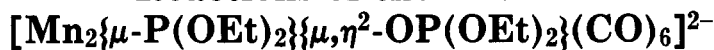


# Redox-Induced P-O and Mn-Mn Bond Cleavages at Dimanganese Carbonyl Centers. Synthesis and Oxidation Reactions of the Dianion



Xiang-Yang Liu, Victor Riera,\* and Miguel A. Ruiz

Departamento de Química Organometálica, Universidad de Oviedo, E-33071 Oviedo, Spain

Maurizio Lanfranchi, Antonio Tiripicchio, and Marisa Tiripicchio-Camellini

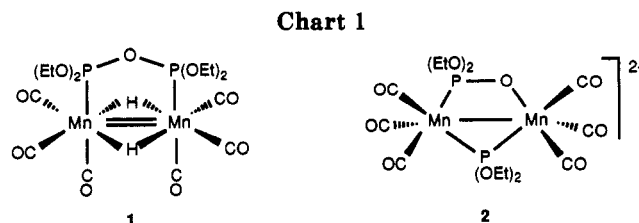
Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffraattometrica del CNR, Università di Parma, Viale delle Scienze 78, I-43100 Parma, Italy

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Chemical reduction of the unsaturated dihydride  $[\text{Mn}_2(\mu\text{-H})_2(\text{CO})_6\{\mu\text{-(EtO)}_2\text{POP}(\text{OEt})_2\}]$  with several reagents (Na-Hg, K, etc.) promotes dihydrogen elimination and an intramolecular P-O bond oxidative addition of the diphosphite ligand, yielding  $[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu,\eta^2\text{-OP}(\text{OEt})_2\}(\text{CO})_6]^{2-}$  (**2**). Chemical oxidation of **2** with 2 equiv of  $[\text{FeCp}_2]\text{PF}_6$  in tetrahydrofuran at  $-80^\circ\text{C}$  results in metal-metal bond cleavage and formation of thermally unstable species, possibly incorporating two tetrahydrofuran molecules. Thermal decomposition of the latter at room temperature yields  $[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu,\eta^2\text{-OP}(\text{OEt})_2\}(\text{CO})_6]$  or, if a phosphine L is present,  $[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu,\eta^2\text{-OP}(\text{OEt})_2\}(\text{CO})_7(\text{L})]$ . If a diphosphine  $\text{L}_2$  is used during oxidation ( $\text{L}_2 = \text{Me}_2\text{PCH}_2\text{PMe}_2$ ,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), two isomers formulated as  $[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu,\eta^2\text{-OP}(\text{OEt})_2\}(\text{CO})_6(\text{L}_2)]$  and  $[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu,\eta^2\text{-OP}(\text{OEt})_2\}(\text{CO})_6(\mu\text{-L}_2)]$  are obtained, but only the latter is isolated when  $\text{L}_2 = (\text{EtO})_2\text{POP}(\text{OEt})_2$ . A possible reaction pathway for the above reactions is proposed on the basis of the compounds isolated and of the detected intermediates. The structures of the new complexes are discussed on the basis of IR and NMR data as well as of the X-ray crystal structures of  $[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu,\eta^2\text{-OP}(\text{OEt})_2\}(\text{CO})_7(\text{PPh}_3)]$  (**4a**) and  $[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu,\eta^2\text{-OP}(\text{OEt})_2\}(\text{CO})_6(\text{Me}_2\text{PCH}_2\text{PMe}_2)]$  (**6a**). Crystals of **4a** are triclinic, space group  $P\bar{1}$  with  $Z = 2$  in a unit cell of dimensions  $a = 21.127(8)$  Å,  $b = 10.503(5)$  Å,  $c = 10.099(6)$  Å,  $\alpha = 65.01(2)^\circ$ ,  $\beta = 73.45(2)^\circ$ , and  $\gamma = 76.05(2)^\circ$ . The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 3711 observed reflections to  $R$  and  $R_w$  values of 0.0425 and 0.0560, respectively. In the molecule the two manganese atoms, displaying an octahedral coordination, are bridged through the P atom by the ethoxyphosphido group and through the P and O atoms by the phosphonate group. The coordinations around the manganese atoms are completed by seven terminal carbonyl ligands and a triphenylphosphine ligand, which is *trans* to the phosphido group and *cis* to the oxygen-donor atom of the phosphonate ligand. Crystals of **6a** are monoclinic, space group  $P2_1/c$  with  $Z = 4$  in a unit cell of dimensions  $a = 14.451(5)$  Å,  $b = 10.469(3)$  Å,  $c = 20.087(7)$  Å, and  $\beta = 91.36(2)^\circ$ . The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 1625 observed reflections to  $R$  and  $R_w$  values of 0.0408 and 0.0542, respectively. The structure of **6a** is very similar to that of **4a**, except that now a diphosphine ligand chelates the manganese atom bearing the O-donor atom of the phosphonate ligand with two P atoms *trans* to the phosphido and carbonyl ligands, respectively.

## Introduction

In our first report on the synthesis and reactivity of the unsaturated dihydride  $[\text{Mn}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-tedip})]$  (**1**) [*tedip* =  $(\text{EtO})_2\text{POP}(\text{OEt})_2$ ] we noted that **1** would react easily with sodium amalgam, presumably yielding the unsaturated dianion  $[\text{Mn}_2(\text{CO})_6(\mu\text{-tedip})]^{2-}$  ( $\text{Mn}=\text{Mn}$ ).<sup>1</sup> However, further investigations, here reported, have revealed that the above reaction yields instead the electron precise dianion  $[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu,\eta^2\text{-OP}(\text{OEt})_2\}(\text{CO})_6]^{2-}$  (**2**), an isomer of the former (Chart 1). The *tedip* ligand has been extensively used by us and others<sup>2</sup> as an efficient instru-



ment in the synthesis of binuclear complexes. Because of the considerable stability of the  $\text{M}-\text{P}(\text{tedip})$  bond, it is usually possible to maintain the nuclearity of  $\text{M}_2(\mu\text{-tedip})$  ( $\text{M} = \text{transition metal}$ ) centers through a great variety of

\* Abstract published in *Advance ACS Abstracts*, February 15, 1994.  
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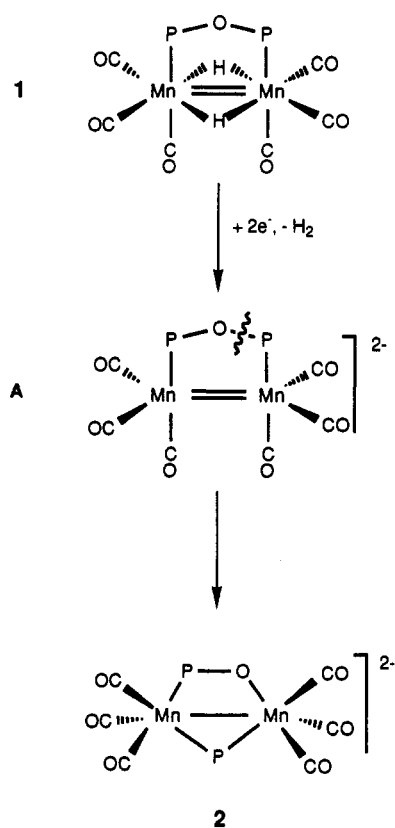
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reactions. For example, we have been able to reduce<sup>3</sup> or halogenate<sup>4</sup> tedip-bridged dimanganese carbonyl species without disruption of the dimetallic unit. The same comment applies to the reactions of compound 1.<sup>5</sup> It was then surprising that a P—O bond cleavage in the tedip ligand had occurred during reduction of dihydride 1. There are several features of interest in this reaction. In the first place, although, for example, backbone P—O hydrolysis in the free tedip ligand is fast and spontaneous in air, the P—O—P linkage becomes quite robust when coordinated to metal centers. In fact, there are only a few precedents of backbone P—O bond cleavages in ligands of the type R<sub>2</sub>POPR<sub>2</sub> (R = alkyl, alkoxy, aryl)<sup>6a-d</sup> and only one of them unambiguously involves the coordinated ligand.<sup>6b</sup> We also note that a related example involving the cage ligand [Pr<sub>2</sub>NPO]<sub>4</sub> coordinated to molybdenum centers has been described recently.<sup>7</sup> On the other hand, the P—O cleavage occurring during the formation of 2 generates an alkoxy substituted phosphido ligand, of which also only a few examples are known.<sup>7-11</sup> These considerations prompted us to further study the reactivity of the anion 2. Its use as a precursor of heterometallic clusters will be reported separately.<sup>12</sup> Of concern in the present study was the possibility of inducing a new P—O bond cleavage by creating an electronic unsaturation in 2. The latter has been accomplished by chemical oxidation of 2 with [FeCp<sub>2</sub>]PF<sub>6</sub>. However, Mn—Mn rather than P—O bond cleavage occurs. Further information about this process, here presented, has been obtained by carrying out the above oxidation reaction in the presence of phosphine ligands.

## Results and Discussion

**Synthesis of Na<sub>2</sub>[Mn<sub>2</sub>{μ-P(OEt)<sub>2</sub>}{μ,η<sup>2</sup>-OP(OEt)<sub>2</sub>}(CO)<sub>6</sub>] (2).** Dihydride 1 reacts readily with sodium amalgam in tetrahydrofuran at room temperature, evolving hydrogen and yielding an orange-brown solution of the dianion 2 (Na<sup>+</sup> salt). The same anion is obtained when other reducing agents are used, such as potassium or an excess of BuLi or Li[HBET<sub>3</sub>], with only minor differences in the IR or <sup>31</sup>P NMR spectra, due to different ion-pair

**Scheme 1. Proposed Pathway for the Formation of Anion 2 [P—O—P = (EtO)<sub>2</sub>POP(OEt)<sub>2</sub>]**



effects.<sup>13</sup> Attempts to isolate compound 2 as a solid were unsuccessful, either by itself or in the presence of bulky cations (for example those from [NEt<sub>4</sub>]Cl or [N(PPh<sub>3</sub>)<sub>2</sub>]Cl). The <sup>31</sup>P NMR spectrum of 2 displays two doublets, one of them ( $\delta = 153.2$  ppm) in the usual region for phosphite ligands coordinated to manganese, and the other at very low field ( $\delta = 419.3$  ppm). The latter is assigned to a diethoxyphosphido ligand bridging the manganese atoms while the former is assigned to a bridging (through O and P atoms) diethyl phosphonate ligand. As will be seen later and elsewhere,<sup>12</sup> this low field/normal field pattern is characteristic of the <sup>31</sup>P NMR spectra of all those derivatives of anion 2 containing the  $\mu$ -P(OEt)<sub>2</sub> and  $\mu, \eta^2$ -OP(OEt)<sub>2</sub> bridging groups. Although the few examples of alkoxyphosphido complexes available usually exhibit highly deshielded <sup>31</sup>P NMR resonances, a closer comparison with our complexes is not possible, as none of them involve manganese atoms. Incidentally, the chemical shift of the phosphido group in 2 seems to be one of the highest reported so far for alkoxyphosphido ligands coordinated to transition metals.<sup>8b</sup>

