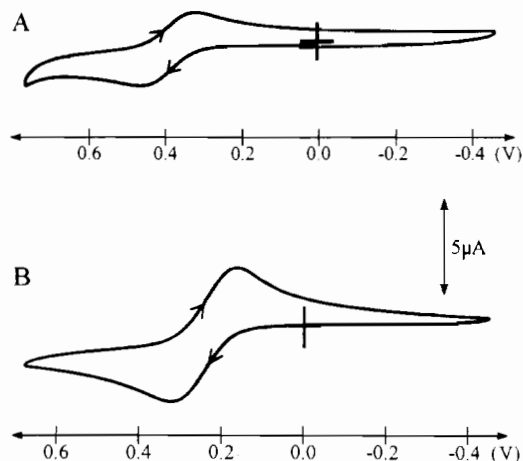


Fig. 5. Cyclic voltammograms for $[\text{Mn}_2(\text{dppm})_2(\text{CO})_6]$ (A) and $[\text{Mn}_2(\text{dcpm})_2(\text{CO})_6]$ (B) in CH_2Cl_2 solution; 0.2 M $(\text{Bu}_4\text{N})(\text{PF}_6)$; Pt bead working electrode; Ag/AgCl quasi-reference electrode and a scan rate of 100 mV s^{-1} .

Table 6
Crystal data and data collection parameters

	1	2	3
Formula	Mn ₂ P ₂ O ₈ C ₃₃ H ₄₆	Mn ₂ P ₄ O ₆ C ₆₈ H ₁₂₀	Mn ₂ P ₄ O ₅ C ₅₅ H ₉₂
Formula weight	742.55	1267.48	1067.12
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	13.097(1)	20.714(5)	11.0309(9)
<i>b</i> (Å)	11.6635(9)	15.856(2)	12.319(2)
<i>c</i> (Å)	23.501(2)	20.910(5)	21.518(2)
α (°)	90	90	83.361(9)
β (°)	101.035(7)	94.34(2)	76.293(7)
γ (°)	90	90	85.646(9)
<i>V</i> (Å ³)	3523.7(9)	6847(4)	2818.1(8)
<i>Z</i>	4	4	2
<i>D</i> _{calc} (g cm ⁻³)	1.400	1.229	1.257
Crystal dimensions (mm)	0.25 × 0.17 × 0.10	0.50 × 0.47 × 0.31	0.16 × 0.15 × 0.14
Temperature (K)	293	293	293
Radiation (wavelength Å)	Cu K α (1.54184)	Mo K α (0.71073)	Cu K α (1.54184)
Monochromator	none	graphite	none
Linear absorption coefficient (cm ⁻¹)	71.31	4.92	50.94
Absorption correction applied	empirical ^a	empirical ^a	empirical ^a
Transmission factors: min., max.	0.50, 1.00	0.65, 1.00	0.65, 1.00
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Scan method	ω -2 θ	ω -2 θ	ω -2 θ
<i>h</i> , <i>k</i> , <i>l</i> limits	-14 to 14, 0 to 12, 0 to 15	0 to 22, 0 to 17, -22 to 22	-11 to 11, -13 to 13, 0 to 23
2 θ Range (°)	4.00–115.00	4.00–45.00	4.00–115.00
Scan width (°)	-0.34 + 0.15 tan(θ)	-0.59 + 0.35 tan(θ)	1.27 + 0.15 tan(θ)
Take-off angle (°)	6.00	2.95	6.00
Programs used	Enraf-Nonius MolEN	Enraf-Nonius MolEN	Enraf-Nonius MolEN
<i>F</i> (000)	1552.0	2744.0	1144.0
<i>p</i> -Factor used in weighting	0.040	0.040	0.040
Data collected	5115	4683	7632
Unique data	5115	4683	7632
Data with <i>I</i> > 3.0 σ (<i>I</i>)	3071	2800	3412
No. variables	406	331	595
Largest shift/e.s.d. in final cycle	0.00	0.01	0.01
<i>R</i>	0.051	0.051	0.047
<i>R</i> _w	0.062	0.065	0.056
Goodness of fit	1.508	1.805	1.324

^aRef. [21].

global migration of carbonyl ligands observed for [Mn₂(dppm)₂(CO)₆]. The stereochemical non-rigidity of [Mn₂(dppm)₂(CO)₆] compared to [Mn₂(dcpm)₂(CO)₆] (2) and parent Mn₂(CO)₁₀ clearly must have an electronic and not a steric rationale.

