Organometallics **2001,** *20,* 3007−3016

Synthesis and Oxidation Reactions of the Unsaturated Anion $[Mn_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)]^{2-}$[†]

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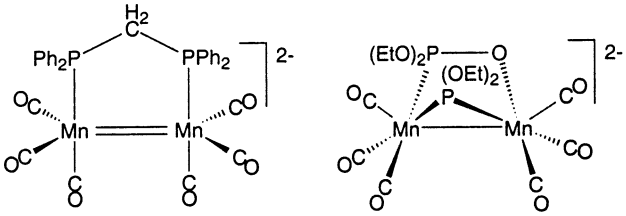
Received February 27, 2001

Chemical reduction of the unsaturated dihydride $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ (dppm = $Ph_2PCH_2PPh_2$) with several reagents (Na−Hg, K, etc.) promotes dihydrogen elimination to yield the deep green anion $[Mn_2(CO)_6(\mu\text{-dppm})]^{2-}$. Oxidation of the latter with $[FeCp_2]PF_6$ (Cp = $\eta^5\text{-}C_5H_5$) gives the CO-bridged species $[Mn_2(\mu\text{-}\eta^1{:}\eta^2\text{-CO})(CO)_6(\mu\text{-dppm})]$ or, if PR_3 is present, the related complexes $[Mn_2(\mu\text{-}\eta^1{:}\eta^2\text{-CO})(CO)_5(PR_3)(\mu\text{-dppm})]$ (R = Ph, OMe). Oxidation of the anion in the presence of nitriles or 1-alkynes gives nitrile or vinylidene-bridged derivatives $[Mn_2(\mu\text{-}\eta^1{:}\eta^2\text{-L})(CO)_6(\mu\text{-dppm})]$ with high yield (L = NCR or CCHR). The complexes having the $(\mu\text{-}\eta^1{:}\eta^2\text{-CO})$ ligand display dynamic behavior in solution and react readily with CO to give the corresponding $[Mn_2(CO)_7L(dppm)]$ (L = CO, PR_3). Diazocompound $CH(SiMe_3)N_2$ also adds readily to $[Mn_2(\mu\text{-}\eta^1{:}\eta^2\text{-CO})(CO)_6(\mu\text{-dppm})]$, but the C−Si bond in the initial product is easily hydrolyzed to yield the diazomethane complex $[Mn_2(\mu\text{-CO})(\mu\text{-}\eta^1{:}\kappa^1\text{-}CH_2N_2)(CO)_6(\mu\text{-dppm})]$. The structure of the new complexes is analyzed in the light of their IR and variable-temperature NMR spectra, and possible reaction pathways for the above oxidation processes are proposed on the basis of the nature of the compounds actually isolated and that of the detected intermediates. The structure of the new compounds $[Mn_2(\mu\text{-}\eta^1{:}\eta^2\text{-CO})(CO)_5\{P(OMe)_3\}(\mu\text{-dppm})]$ and $[Mn_2(CO)_7(PPh_3)(\mu\text{-dppm})]$ has been solved through single-crystal X-ray diffraction studies.

Introduction

Organometallic compounds having multiple metal−metal bonds are species of interest because of the high reactivity they usually display toward a great variety of molecules under mild conditions.[1] Relevant examples of this sort of molecules are the triply bonded cyclopentadienyl dimers $[M_2Cp_2(CO)_4]$ (M = Mo, W; Cp = $\eta^5\text{-}C_5H_5$)[2] or the osmium dihydride $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.[3] Attempts to synthesize new compounds within this class of species by using decarbonylation or other ligand elimination reactions from suitable precursors often fail to give the desired result. In part this is because the primary unsaturated dimetal center being generated is reactive enough so as to activate bonds in the surrounding ligands, thus relieving both coordination and electronic deficiency. For example, we have found previously that removal of CO in the electron precise dimers $[M_2Cp_2(CO)_4(\mu\text{-}L_2)]$ [M = Mo, W; L = $Ph_2PCH_2PPh_2$, dppm; $(EtO)_2POP(OEt)_2$, tedip] can induce either C−H, P−C, or P−O bond cleavages in the cyclopentadienyl or phosphorus-donor ligands, depending on the complex and reaction conditions.[4] This is also the case of the reduction of the unsaturated dihydride $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})]$, which yields the P−O cleavage product $[Mn_2\{\mu\text{-}P(OEt)_2\}\{\mu\text{-}OP(OEt)_2\}(CO)_6]^{2-}$ (Chart 1).[5] By contrast, reduction of the dppm-bridged analogue $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ causes no cleavage in the phosphorus ligand but yields the doubly bonded anion $[Mn_2(CO)_6(\mu\text{-dppm})]^{2-}$ (**1**) (Chart 1).[6] Although previous results by

Chart 1



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[†] Dedicated to Prof. R. Usón on the occasion of his 75th birthday.