The formation of anion 2 from dihydride 1 requires both H<sub>2</sub> elimination and P—O bond cleavage steps. The fact that both reducing and/or deprotonating reagents promote this reaction makes reasonable the assumption that H<sub>2</sub> elimination (through reduction or deprotonation) could be the first step (Scheme 1), yielding the anionic intermediate A. In contrast with dihydride 1, intermediate A is not only electronically but also coordinatively unsaturated. Then, it would experience an intramolecular backbone P—O bond oxidative addition so as to relieve these unsaturations. It is interesting to note that the alkoxyphosphido complexes [Fe<sub>2</sub>{μ-P(OEt)<sub>2</sub>}{μ-CH<sub>2</sub>P-

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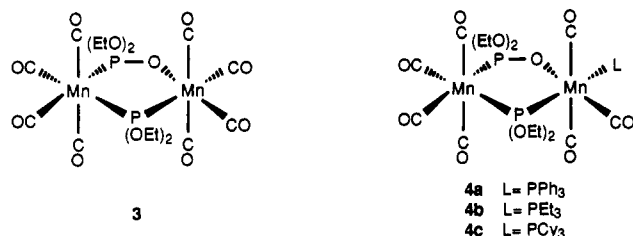
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Chart 2

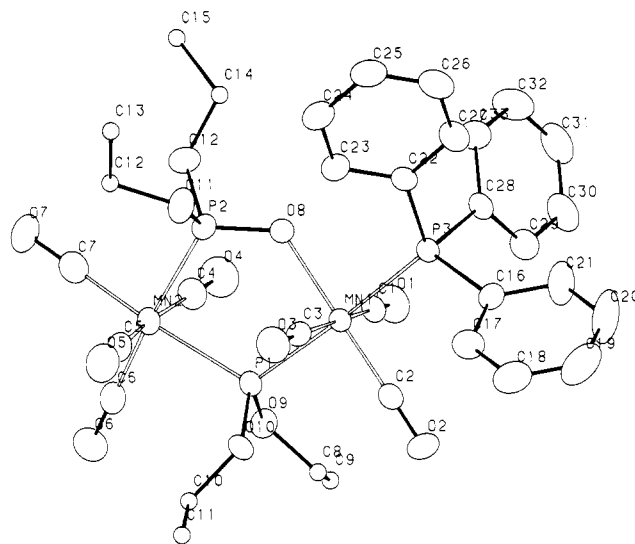


(OEt)<sub>2</sub>(CO)<sub>6</sub>)<sup>9</sup> and [Fe<sub>2</sub>Cp<sub>2</sub>{μ-P(OPh)<sub>2</sub>}{μ-N(Ph)P(OPh)<sub>2</sub>}]<sup>10</sup> were also obtained through related backbone P–C and P–N bond cleavages, respectively. Moreover these cleavages occurred during decarbonylation experiments, a type of reaction which also involves coordinatively and electronically unsaturated intermediates. In summary, we believe that the combination of electronic and coordinative unsaturation in intermediate **A** is the main driving force for the P–O oxidative addition leading to anion **2**.

The above ideas, added to the fact that only five ligands surround each manganese center in anion **2** (ignoring the metal–metal bond), suggested to us that removal of two electrons from **2** would surely generate a highly reactive neutral intermediate (now electronically as well as coordinatively unsaturated), which perhaps would experience a new P–O oxidative addition. The results of these reactions, next described, proved that other processes take place instead.

**Oxidation Reactions of Anion 2.** Compound **2** reacts almost instantaneously in tetrahydrofuran at –80 °C with 2 equiv of [FeCp]<sub>2</sub>PF<sub>6</sub> to give yellow-orange intermediate species, which at room temperature quickly transform into [Mn<sub>2</sub>{μ-P(OEt)<sub>2</sub>}{μ,η<sup>2</sup>-OP(OEt)<sub>2</sub>}(CO)<sub>8</sub>] (**3**). As expected, improved yields of **3** are obtained when the reaction is performed in the presence of CO. On the other hand, when this reaction is carried out in the presence of 1 equiv of phosphine (L), the corresponding heptacarbonylic species [Mn<sub>2</sub>{μ-P(OEt)<sub>2</sub>}{μ,η<sup>2</sup>-OP(OEt)<sub>2</sub>}(CO)<sub>7</sub>(L)] (**4a–c**) are obtained [L = PPh<sub>3</sub> (**4a**); L = PEt<sub>3</sub> (**4b**); L = PCy<sub>3</sub> (**4c**); Cy = C<sub>6</sub>H<sub>11</sub>]. Again, intermediate species can be detected by IR spectroscopy, but discussion about their nature will be made later on.

The structure of **4a** has been determined by an X-ray diffraction study and is shown in Figure 1 together with the atom-numbering scheme. A summary of relevant bond distances and angles is given in Table 3. In the molecule the two manganese atoms, displaying an octahedral coordination, are bridged through the P(1) atom by the ethoxyphosphido group and through the P(2) and O(8) atoms by the phosphonate group. The coordinations around the manganese atoms are completed by seven



**Figure 1.** Molecular structure of **4a**, with the atom-numbering scheme.

terminal carbonyl ligands and the P(3) atom from the triphenylphosphine ligand, which is *trans* to the phosphido group and *cis* to the oxygen-donor atom of the phosphonate ligand. The intermetallic separation, 3.926(2) Å, is clearly nonbonding, as expected after consideration of the ean rule for this molecule. The P(1), P(2), and O(8) bridging atoms together with the metal atoms form a puckered pentaatomic ring. The Mn(2)–P(2) and Mn(1)–O(8) bond lengths, involving the phosphonate ligand, are 2.280(2) and 2.069(4) Å, respectively. The phosphido bridge is asymmetrical as the two Mn–P bond lengths are significantly different [Mn(1)–P(1) = 2.288(2) and Mn(2)–P(1) = 2.350(2) Å] and the Mn(1)–P(1)–Mn(2) angle is 115.7(1)°. The shorter one involves the manganese atom bearing the O-donor atom of the phosphonate ligand, whereas the longer one corresponds to the manganese atom bonded to the P atom of the same ligand. This asymmetry in the phosphido bridge probably compensates for the higher electron donor ability of P relative to O in the phosphonate group. Additionally, *trans* influence effects<sup>14</sup> probably operate in the same direction, as the longer distance is associated with the better π acceptor *trans* ligand (CO *vs* PPh<sub>3</sub>). Finally, it should be noted that the P(2)–O(8) bond length in the phosphonate group, 1.511(5) Å, is slightly shorter than the usual single-bond values (for example, P(2)–O(11) = 1.600(6) or P(2)–O(12) = 1.594(5) Å), an observation which can be interpreted as arising from a significant π-bonding contribution to this P–O linkage.<sup>15</sup>

Spectroscopic data for **4a** are fully consistent with its solid structure. Furthermore, the great similitude in these data for complexes **4a–c** (Tables 1 and 2) indicate that

**Table 1.** IR Data for New Compounds<sup>a</sup>

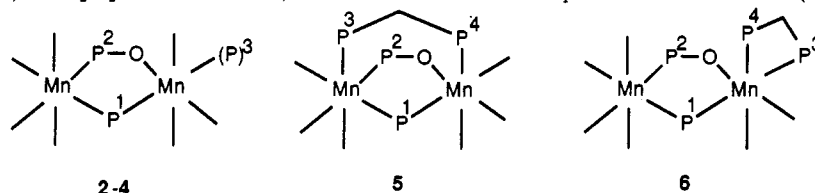
compound	$\nu(\text{CO})$ , cm <sup>-1</sup>
$\text{Na}_2[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu\text{-OP}(\text{OEt})_2\}(\text{CO})_6]$ ( <b>2</b> )	1959 (s), 1901 (vs), 1857 (s), 1834 (s), 1819 (s), 1786 (w, sh) <sup>b</sup>
$[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu\text{-OP}(\text{OEt})_2\}(\text{CO})_8]$ ( <b>3</b> )	2069 (m), 2010 (vs), 1981 (s), 1948 (m)
$[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu\text{-OP}(\text{OEt})_2\}(\text{CO})_7(\text{PPh}_3)]$ ( <b>4a</b> )	2072 (m), 2037 (w), 1999 (s), 1984 (vs), 1972 (s), 1949 (m), 1911 (m)
$[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu\text{-OP}(\text{OEt})_2\}(\text{CO})_7(\text{PEt}_3)]$ ( <b>4b</b> )	2071 (m), 2031 (w), 1998 (s), 1982 (vs), 1971 (s), 1944 (m), 1901 (s)
$[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu\text{-OP}(\text{OEt})_2\}(\text{CO})_7(\text{PCy}_3)]$ ( <b>4c</b> )	2070 (m), 2027 (w), 1997 (s), 1982 (vs), 1969 (s), 1939 (m), 1895 (s)
$[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu\text{-OP}(\text{OEt})_2\}(\text{CO})_6(\mu\text{-dmpm})]$ ( <b>5a</b> )	2027 (m), 2008 (vs), 1953 (s), 1937 (m), 1925 (m), 1903 (m), 1898 (m)
$[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu\text{-OP}(\text{OEt})_2\}(\text{CO})_6(\mu\text{-dppm})]$ ( <b>5b</b> )	2027 (s), 2009 (vs), 1955 (s, sh), 1951 (s), 1934 (s), 1927 (m, sh), 1914 (m), 1908 (m)
$[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu\text{-OP}(\text{OEt})_2\}(\text{CO})_6(\mu\text{-tedip})]$ ( <b>5c</b> )	2039 (s), 2020 (vs), 1969 (s), 1962 (s, sh), 1948 (m, sh), 1943 (s), 1919 (s), 1909 (w, sh)
$[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu\text{-OP}(\text{OEt})_2\}(\text{CO})_6(\text{dmpm})]$ ( <b>6a</b> )	2064 (m), 1998 (s), 1992 (m, sh), 1972 (s, sh), 1967 (vs), 1959 (s), 1936 (m), 1853 (s)
$[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu\text{-OP}(\text{OEt})_2\}(\text{CO})_6(\text{dppm})]$ ( <b>6b</b> )	2065 (s), 1998 (m), 1991 (s), 1986 (s), 1977 (s), 1966 (m, sh), 1960 (vs), 1935 (m), 1864 (m)
$[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu\text{-OP}(\text{OEt})_2\}(\text{CO})_6(\text{tedip})]$ ( <b>6c</b> )	2067 (m), 1993 (s), 1986 (vs), 1977 (s), 1963 (s), 1884 (m, br) <sup>c</sup>

<sup>a</sup> Recorded in petroleum ether solution, unless otherwise stated. <sup>b</sup> In tetrahydrofuran solution. <sup>c</sup> Tentative assignment (see text).