2.3. Electrochemical studies

As a further probe of the influence of the dcpm ligand on the chemistry of di-metal centers, we have compared the electrochemical behavior of the complexes [Mn₂(dppm)₂(CO)₆] and [Mn₂(dcpm)₂(CO)₆] (2) using cyclic voltammetric methods. Both complexes show an accessible one-electron oxidation wave in CH₂Cl₂ solvent using 0.2 M[(Bu₄N)(PF₆)] as supporting electrolyte (Fig. 5). Both of the waves are close to being reversible on the electrochemical time scale, and appear at +0.38 V (versus an Ag/AgCl quasi-reference electrode at a Pt bead working electrode) for the dppm complex and at +0.25 V for the dcpm analogue. Hence, it can be

seen that the dcpm ligands lead to an increase in the ease of oxidation of 130 mV in this particular system.

3. Experimental

3.1. Preparation of [Mn₂(CO)₈(dcpm)] (1)

A mixture of [Mn₂(CO)₁₀] (0.24 g, 0.62 mmol) and dcpm (0.25 g, 0.62 mmol) in 20 ml of cyclohexane was refluxed for 12 h. The solution was allowed to cool to room temperature before being evaporated to dryness in vacuo. The resulting material was purified by carefully layering hexane over a concentrated solution of the crude solid in chloroform. Yield 0.10 g (0.13 mmol, 22% based on [Mn₂(CO)₁₀]. ³¹P NMR (C₆D₆, 22 °C, ppm): δ 64.3 (br. singlet). ¹³C NMR (C₆D₆, 22 °C, ppm): δ 220.5 (br. singlet, 4CO), 223.2 (br. singlet, 2CO), 230.5 (br. singlet, 2CO).

3.2. Preparation of $[\text{Mn}_2(\text{CO})_6(\text{dcpm})_2]$ (2)

A mixture of $[\text{Mn}_2(\text{CO})_{10}]$ (2.02 g, 5.18 mmol) and dcpm (4.50 g, 11.0 mmol) in 25 ml of cyclohexane was refluxed for 18 h. The solution was allowed to cool to room temperature before the solvent was removed in vacuo. The resulting crude solid was washed with about 15 ml of hot hexane. The bright orange solid that results was dried again under vacuum to give essentially pure **2**. Recrystallization by layering a saturated chloroform solution with hexane produced crystals of X-ray quality. ^{31}P NMR (C_6D_6 , 22 °C, ppm): δ 71.5 (singlet). ^{13}C NMR (C_6D_6 , 22 °C, ppm): δ 26.3 (br. singlet, cyclohexyl), 27.8 (br. singlet, cyclohexyl), 30.3 (br. singlet, cyclohexyl), 41.2 (br. singlet, methylene), 231.7 (triplet, $J=10.4$ Hz, 2 axial carbonyl), 242.1 (triplet, $J=10.15$ Hz, 4 equatorial carbonyl).

3.3. Preparation of $[\text{Mn}_2(\mu\text{-CO})(\text{CO})_4(\text{dcpm})_2]$ (3)

A solution of 0.3 g of $[\text{Mn}_2(\text{CO})_6(\text{dcpm})_2]$ (**2**) (0.3 mmol) in 5 ml of benzene was placed in a quartz tube (10 mm diameter) fitted with a nitrogen adapter. A partial vacuum was applied to the solution prior to its exposure to broadband radiation from a mercury arc lamp for 5 h, periodically purging the solution with nitrogen and reestablishing a partial vacuum. After the solution was allowed to cool, the solvent was removed under vacuum and the crude solid was washed with small portions of pentane. The compound $[\text{Mn}_2(\mu\text{-CO})(\text{CO})_4(\text{dcpm})_2]$ (**3**) is formed in approximately 70% yield. Although the compound is difficult to purify, orange crystals suitable for X-ray analysis were obtained by recrystallization from benzene. ^{31}P NMR (C_6D_6 , 22 °C, ppm): two resonances at δ 67.7 and 81.4 forming an AA'BB' pattern. ^{13}C NMR (C_6D_6 , 22 °C, ppm): δ 26–31 (br. multiplets, cyclohexyl), δ 40.8 (triplet, $J=10.3$ Hz, methylene), δ 222.8 (br. singlet, terminal carbonyl).

4. Crystallographic studies

Details of the crystallographic studies and crystal data are contained in Table 6. For full experimental details of the crystallographic study see Section 5.

5. Supplementary material

Full listings of bond distances and angles and observed and calculated structure factors and experimental details of the crystallographic studies are available from the authors on request.

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