Table 2. <sup>31</sup>P{<sup>1</sup>H} NMR Data for New Compounds<sup>a</sup>

compd	δ, ppm				J <sub>P,P</sub> , Hz					
	P(1)	P(2)	P(3)	P(4)	J <sub>1,2</sub>	J <sub>1,3</sub>	J <sub>1,4</sub>	J <sub>2,3</sub>	J <sub>2,4</sub>	J <sub>3,4</sub>
2 <sup>b</sup>	419.3 (d)	153.2 (d)			60					
3 <sup>c</sup>	344.8 (br)	169.8 (vbr)								
4a	349.3 (d)	169.7 (br)	54.0 (dd)		<10 <sup>d</sup>	50		30		
4b	349.6 (d)	168.8 (br)	46.8 (dd)		<10 <sup>d</sup>	41		27		
4c <sup>c</sup>	352.1 (br)	171.0 (vbr)	59.6 (br)							
5a	372.8 (ddd)	180.9 (d, br)	22.5 (ddd)	24.8 (dd)	7	36	48	78	<10 <sup>d</sup>	28
5b	368.9 (ddd)	169.3 (dd)	40.2 (ddd)	35.0 (dd)	32	32	46	67	<10 <sup>d</sup>	34
5c	362.1 (ddd)	174.8 (d, br)	158.3 (vbr)	151.9 (dd)	9	55	74	111	<10 <sup>d</sup>	27
6a	355.2 (ddd)	173.3 (br)	11.3 (ddd)	-3.6 (dd)	13	90	62	33	<5 <sup>d</sup>	73
6b	353.6 (dd)	168.5 (br)	30.8 (ddd)	6.4 (dd)	<15 <sup>d</sup>	97	50	27	<5 <sup>d</sup>	15

<sup>a</sup> Measured at 121.5 MHz, in CD<sub>2</sub>Cl<sub>2</sub> solution at 213 K, unless otherwise stated. Phosphorus atoms are labeled (P(1) to P(4)) according to the figures shown below.



<sup>b</sup> In tetrahydrofuran; C<sub>6</sub>D<sub>6</sub> solution (9:1), at room temperature. <sup>c</sup> Room temperature. <sup>d</sup> Estimated upper limit, considering the lowest half-width of the experimental lines involved.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 4a

Mn(1)-P(1)	2.288(2)	Mn(2)-P(1)	2.350(2)
Mn(1)-P(3)	2.341(2)	Mn(2)-P(2)	2.280(2)
Mn(1)-O(8)	2.069(4)	Mn(2)-C(4)	1.846(10)
Mn(1)-C(1)	1.856(9)	Mn(2)-C(5)	1.823(10)
Mn(1)-C(2)	1.772(5)	Mn(2)-C(6)	1.841(7)
Mn(1)-C(3)	1.837(8)	Mn(2)-C(7)	1.821(7)
P(1)-O(9)	1.630(5)	O(3)-C(3)	1.144(11)
P(1)-O(10)	1.624(5)	O(4)-C(4)	1.126(13)
P(2)-O(8)	1.511(5)	O(5)-C(5)	1.138(13)
P(2)-O(11)	1.600(6)	O(6)-C(6)	1.128(8)
P(2)-O(12)	1.594(5)	O(7)-C(7)	1.156(9)
P(3)-C(16)	1.835(6)	O(9)-C(8)	1.421(9)
P(3)-C(22)	1.837(6)	O(10)-C(10)	1.438(9)
P(3)-C(28)	1.830(8)	O(11)-C(12)	1.465(12)
O(1)-C(1)	1.136(11)	O(12)-C(14)	1.443(9)
O(2)-C(2)	1.153(6)		
C(2)-Mn(1)-C(3)	90.5(3)	C(6)-Mn(2)-C(7)	93.6(4)
C(1)-Mn(1)-C(3)	174.2(3)	C(4)-Mn(2)-C(5)	171.1(4)
C(1)-Mn(1)-C(2)	91.0(3)	C(5)-Mn(2)-C(7)	94.7(4)
O(8)-Mn(1)-C(3)	91.7(2)	C(5)-Mn(2)-C(6)	94.6(4)
O(8)-Mn(1)-C(2)	177.7(2)	P(2)-Mn(2)-C(6)	173.6(3)
O(8)-Mn(1)-C(1)	86.8(2)	C(4)-Mn(2)-C(7)	92.3(4)
P(3)-Mn(1)-C(3)	92.6(2)	C(4)-Mn(2)-C(6)	90.5(4)
P(3)-Mn(1)-C(2)	91.7(2)	P(2)-Mn(2)-C(7)	90.2(3)
P(3)-Mn(1)-C(1)	93.0(2)	P(2)-Mn(2)-C(5)	90.2(2)
P(3)-Mn(1)-O(8)	88.9(1)	P(2)-Mn(2)-C(4)	84.2(2)
P(1)-Mn(1)-C(3)	86.3(2)	P(1)-Mn(2)-C(6)	89.8(3)
P(1)-Mn(1)-C(2)	91.0(2)	P(1)-Mn(2)-C(5)	86.5(2)
P(1)-Mn(1)-C(1)	88.1(2)	P(1)-Mn(2)-C(4)	86.2(2)
P(1)-Mn(1)-O(8)	88.4(1)	P(1)-Mn(2)-P(2)	86.3(1)
P(1)-Mn(1)-P(3)	177.0(1)	P(1)-Mn(2)-C(7)	176.3(3)
Mn(2)-P(2)-O(8)	117.1(2)	Mn(1)-O(8)-P(2)	126.2(3)
Mn(1)-P(1)-Mn(2)	115.7(1)		

they all are isostructural. In fact all 3 and 4a-c display very similar <sup>31</sup>P chemical shifts for the phosphido and phosphonate groups (ca. 350 ppm and ca. 170 ppm, respectively). As expected, the phosphorus atom of the phosphine group in complexes 4 is strongly coupled with the phosphido phosphorus (P<sup>1</sup> in Table 2) atom (*trans* coupling) and, to a lesser extent, with the phosphonate group (P<sup>2</sup>). Coupling between the ring phosphorus atoms

was not observed, in contrast with that found for 2, but an upper limit of ca. 10 Hz has been estimated by considering the width of the lines in the spectra (Table 2). In any case, the low value for this coupling can be related to the absence of a metal-metal bond in complexes 3 and 4, which thus eliminates one of three-bond pathways connecting P<sup>1</sup> and P<sup>2</sup>. Mutual cancelation of the couplings arising from alternative pathways connecting phosphorus atoms in five-membered ring systems has been observed in dimolybdenum complexes bridged by PPh<sub>2</sub> and CH<sub>2</sub>-PPh<sub>2</sub> ligands.<sup>16</sup>

The IR spectra of complexes 3 and 4 in the carbonyl stretching region can be interpreted as arising from mononuclear *cis*-Mn(CO)<sub>4</sub> and *mer*-Mn(CO)<sub>3</sub> oscillators.<sup>17</sup> This is justified on the grounds that the large separation between the manganese centers is expected to result in minimal interactions between carbonyl groups bonded to different manganese atoms. Moreover, the presence of just four ν<sub>st</sub>(CO) bands in the IR spectrum of 3 indicates that the combined electronic influence of both the phosphido and the phosphonate group is roughly the same for either manganese center. This is only possible if the intrinsic asymmetry of the phosphonate group can be counterbalanced by an asymmetric coordination of the phosphido ligand, in agreement with the structural data of 4a discussed above.

The formation of complexes 3 and 4 requires some decomposition of the initial product resulting after the oxidation of 2, so as to provide the extra CO ligands required. Unexpectedly, the use of larger amounts of phosphine ligand did not suppress efficiently this decomposition. For example, the oxidation of 2 in the presence of 2 equiv of PPh<sub>3</sub> still yielded 4a as a major product, along with other disubstituted complexes which have not been characterized. However, the use of diphosphine ligands proved to be more efficient in this respect, with the added benefit of a higher selectivity.

Compound 2 reacts rapidly in tetrahydrofuran at -80 °C with 2 equiv of [FeCp<sub>2</sub>]PF<sub>6</sub> in the presence of 1 equiv

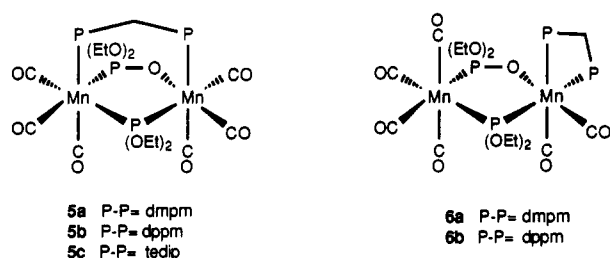
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(17) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, U.K., 1975.

Chart 3

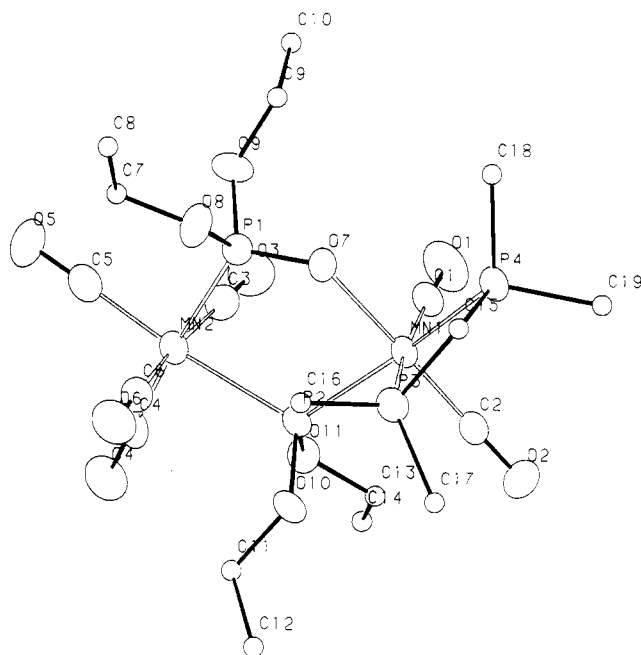


of diphosphine ligand ( $L_2$ ) to give a mixture of two hexacarbonylic species, which have been identified as the diphosphine-bridged complexes  $[Mn_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu,\eta^2\text{-OP}(\text{OEt})_2\}(\text{CO})_6(\mu\text{-}L_2)]$  (**5a-c**) (**a**,  $L_2 = \text{Me}_2\text{PCH}_2\text{PMe}_2$  or dmpm; **b**,  $L_2 = \text{Ph}_2\text{PCH}_2\text{PPh}_2$  or dppm; **c**,  $L_2 = (\text{EtO})_2\text{-POP}(\text{OEt})_2$  or tedip) and the chelate complexes  $[Mn_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu,\eta^2\text{-OP}(\text{OEt})_2\}(\text{CO})_6(L_2)]$  (**6a-b**). In contrast with the reactions previously discussed, no intermediate species are detected by IR monitoring of the corresponding reaction mixtures.

When  $L_2 = \text{tedip}$ , trace amounts of a complex exhibiting an IR spectrum resembling that of the chelate complexes **6a,b** was obtained. Although this species, labeled **6c**, has not been fully characterized, it is supposed to have a structure similar to that of the other chelate complexes. That **6c** is formed in such a low amount is not surprising, given the well-known reluctance of the phosphorus ligands with P-O-P skeletons to act as chelating agents.<sup>2</sup> In fact, only a few examples of the latter are known,<sup>6b,18</sup> and they usually combine large-size metals with bulky groups at the phosphorus atoms, two factors which favor chelate coordination and are absent in our case.<sup>19</sup> On the other hand, the ratio 5:6 (*ca.* 1:2) for the other diphosphine complexes is slightly higher for dmpm, as expected on these grounds.<sup>19</sup> However, this might be accidental, as the observed ratio 5:6 in the above reactions is probably kinetic in origin (see below).

The IR spectra of the diphosphine-bridged species **5** (Table 1) display two strong  $\nu_{\text{st}}(\text{CO})$  bands in the 2050–2000- $\text{cm}^{-1}$  region, as usually found for many  $[Mn_2(\mu\text{-X})(\mu\text{-Y})(\text{CO})_6(\mu\text{-}L_2)]$  complexes prepared in our laboratory (X, Y = H, halide,  $\text{PR}_2$ , SR, etc.). However, all complexes **5** display more than six  $\nu_{\text{st}}(\text{CO})$  bands in petroleum ether solution. This is interpreted as due to the presence of more than one conformational isomer in solution, as the low temperature NMR spectra were only indicative of single species in solution. Puckering of the different rings in these molecules (five- to seven-membered ones) might be responsible for this.

The  $^3\text{P}\{^1\text{H}\}$  NMR spectra of complexes **5** (Table 2) show regular trends and were assigned on the single assumption that only one of the diphosphine phosphorus atoms should exhibit an appreciable coupling with the phosphonate phosphorus atom (in other words,  $J_{24}$  in Table 2 is expected to be very small). The P-P couplings thus resulting are entirely consistent with a stronger coordination of the phosphido ligand to the manganese atom bearing the O-end of the phosphonate ligand, as found in the crystal structure



**Figure 2.** Molecular structure of **6a**, with the atom-numbering scheme.

of **4a**. Thus, under this assumption, the orderings  $J_{14} > J_{13}$  and  $J_{32} > J_{31}$  are expected, as observed for all complexes **5** (actually,  $J_{14} \approx 3/2J_{13}$  and  $J_{32} \approx 2J_{31}$ ; see Table 2).

The spectroscopic data for the chelate complexes **6a** and **6b** indicate that they are isostructural. Besides, we have confirmed the molecular geometry through an X-ray diffraction study on the dmpm complex **6a**. Its structure is depicted in Figure 2 together with the atom-numbering scheme. A summary of relevant bond distances and angles is given in Table 4. The molecule is very similar to the heptacarbonylic complex **4a** except that now a chelating dmpm ligand is coordinated to the manganese atom bearing the O-end of the phosphonate ligand. The P(3) and P(4) atoms of the diphosphine ligand are placed *trans* to one carbonyl ligand and to the P(2) atom of the phosphido group, respectively, and correspondingly the Mn(1)–P(3) bond length, 2.315(3) Å, is longer than Mn(1)–P(4), 2.274(3) Å. Structural features in the MnPOMnP ring are strictly comparable to those found in **4a**. The Mn(1)–Mn(2) separation is 3.913(2) Å, and the Mn(2)–P(1) and Mn(1)–O(7) bond lengths, involving the phosphonate ligand, are 2.279(3) and 2.059(6) Å, respectively. The phosphido bridge is asymmetrical with the Mn(1)–P(2) bond length, 2.252(3) Å, shorter than Mn(2)–P(2), 2.364(3) Å, and the Mn(1)–P(2)–Mn(2) angle is 115.9(1)°. Moreover the P(1)–O(7) bond length in the phosphonate group, 1.495(6) Å, is still shorter than the P(1)–O(8) and P(1)–O(9) ones, 1.600(7) and 1.579(7) Å, respectively.

The spectroscopic data in solution for complexes **6** are consistent with the solid state structure of **6a**. As discussed for complexes **4**, the IR spectra can be roughly interpreted as arising from isolated metal fragments. In the case of complexes **6**, the *cis*-Mn(CO)<sub>4</sub> oscillator is identified by the presence of a medium to strong  $\nu_{\text{st}}(\text{CO})$  band at *ca.* 2065  $\text{cm}^{-1}$ , very close to the values found for **3** or **4**. On the other hand, the *cis*-Mn(CO)<sub>2</sub> group is surely responsible for the bands of *ca.* 1935 and 1860  $\text{cm}^{-1}$ . However, as was the case for complexes **5**, the chelate compounds **6** exhibit more than six  $\nu_{\text{st}}(\text{CO})$  bands in their IR spectra, when recorded in petroleum ether solution. Again, the presence of conformational isomers in solution must be suspected,

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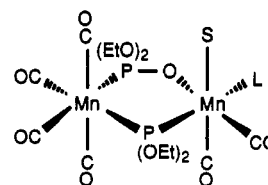
Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 6a

Mn(1)-P(2)	2.252(3)	Mn(2)-P(1)	2.279(3)
Mn(1)-P(3)	2.315(3)	Mn(2)-P(2)	2.364(3)
Mn(1)-P(4)	2.274(3)	Mn(2)-C(3)	1.832(11)
Mn(1)-O(7)	2.059(6)	Mn(2)-C(4)	1.791(12)
Mn(1)-C(1)	1.772(11)	Mn(2)-C(5)	1.809(11)
Mn(1)-C(2)	1.735(10)	Mn(2)-C(6)	1.813(11)
P(1)-O(7)	1.495(6)	O(1)-C(1)	1.153(13)
P(1)-O(8)	1.600(7)	O(2)-C(2)	1.169(13)
P(1)-O(9)	1.579(7)	O(3)-C(3)	1.144(14)
P(2)-O(10)	1.629(7)	O(4)-C(4)	1.162(15)
P(2)-O(11)	1.631(7)	O(5)-C(5)	1.156(14)
P(3)-C(15)	1.805(11)	O(6)-C(6)	1.137(14)
P(3)-C(16)	1.792(12)	O(8)-C(7)	1.402(14)
P(3)-C(17)	1.798(11)	O(9)-C(9)	1.407(15)
P(4)-C(15)	1.816(11)	O(10)-C(11)	1.452(12)
P(4)-C(18)	1.801(11)	O(11)-C(13)	1.422(13)
P(4)-C(19)	1.812(11)		
C(1)-Mn(1)-C(2)	90.6(5)	C(5)-Mn(2)-C(6)	93.0(5)
O(7)-Mn(1)-C(2)	173.8(4)	C(3)-Mn(2)-C(6)	173.7(5)
O(7)-Mn(1)-C(1)	95.1(4)	C(4)-Mn(2)-C(5)	94.3(5)
P(4)-Mn(1)-C(2)	92.6(4)	C(4)-Mn(2)-C(6)	93.0(5)
P(4)-Mn(1)-C(1)	96.6(4)	C(3)-Mn(2)-C(5)	92.5(5)
P(4)-Mn(1)-O(7)	84.2(2)	C(3)-Mn(2)-C(4)	89.5(5)
P(3)-Mn(1)-C(2)	89.7(4)	P(2)-Mn(2)-C(6)	90.9(4)
P(3)-Mn(1)-C(1)	168.9(4)	P(2)-Mn(2)-C(5)	174.7(4)
P(3)-Mn(1)-O(7)	84.3(2)	P(2)-Mn(2)-C(4)	89.1(4)
P(3)-Mn(1)-P(4)	72.4(1)	P(2)-Mn(2)-C(3)	83.4(4)
P(2)-Mn(1)-C(2)	94.0(4)	P(1)-Mn(2)-C(6)	89.3(4)
P(2)-Mn(1)-C(1)	95.4(4)	P(1)-Mn(2)-C(5)	90.6(4)
P(2)-Mn(1)-O(7)	88.1(2)	P(1)-Mn(2)-C(3)	87.6(4)
P(2)-Mn(1)-P(4)	166.3(1)	P(1)-Mn(2)-C(4)	174.5(4)
P(2)-Mn(1)-P(3)	95.6(1)	P(1)-Mn(2)-P(2)	85.9(1)
Mn(2)-P(1)-O(7)	118.1(3)	Mn(1)-O(7)-P(1)	128.9(4)
Mn(1)-P(2)-Mn(2)	115.9(1)		

as no evidence of more than a single species in each case is obtained from the low temperature NMR spectra. These isomers derive from the presence of a diphosphine phosphorus atom [P(3) in Figure 2] *cis* to the bridging groups and the fact that the latter define a puckered Mn<sub>2</sub>P<sub>2</sub>O ring. As a result, nonequivalent conformations of this ring are possible.

The <sup>31</sup>P NMR spectra of complexes 6 (Table 2) have been assigned under the single assumption used for 5 (here  $J_{24} \approx 0$ ). The alternative assumption based on the usual finding that  $^2J(\text{PP})$  is higher for *trans* than for *cis* relative arrangements about the metal<sup>20</sup> (in our case  $J_{13} > J_{14}$ ) leads to the same results. As was the case for complexes 3-5, coupling between phosphido and phosphonate phosphorus atoms remains very small. Finally, the relative <sup>31</sup>P chemical shifts for the diphosphine ligands in complexes 5 and 6 are consistent with their bridging or chelating nature, respectively. Thus, it is well established that the formation of four-membered rings through chelate coordination of diphosphine ligands brings about a considerable shielding effect on the phosphorus atoms involved.<sup>21</sup> This effect is expected to be much smaller in the considerably less strained bridging diphosphines. Therefore, comparison of the chemical shifts of P<sup>4</sup> in complexes 5 and 6 (same coordination position, but bridging *vs* chelate coordination, Table 2) should yield  $\delta(\text{P}^4)$  (5) >  $\delta(\text{P}^4)$  (6). In fact, this is what we find, the differences being 28.4 and 28.6 ppm for the dmpm and dppm complexes, respectively. This analysis cannot be extended to the chemical shifts of P<sup>3</sup>, as they also

Chart 4



correspond to a distinct coordination position in 5 and 6 (*cis* or *trans* to the phosphido groups, respectively).

**Intermediate Species and Reaction Pathways in the Oxidation of Anion 2.** The oxidation reactions of anion 2 discussed above imply considerable reorganization at the dimanganese center. In all cases, two new ligands are incorporated to the dimetallic center and the Mn-Mn bond is cleaved, so those reactions are obviously complex. In spite of this, some intermediate species are detected by IR spectroscopy, and they provide some ideas about the way these reactions occur. As we have stated previously, intermediate species were detected through IR spectroscopy during the formation of complexes 3 and 4, but not in the case of the diphosphine compounds. All these intermediates are unstable at room temperature and yield the final complexes within less than 1 h, but several experiments, next discussed, indicate a considerable lifetime at low temperature (at least several hours below -30 °C).

The intermediate detected during the formation of compound 4a proved to be easier to handle, so that both its IR and <sup>31</sup>P NMR spectra could be unambiguously identified. The latter (in tetrahydrofuran: C<sub>6</sub>D<sub>6</sub>, 9:1, at -70 °C) exhibits a somewhat broad phosphonate resonance at 175.6 ppm whereas the phosphido group appears as a doublet at 351.7 ppm ( $J_{\text{PP}} = 157$  Hz) and the triphenylphosphine ligand appears as doublet of doublets at 53.8 ppm ( $J_{\text{PP}} = 157$  and 31 Hz). Its IR spectrum exhibits six  $\nu_{\text{st}}(\text{CO})$  bands [2062 (m), 1989 (s), 1972 (s), 1952 (vs), 1922 (m), 1843 (m)]. The above data resemble those of the hexacarbonylic complexes 6, but it is clear from the <sup>31</sup>P spectrum that the precursor of 4a has a single PPh<sub>3</sub> ligand. In addition, the following experimental observations suggest that the referred intermediate contains also a coordinated tetrahydrofuran molecule: (a) the intermediate complex can be regenerated by UV irradiation of 4a at -30 °C for 20 min in tetrahydrofuran; (b) removal of solvent from the latter solution leads to complete disappearance of this intermediate; (c) UV irradiation of 4a at -30 °C in petroleum ether gives a mixture of products, but none of them is the referred intermediate. Therefore, it seems reasonable to formulate the precursor of 4a as [(CO)<sub>4</sub>Mn{ $\mu$ -P(OEt)<sub>2</sub>}{ $\mu, \eta^2$ -OP(OEt)<sub>2</sub>}Mn(CO)<sub>2</sub>(PPh<sub>3</sub>)(S)] (S = tetrahydrofuran), and a similar structure is proposed for the intermediates detected in the formation of compounds 4b,c (Chart 4, L = PPh<sub>3</sub>, PEt<sub>3</sub>, PCy<sub>3</sub>).

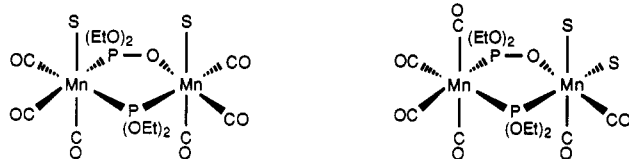
The proposed structure for the precursors of complexes 4 is fully consistent with the spectroscopic data previously discussed and with the final geometry exhibited by complexes 4. However, it is clear that those intermediates are not the primary species formed in the oxidation reactions of anion 2. The formation of the octocarbonylic complex 3 provides some complementary, though incomplete, information in this respect.

The intermediate leading to complex 3 is more unstable than the ones previously discussed. In spite of this, a separate experiment strongly suggests the presence of only

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(21) Garrou, P. E. *Chem. Rev.* 1981, 81, 229.

Chart 5



six carbonyls in this intermediate species: When anion **2** is oxidized with  $[\text{FeCp}_2]\text{PF}_6$ , the reaction mixture stirred for 20 min at  $-75^\circ\text{C}$  (IR at this step showing the presence of **3** and its intermediate), and then 1 equiv of  $\text{PPh}_3$  added, the IR spectrum of the resulting mixture shows the presence of **4a** and its corresponding intermediate (Chart 4). Thus, it seems that both intermediates (those of **3** and **4a**) are hexacarbonylic species, the one of **3** reacting quickly with a molecule of  $\text{PPh}_3$  at low temperature to generate the precursor of **4a**. Therefore, a formulation  $[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu,\eta^2\text{-OP}(\text{OEt})_2\}(\text{CO})_6(\text{S})_2]$  (S = tetrahydrofuran) would be consistent with the above observations. There are related precedents of tetrahydrofuran adducts in manganese(I) or rhenium(I) carbonyl complexes which include, for example, the complexes  $[\text{M}_2(\mu\text{-X})_2(\text{CO})_6(\text{S})_2]$  (M = Mn, X = Cl;<sup>22</sup> M = Re, X = Br<sup>23</sup>). The latter species contain  $\text{M}(\text{CO})_3(\text{S})$  units bridged by halide ligands. This might be the case for the precursor of **3** (Chart 5, left), because strong bands in the expected region are observed in its IR spectrum. However, we also note in the latter spectrum the presence of weak  $\nu_{\text{st}}(\text{CO})$  bands at 2069 and  $1836\text{ cm}^{-1}$ . This could be explained if a second isomer, made from  $\text{Mn}(\text{CO})_4$  and  $\text{Mn}(\text{CO})_2$  units, were also present (Chart 5, right). It is not difficult to imagine that these isomers (and even some other one) could interconvert easily in tetrahydrofuran solution.

Although the present hypothesis has little experimental support, it is not unreasonable. Moreover, it allows a rationalization of the oxidation reactions of dianion **2** previously discussed. Thus, the intermediate species detected during formation of **3** (possibly **A** and **B** in Scheme 2) would be formed initially in all the reactions discussed. Their formation would be preferred over other processes (for example, the formation of a new metal-metal bond, Scheme 2). This is not uncommon, as, in many instances, chemical oxidation of singly metal-metal bonded carbonyl dimers leads to mononuclear cations incorporating solvent molecules or other ligands.<sup>24,25</sup> In our case, however, dimer degradation would be prevented by the presence of the bridging ligands. Upon reaction with CO, either **A** or **B** would yield **3**. On the other hand, either **A** or **B** would rapidly react with phosphine ligands. Initial substitution at the manganese atom bearing the O-end of the phosphonate group seems more likely on steric grounds. That would give intermediate **C** or **D**, respectively. As was discussed for **A** and **B**, it is not unlikely than **C** and **D** can interconvert, but now **C** should be thermodynamically favored on steric grounds. We recall here that when  $\text{L} = \text{PPh}_3$ , intermediate **C** is the unique species detected by  $^{31}\text{P}$  NMR spectroscopy. Replacement of the remaining tetrahydrofuran molecule in **C** by CO, or

the uncoordinated end of the diphosphine ligands, would yield respectively complexes **4** and **6**. Finally, complexes **5** would follow from **D** in an analogous way. As the transformations **C** to **6** and **D** to **5** are intramolecular, they can be relatively fast, and then it is not surprising that no intermediates are detected in the reactions with diphosphines, in contrast with the other ones (that is, **C** and **D** are short-lived species when  $\text{L} = \text{diphosphine}$ ). Moreover, if the final steps in the formation of **5** and **6** are fast, then the observed ratio **5**:**6** (ca. 1:2) would follow from the rates at which **C** and **D** are formed, and therefore would have a kinetic origin. In contrast with this, the diphosphine-bridged complexes **5** seem to be thermodynamically favored over **6**, at least at high temperatures. Thus, when a mixture of **5b** and **6b** was heated at  $65^\circ\text{C}$  in petroleum ether for 2 h, almost complete transformation into **5b** was observed.

In summary, and in spite of the uncertainties discussed above, we can extract several conclusions concerning the chemical oxidation of dianion **2** in tetrahydrofuran: (i) It does not lead to a doubly metal-metal bonded species but rather to non metal-metal bonded species containing two coordinated tetrahydrofuran molecules. (ii) The latter solvated complexes are thermally unstable species which react easily with mono- or bidentate phosphorus-donor ligands at low temperature, whereupon one or two tetrahydrofuran molecules are rapidly displaced respectively. (iii) The above reactions occur selectively at the manganese center bearing the O-donor atom of the phosphonate ligand present in **2**.

## Experimental Section

**General Considerations.** All manipulations and reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were purified according to standard literature procedures<sup>26</sup> and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range  $60\text{--}65^\circ\text{C}$ . Compound **1**,<sup>56</sup>  $[\text{FeCp}_2]\text{PF}_6$ ,<sup>27</sup> and  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ <sup>28</sup> were prepared according to literature procedures. Other phosphorus donor ligands were purchased from the usual commercial suppliers and used as received. Filtrations were carried out using diatomaceous earth. Alumina for column chromatography was deactivated by appropriate addition of water to the commercial material (Aldrich, neutral activity I). Jacketed columns were used, being refrigerated either by tap water or by a closed 2-propanol circuit kept at the desired temperature with a cryostat, as appropriate. All other manipulations were carried out at room temperature unless otherwise indicated. The photochemical reactions on compound **4a** were performed using jacketed Schlenk tubes.  $^1\text{H}$  (300.13-MHz),  $^{31}\text{P}$  (121.50-MHz), and  $^{13}\text{C}$  (75.47-MHz) NMR spectra were measured with a Bruker AC300 spectrometer. Chemical shifts ( $\delta$ ) are given in ppm, relative to internal TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or external 85%  $\text{H}_3\text{PO}_4$  aqueous solution ( $^{31}\text{P}$ ), with positive values for frequencies higher than that of the reference. Coupling constants ( $J$ ) are given in hertz.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were routinely recorded on solutions containing a small amount of tris(acetylacetonato)chromium(III) as a relaxation reagent.

**Preparation of Tetrahydrofuran Solutions of  $\text{Na}_2[\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}\{\mu,\eta^2\text{-OP}(\text{OEt})_2\}(\text{CO})_6]$  (**2**).** In a typical experiment, compound **1** (0.054 g, 0.1 mmol) in tetrahydrofuran (10 mL) was stirred with an excess of 1% sodium amalgam (ca. 1 mL, 5 mmol of Na) for 30 min, affording an orange solution. The latter was filtered using a cannula and was then ready for further use.  $^{31}\text{P}$ -

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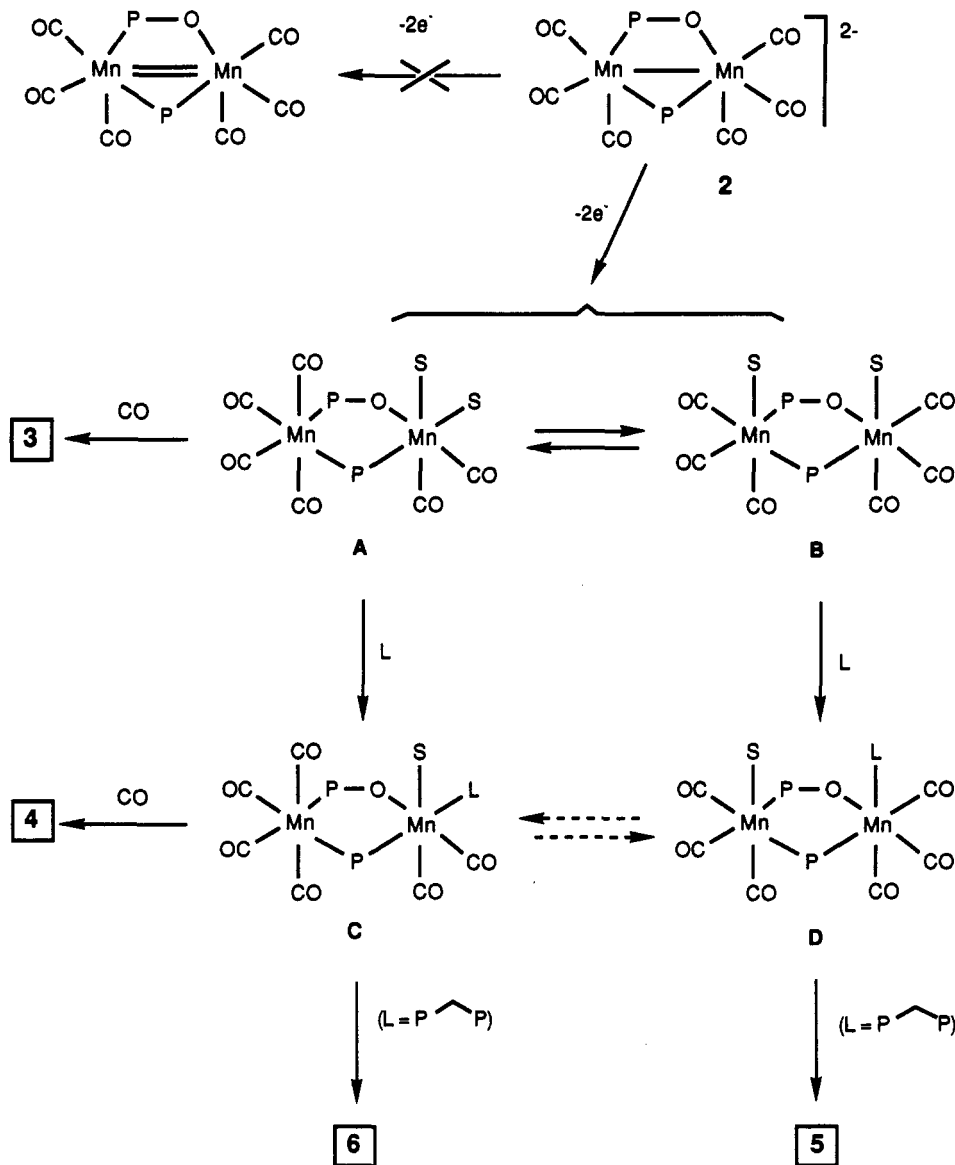
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**Scheme 2. Proposed Pathways for the Oxidation Reactions of Anion 2 in Tetrahydrofuran (S) [P-O = (EtO)<sub>2</sub>PO; μ-P = P(OEt)<sub>2</sub>; L = Phosphine or Diphosphine (P-P) Ligand]**



<sup>1</sup>H} spectroscopy showed the presence of a single species in this solution, and thus a 100% yield in the formation of 2 was assumed.

**Preparation of [Mn<sub>2</sub>{μ-P(OEt)<sub>2</sub>}{μ,η<sup>2</sup>-OP(OEt)<sub>2</sub>}(CO)<sub>8</sub>] (3).** Solid [FeCp<sub>2</sub>][PF<sub>6</sub>] (33 mg, 0.1 mmol) was added to a stirred tetrahydrofuran solution of 2 (0.05 mmol, prepared from 0.027 g of 1) at -80 °C. Carbon monoxide was then gently bubbled through the solution, and the mixture was allowed to reach room temperature. Solvent was then removed in vacuum, and the yellow-orange residue was extracted with petroleum ether (3 × 3 mL) and chromatographed on an alumina column (activity III, 3 × 20 cm). Ferrocene was first eluted using petroleum ether. Elution with dichloromethane-petroleum ether (1:5) gave a yellow fraction which yielded, after removal of solvent in vacuum, compound 3 as a yellow microcrystalline solid (0.023 g, 80%). Anal. Calcd for C<sub>16</sub>H<sub>20</sub>Mn<sub>2</sub>O<sub>13</sub>P<sub>2</sub>: C, 32.45; H, 3.40. Found: C, 31.94; H, 3.45. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 4.12 (q, J<sub>HH</sub> = J<sub>PH</sub> = 7, 4H, OCH<sub>2</sub>), 3.95 (m, 4H, OCH<sub>2</sub>), 1.43, 1.27 (2 × t, J<sub>HH</sub> = 7, 2 × 6H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 218.2, 216.2, 214.1, 210.7 (4 × m, br, Mn-CO), 64.8 (d, J<sub>PC</sub> = 12, OCH<sub>2</sub>), 60.0 (d, J<sub>PC</sub> = 9, OCH<sub>2</sub>), 16.2 (d, J<sub>PC</sub> = 6, Me), 16.0 (d, J<sub>PC</sub> = 6, Me).

**Preparation of [Mn<sub>2</sub>{μ-P(OEt)<sub>2</sub>}{μ,η<sup>2</sup>-OP(OEt)<sub>2</sub>}(CO)<sub>7</sub>(PPh<sub>3</sub>)] (4a).** Solid [FeCp<sub>2</sub>][PF<sub>6</sub>] (0.066 g, 0.2 mmol) was added to a stirred tetrahydrofuran solution containing 0.1 mmol of 2 (prepared from 0.054 g of 1) and PPh<sub>3</sub> (0.026 g, 0.1 mmol) at -80 °C. The solution was then allowed to reach room temperature

and further stirred for 1 h. Solvent was then removed in vacuum, and the yellow-orange residue was extracted with petroleum ether (5 × 3 mL) and chromatographed on an alumina column (activity III, 3 × 20 cm). Ferrocene was first eluted using petroleum ether. Elution with dichloromethane-petroleum ether (1:4) gave a yellow fraction which yielded, after removal of solvent in vacuum, compound 4a as a yellow microcrystalline solid (0.050 g, 63%). The crystals used in the X-ray study were grown from a petroleum ether solution at -20 °C. Anal. Calcd for C<sub>33</sub>H<sub>35</sub>Mn<sub>2</sub>O<sub>12</sub>P<sub>3</sub>: C, 47.96; H, 4.27. Found: C, 48.30; H, 4.25. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.64-7.38 (m, 15H, Ph), 4.10, 3.60 (2 × m, 2 × 4H, OCH<sub>2</sub>), 1.38, 1.12 (2 × t, J<sub>HH</sub> = 7, 2 × 6H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 218 K): δ 222.4 (m, br, Mn-CO) 217.1 (m, br, 2 × Mn-CO), 214.7 (t, J<sub>PC</sub> = 18, 2 × Mn-CO), 212.0 (m, br, 2 × Mn-CO), 63.6 (d, J<sub>PC</sub> = 10, 2 × OCH<sub>2</sub>), 59.4 (d, J<sub>PC</sub> = 6, 2 × OCH<sub>2</sub>), 16.5 (s, Me).

**Preparation of [Mn<sub>2</sub>{μ-P(OEt)<sub>2</sub>}{μ,η<sup>2</sup>-OP(OEt)<sub>2</sub>}(CO)<sub>7</sub>(PEt<sub>3</sub>)] (4b).** The procedure is completely analogous to that described for 4a, except that 15 μL of PEt<sub>3</sub> (ca. 0.1 mmol) was used. Complex 4b was eluted from the chromatography column using dichloromethane-petroleum ether (1:5). Removal of solvent under vacuum yielded pure (by <sup>31</sup>P spectroscopy) complex 4b as an oily yellow residue (ca. 0.040 g). Attempts to crystallize this highly soluble substance always yielded oily materials. Thus, satisfactory elemental microanalysis could not be obtained. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 4.22, 3.83 (2 × m, 2 × 4H, OCH<sub>2</sub>), 1.57 (q, J<sub>HH</sub>



Table 5. Experimental Data for the X-ray Diffraction Studies

	4a	6a
mol formula	C <sub>33</sub> H <sub>35</sub> Mn <sub>2</sub> O <sub>12</sub> P <sub>3</sub>	C <sub>19</sub> H <sub>34</sub> Mn <sub>2</sub> O <sub>11</sub> P <sub>4</sub>
mol wt	826.43	672.24
cryst syst	triclinic	monoclinic
space group	P $\bar{1}$	P2 <sub>1</sub> /c
radiatn ( $\lambda$ , Å)	graphite monochromated Mo K $\alpha$ (0.710 73)	
a, Å	21.127(8)	14.451(5)
b, Å	10.503(5)	10.469(3)
c, Å	10.099(6)	20.087(7)
$\alpha$ , deg	65.01(2)	
$\beta$ , deg	73.45(2)	91.36(2)
$\gamma$ , deg	76.05(2)	
V, Å <sup>3</sup>	1928(2)	3038(2)
Z	2	4
D <sub>calcd</sub> , g cm <sup>-3</sup>	1.424	1.470
F(000)	848	1384
cryst dimens, mm	0.20 × 0.25 × 0.30	0.25 × 0.28 × 0.35
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	8.36	10.90
2 $\theta$ range, deg	6–50	6–48
reflectns measd	$\pm h, \pm k, l$	$\pm h, k, l$
total no. of unique data	6809	4791
no. of unique obsd data	3711 [ $I > 2\sigma(I)$ ]	1625 [ $I > 2\sigma(I)$ ]
R	0.0425	0.0408
R <sub>w</sub>	0.0560	0.0542

=  $J_{PH} = 7.5$ , 6 H, PCH<sub>2</sub>), 1.32, 1.23 (2 × t,  $J_{HH} = 7$ , 2 × 6H, OCH<sub>2</sub>CH<sub>3</sub>), 0.98 (dt,  $J_{PH} = 15$ ,  $J_{HH} = 7.5$ , 9H, PCH<sub>2</sub>CH<sub>3</sub>).

**Preparation of [Mn<sub>2</sub>{ $\mu$ -P(OEt)<sub>2</sub>]<sub>2</sub>{ $\mu$ , $\eta^2$ -OP(OEt)<sub>2</sub>(CO)<sub>7</sub>(PCy<sub>3</sub>)] (4c).** The procedure is completely analogous to that described for 4a, except that 0.028 g (0.1 mmol) of PCy<sub>3</sub> was used. Complex 4c was eluted from the chromatography column using dichloromethane–petroleum ether (1:4). Removal of solvent under vacuum yielded complex 4c as a yellow microcrystalline solid (0.060 g, 71%). Anal. Calcd for C<sub>38</sub>H<sub>55</sub>Mn<sub>2</sub>O<sub>12</sub>P<sub>3</sub>: C, 46.93; H, 6.33. Found: C, 46.55; H, 6.20. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.21, 3.88 (2 × m, 2 × 4H, OCH<sub>2</sub>), 2.13–1.28 (complex, 23H, C<sub>6</sub>H<sub>11</sub> and Me).

**Chemical Oxidation of 2 in the Presence of Me<sub>2</sub>PCH<sub>2</sub>PMe<sub>2</sub>.** Solid [FeCp<sub>2</sub>][PF<sub>6</sub>] (0.132 g, 0.4 mmol) and 31  $\mu$ L of Me<sub>2</sub>PCH<sub>2</sub>PMe<sub>2</sub> (dmpm, 0.027 g, 0.2 mmol) were added to a stirred tetrahydrofuran solution containing 0.2 mmol of 2 (prepared from 0.108 g of 1) at –80 °C. The solution was then allowed to reach room temperature and further stirred for 2 h. Solvent was then removed in vacuum, and the yellow-orange residue was extracted with petroleum ether (5 × 3 mL) and chromatographed at –40 °C on an alumina column (activity III, 3 × 20 cm). Ferrocene was first eluted using dichloromethane–petroleum ether (1:8). Elution with dichloromethane–petroleum ether (1:3) gave a yellow fraction which yielded, after removal of solvent in vacuum, compound [Mn<sub>2</sub>{ $\mu$ -P(OEt)<sub>2</sub>]<sub>2</sub>{ $\mu$ , $\eta^2$ -OP(OEt)<sub>2</sub>(CO)<sub>6</sub>(Me<sub>2</sub>PCH<sub>2</sub>PMe<sub>2</sub>)] (6a) as a yellow microcrystalline solid (0.054 g, 40%). Elution with dichloromethane–petroleum ether (2:3) gave another yellow fraction yielding, after similar workup, complex [Mn<sub>2</sub>{ $\mu$ -P(OEt)<sub>2</sub>]<sub>2</sub>{ $\mu$ , $\eta^2$ -OP(OEt)<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -Me<sub>2</sub>PCH<sub>2</sub>PMe<sub>2</sub>)] (5a) as a yellow solid (0.025 g, 19%). The crystals used in the X-ray study of 6a were grown from a petroleum ether solution at –20 °C. Anal. Calcd for C<sub>19</sub>H<sub>34</sub>Mn<sub>2</sub>O<sub>11</sub>P<sub>4</sub>, 5a or 6a: C, 33.95; H, 5.10. Found for 5a: C, 34.30; H, 5.51. Found for 6a: C, 33.52; H, 5.05. Spectroscopic data for 5a: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.33–3.76 (complex 10H, CH<sub>2</sub>), 1.43–1.03 (complex, 24H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 213 K):  $\delta$  223.0, 221.0, 220.0, 218.0 (4 × m, br, Mn–CO), 63.8, 61.4 (2 × s, OCH<sub>2</sub>), 58.5 (d,  $J_{PC} = 10$ , OCH<sub>2</sub>), 27.7 (br, PCH<sub>2</sub>), 20.7 (d,  $J_{PC} = 29$ , PCH<sub>3</sub>), 19.7 (d,  $J_{PC} = 25$ , PCH<sub>3</sub>), 16.7 (d,  $J_{PC} = 31$ , PCH<sub>3</sub>), 16.5, 15.9 (2 × s, OCH<sub>2</sub>CH<sub>3</sub>). Spectroscopic data for 6a: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.65–3.85 (complex, 8H, OCH<sub>2</sub>), 2.45 (m, 2H, PCH<sub>2</sub>), 1.43–1.15 (complex, 24H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 213 K):  $\delta$  229.2, 223.3, 213.8, 211.5 (4 × m, br, 4 × Mn–CO), 218.3 (br, 2 × Mn–CO), 64.0 (d,  $J_{PC} = 9$ , OCH<sub>2</sub>), 63.0 (d,  $J_{PC} = 11$ , OCH<sub>2</sub>), 59.6 (d,  $J_{PC} = 6$ , OCH<sub>2</sub>), 59.3 (d,  $J_{PC} = 8$ , OCH<sub>2</sub>), 43.3 (t, br,  $J_{PC} = 16$ , PCH<sub>2</sub>), 17.0 (d,  $J_{PC} = 5$ , Me), 16.8 (d,  $J_{PC} = 5$ , 2 × Me), 16.7 (d,  $J_{PC} = 6$ , 2 × Me), 15.4 (s, br, Me), 14.3 (dd,  $J_{PC} = 20$ , 2, Me), 11.6 (br, Me).

Table 6. Atomic Coordinates ( $\times 10^4$ ) and Isotropic Thermal Parameters ( $\text{\AA}^2 \times 10^4$ ) for the Non-Hydrogen Atoms of Complex 4a

atom	x/a	y/b	z/c	U
Mn(1)	2909.9(4)	3960.0(9)	1174.8(9)	367(4) <sup>a</sup>
Mn(2)	977.3(4)	4897.0(10)	1397.0(10)	496(4) <sup>a</sup>
P(1)	2055.3(7)	5400.9(17)	52.7(17)	432(7) <sup>a</sup>
P(2)	1489.4(8)	3014.7(18)	3102.8(18)	470(7) <sup>a</sup>
P(3)	3745.5(7)	2399.8(16)	2405.2(15)	365(6) <sup>a</sup>
O(1)	2850(2)	6133(5)	2408(6)	708(27) <sup>a</sup>
O(2)	3895(2)	5334(4)	–1465(5)	595(22) <sup>a</sup>
O(3)	2824(3)	2014(5)	–206(5)	718(27) <sup>a</sup>
O(4)	1092(3)	6490(7)	3130(7)	916(34) <sup>a</sup>
O(5)	1109(3)	3138(7)	–337(6)	892(35) <sup>a</sup>
O(6)	393(3)	7551(6)	–770(7)	959(31) <sup>a</sup>
O(7)	–350(3)	4125(7)	3261(6)	931(33) <sup>a</sup>
O(8)	2206(2)	3052(4)	3059(4)	471(18) <sup>a</sup>
O(9)	1979(2)	7092(4)	–319(5)	552(20) <sup>a</sup>
O(10)	2249(2)	5324(5)	–1591(4)	536(21) <sup>a</sup>
O(11)	1519(2)	1492(5)	3068(5)	665(24) <sup>a</sup>
O(12)	1063(2)	2880(5)	4726(5)	678(23) <sup>a</sup>
C(1)	2881(3)	5287(7)	1961(6)	455(28) <sup>a</sup>
C(2)	3507(3)	4799(6)	–419(7)	409(27) <sup>a</sup>
C(3)	2856(3)	2741(7)	349(6)	465(28) <sup>a</sup>
C(4)	1045(3)	5891(8)	2473(8)	597(35) <sup>a</sup>
C(5)	1049(3)	3824(8)	324(7)	608(35) <sup>a</sup>
C(6)	620(3)	6539(8)	39(9)	666(37) <sup>a</sup>
C(7)	165(4)	4436(8)	2545(8)	688(39) <sup>a</sup>
C(8)	2495(4)	7937(8)	–1213(9)	736(21)
C(9)	2362(6)	9245(11)	–929(12)	1212(34)
C(10)	1853(3)	6037(7)	–2713(7)	617(18)
C(11)	2073(4)	5387(9)	–3817(9)	809(23)
C(12)	905(4)	908(10)	3383(10)	911(25)
C(13A)	1036(8)	–684(19)	4109(25)	936(84)
C(13B)	1107(12)	–322(27)	2949(40)	1232(110)
C(14)	1312(4)	1925(9)	6049(9)	848(23)
C(15)	747(5)	1630(11)	7372(11)	1159(30)
C(16)	4562(3)	2181(6)	1195(7)	450(28) <sup>a</sup>
C(17)	4592(3)	2005(7)	–99(7)	566(32) <sup>a</sup>
C(18)	5184(4)	1751(8)	–1001(8)	732(39) <sup>a</sup>
C(19)	5764(4)	1705(9)	–650(11)	954(53) <sup>a</sup>
C(20)	5751(4)	1875(11)	621(12)	1142(68) <sup>a</sup>
C(21)	5153(3)	2127(9)	1539(9)	823(46) <sup>a</sup>
C(22)	3635(3)	529(6)	3494(6)	399(25) <sup>a</sup>
C(23)	3076(3)	20(7)	3563(7)	527(29) <sup>a</sup>
C(24)	3008(4)	–1390(7)	4346(7)	643(35) <sup>a</sup>
C(25)	3483(4)	–2316(7)	5103(7)	655(35) <sup>a</sup>
C(26)	4040(4)	–1839(7)	5037(7)	671(37) <sup>a</sup>
C(27)	4122(3)	–442(7)	4237(7)	571(33) <sup>a</sup>
C(28)	3928(3)	2944(6)	3740(6)	402(26) <sup>a</sup>
C(29)	4228(3)	4132(7)	3233(8)	581(34) <sup>a</sup>
C(30)	4342(4)	4605(8)	4238(9)	695(42) <sup>a</sup>
C(31)	4153(4)	3903(9)	5714(10)	767(46) <sup>a</sup>
C(32)	3844(4)	2727(10)	6243(9)	835(47) <sup>a</sup>
C(33)	3727(3)	2236(8)	5273(7)	627(35) <sup>a</sup>

<sup>a</sup> Equivalent isotropic U defined as one-third of the trace of the orthogonalized U<sub>ij</sub> tensor.

**Chemical Oxidation of 2 in the Presence of Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>.** The procedure is completely analogous to that described for the previous alkyldiphosphine, except that 0.077 g of Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (0.2 mmol) was used. Elution with dichloromethane–petroleum ether (1:2) gave a yellow fraction which yielded, after removal of solvent in vacuum, compound [Mn<sub>2</sub>{ $\mu$ -P(OEt)<sub>2</sub>]<sub>2</sub>{ $\mu$ , $\eta^2$ -OP(OEt)<sub>2</sub>(CO)<sub>6</sub>(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)] (6b) as a yellow microcrystalline solid (0.064 g, 35%). Elution with dichloromethane–petroleum ether (2:1) gave another yellow fraction yielding, after similar workup, complex [Mn<sub>2</sub>{ $\mu$ -P(OEt)<sub>2</sub>]<sub>2</sub>{ $\mu$ , $\eta^2$ -OP(OEt)<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)] (5b) as a yellow solid (0.028 g, 15%). Anal. Calcd for C<sub>39</sub>H<sub>42</sub>Mn<sub>2</sub>O<sub>11</sub>P<sub>4</sub>, 5b or 6b: C, 50.89; H, 4.60. Found for 5b: C, 50.96; H, 4.79. Found for 6b: C, 51.22; H, 4.92. Spectroscopic data for 5b: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.57–6.88 (m, 20H, Ph), 4.22–3.61 (complex, 9H, CH<sub>2</sub>), 3.06 (q of d,  $J_{PH} = J_{HH} = 14$ ,  $J_{PH} = 6$ , 1H, PCH<sub>2</sub>), 1.42, 1.41, 1.28, 1.25, (4 × t,  $J_{HH} = 7$ , 4 × 3H, Me). Spectroscopic data for 6b: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.91–6.85 (m, 20H, Ph), 4.77–3.41 (complex, 10H, CH<sub>2</sub>), 1.44, 1.15, 1.08, 1.03 (4 × t,  $J_{HH} = 7$ , 4 × 3H, Me).

**Table 7. Atomic Coordinates ( $\times 10^4$ ) and Isotropic Thermal Parameters ( $\text{\AA}^2 \times 10^4$ ) for the Non-Hydrogen Atoms of Complex 6a**

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i>
Mn(1)	2625.6(9)	827.5(13)	5857.3(7)	414(6) <sup>a</sup>
Mn(2)	2321.0(10)	3336.2(15)	7279.3(7)	506(6) <sup>a</sup>
P(1)	3337(2)	1672(3)	7321(1)	486(10) <sup>a</sup>
P(2)	1770(2)	2429(3)	6268(1)	442(10) <sup>a</sup>
P(3)	1710(2)	-802(3)	6258(1)	521(10) <sup>a</sup>
P(4)	3356(2)	-1050(3)	5653(1)	517(10) <sup>a</sup>
O(1)	4007(5)	2473(8)	5251(4)	935(38) <sup>a</sup>
O(2)	1598(5)	707(7)	4599(4)	809(34) <sup>a</sup>
O(3)	3641(6)	4684(7)	6407(4)	858(38) <sup>a</sup>
O(4)	1022(6)	5489(8)	7092(5)	1025(42) <sup>a</sup>
O(5)	3180(6)	4480(8)	8495(4)	889(38) <sup>a</sup>
O(6)	1015(5)	1784(9)	8045(4)	963(40) <sup>a</sup>
O(7)	3288(4)	705(5)	6774(3)	488(24) <sup>a</sup>
O(8)	3297(5)	756(6)	7958(3)	669(28) <sup>a</sup>
O(9)	4336(4)	2279(6)	7374(3)	643(28) <sup>a</sup>
O(10)	706(4)	1918(6)	6292(3)	562(27) <sup>a</sup>
O(11)	1651(4)	3726(5)	5824(3)	546(26) <sup>a</sup>
C(1)	3468(7)	1833(10)	5502(5)	556(43) <sup>a</sup>
C(2)	2012(7)	774(10)	5105(5)	511(40) <sup>a</sup>
C(3)	3133(8)	4156(10)	6738(6)	595(45) <sup>a</sup>
C(4)	1517(8)	4623(12)	7162(6)	736(53) <sup>a</sup>
C(5)	2850(7)	4014(10)	8024(6)	635(47) <sup>a</sup>
C(6)	1508(7)	2392(11)	7746(6)	649(48) <sup>a</sup>
C(7)	3452(8)	1191(11)	8611(6)	919(41)
C(8)	3753(9)	129(12)	9044(6)	1132(47)
C(9)	5134(9)	1527(14)	7301(7)	1120(49)
C(10)	5921(8)	2238(12)	7105(6)	1104(46)
C(11)	-55(7)	2734(10)	6484(5)	739(34)
C(12)	-939(7)	2097(10)	6297(5)	831(38)
C(13)	1427(8)	3675(11)	5132(5)	758(37)
C(14)	1340(9)	5014(12)	4869(6)	1090(46)
C(15)	2563(7)	-2028(11)	6122(6)	816(38)
C(16)	1389(8)	-973(11)	7110(6)	957(42)
C(17)	676(7)	-1319(11)	5821(6)	978(43)
C(18)	4502(7)	-1406(11)	5974(5)	816(36)
C(19)	3369(8)	-1736(12)	4825(5)	918(40)

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Chemical Oxidation of 2 in the Presence of (EtO)<sub>2</sub>POP-(OEt)<sub>2</sub>.** The procedure is completely analogous to that described for the previous diphosphines, except that 50  $\mu$ L of (EtO)<sub>2</sub>POP-(OEt)<sub>2</sub> (0.052 g, 0.2 mmol) was used. Elution with dichloromethane-petroleum ether (1:3) gave a yellow fraction containing trace amounts of a compound possibly related to complex 6a or 6b (see Discussion). Elution with dichloromethane-petroleum ether (2:1) gave another yellow fraction. Removal of solvent from this solution yielded complex [Mn<sub>2</sub>{ $\mu$ -P(OEt)<sub>2</sub>}{ $\mu$ , $\eta^2$ -OP-(OEt)<sub>2</sub>}(CO)<sub>6</sub>{ $\mu$ -(EtO)<sub>2</sub>POP(OEt)<sub>2</sub>}] (5c) as a yellow solid (0.080 g, 51%). Anal. Calcd for C<sub>22</sub>H<sub>40</sub>Mn<sub>2</sub>O<sub>16</sub>P<sub>4</sub>, 5c: C, 33.26; H, 5.08. Found: C, 32.80; H, 5.30. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.35-3.75 (complex, 16H, OCH<sub>2</sub>), 1.38, 1.26, 1.21, 1.15, 1.14, 1.04 (6  $\times$  t,  $J_{\text{HH}}$  = 7, 6  $\times$  3H, Me), 1.06 (t,  $J_{\text{HH}}$  = 7, 6H, Me).

**X-ray Data Collection, Structure Determination, and Refinement for Compounds 4a and 6a.** The crystallographic data for both compounds are summarized in Table 5. Data were collected at room temperature (22  $^{\circ}$ C) on a Philips 1100 PW diffractometer, using graphite-monochromated Mo K $\alpha$  radiation

and the  $\theta/2\theta$  scan type. The reflections for both 4a and 6a were collected with a variable scan speed of 3-12 $^{\circ}$  min<sup>-1</sup> and a scan width from ( $\theta = 0.60$ ) $^{\circ}$  to ( $\theta + 0.60 + 0.346 \tan \theta$ ) $^{\circ}$ . One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed following Lehmann and Larsen.<sup>29</sup> Intensities were corrected for Lorentz and polarization effects. No correction for absorption was applied. Only the observed reflections were used in the structure solutions and refinements.

Both structures were solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic thermal parameters and then with anisotropic thermal parameters for the non-hydrogen atoms, with the exception of the carbons of the ethyl groups (4a), and of the ethyl groups and of the dmpm ligand (6a). The terminal carbon (C (13)) of one of the ethyl groups in 4a was found disordered and distributed in two positions of almost equal occupancy factor. All hydrogen atoms, with the exception of those in the disordered ethyl group, were placed at their geometrically calculated positions (C-H = 0.96  $\text{\AA}$ ) and refined "riding" the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 434 (4a) and 263 (6a) variables; after the last cycles, no parameters shifted by more than 1.27 (4a) and 1.05 (6a) esd. The highest remaining peak in the final difference map was equivalent to about 0.51 (4a) and 0.36 (6a) e/ $\text{\AA}^3$ . In the final cycles of refinement a weighting scheme  $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$  was used; at convergence the *K* and *g* values were 0.741 and 0.0043 (4a) and 0.643 and 0.0093 (6a), respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 30. All calculations were carried out on the GOULD POWERNODE 6040 of the "Centro di Studio per la Strutturistica Diffraattometrica" del CNR, Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.<sup>31</sup> The final atomic coordinates for the non-hydrogen atoms are given in Table 6 (4a) and 7 (6a). The atomic coordinates of the hydrogen atoms are given in Tables SI (4a) and SII (6a), the thermal parameters, in Tables SIII (4a) and SIV (6a).

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**Supplementary Material Available:** Tables of hydrogen atom coordinates (Tables SI and SII), thermal parameters for the non-hydrogen atoms (Tables SIII and SIV), and complete bond distances and angles (Tables SV and SVI) (9 pages). Ordering information is given on any current masthead page.

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