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10.1021/om0101590 CCC: $20.00
Publication on Web 06/05/2001

Table 1. IR Data for New Compounds[a]

compound	ν_{st}(CO)/cm^{-1}
$[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$	2031 (s), 2000 (s), 1948 (s), 1920 (vs)
$Na_2[Mn_2(CO)_6(\mu\text{-dppm})]$ (**1**)	1888 (s), 1841 (vs), 1817 (s), 1787 (s)
$[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CO})(CO)_6(\mu\text{-dppm})]$ (**2**)	2034 (vs), 1987 (s), 1961 (s), 1934 (s, sh) 1922 (s), 1709 (w)[b]
$[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CO})(CO)_5(\mu\text{-dppm})(PPh_3)]$ (**3a**)	1997 (s), 1939 (vs), 1919 (s), 1892 (s), 1866 (m), 1665 (w)
$[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CO})(CO)_5(\mu\text{-dppm})\{P(OMe)_3\}]$ (**3b**)	2006 (s), 1948 (vs), 1925 (s), 1897 (s), 1870 (m), 1669 (w)[b]
$[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-NC}^tBu)(CO)_6(\mu\text{-dppm})]$ (**4a**)	2018 (s), 1964 (vs), 1943 (m), 1910 (m), 1902 (m), 1886 (w)
$[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-NCPh})(CO)_6(\mu\text{-dppm})]$ (**4b**)	2020 (vs), 1969 (s), 1946 (m), 1913 (m), 1907 (m), 1891 (w)
$[Mn_2(CO)_7(\mu\text{-dppm})(PPh_3)]$ (**5a**)	2033 (s), 1949 (vs), 1915 (m), 1873 (m)[b]
$[Mn_2(CO)_7(\mu\text{-dppm})\{P(OMe)_3\}]$ (**5b**)	2034 (s), 1950 (vs), 1923 (m), 1896 (m), 1880 (m, sh)[b]
$[Mn_2(\mu\text{-}CH_2N_2)(\mu\text{-CO})(CO)_6(\mu\text{-dppm})]$ (**6**)	2032 (vs), 1995 (vs), 1962 (s), 1934 (m), 1922 (w, sh), 1871 (w)[c]

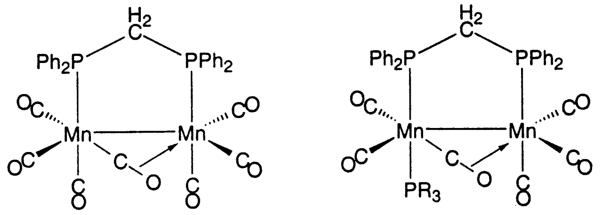
[a] Recorded in tetrahydrofuran solution, unless otherwise stated. [b] In dichloromethane solution. [c] 1653 (w) cm^{-1} [ν(N−N)].

us[4] and others[7] indicate that backbone P−C cleavage in the dppm ligand is a thermal process facilitated by the presence of unsaturation at a dimetallic center, anion **1** is surprisingly stable in this respect, showing no change even in refluxing tetrahydrofuran. This cannot be conciliated either with recent results on diruthenium complexes, which suggest that an increase in electron density at the dimetallic center might actually facilitate the backbone P−C cleavage of the dppm ligand.[8] In this context we decided to study the oxidation reactions of dianion **1** in order to test the effect of increasing the formal unsaturation in the molecule while at the same time reducing its negative charge. The results of that study, here presented, indicate that no cleavage of the dppm is induced in this way, which tend to force coordination of the CO ligand in a η^1:η^2 fashion instead. Further information on the processes involved has been obtained by carrying out the oxidation of **1** in the presence of ligands such as phosphines, nitriles, or isocyanides. The latter reactions also represent a good synthetic approach to new complexes not available through alternative, more conventional routes. Part of this work appeared in a communication.[6]

Results and Discussion

Synthesis of $Na_2[Mn_2(CO)_6(\mu\text{-dppm})]$ (1). Dihydride $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ reacts readily with sodium amalgam in tetrahydrofuran at room temperature, presumably evolving hydrogen, to yield a dark green solution of the dianion **1** (Na^+ salt). The same anion is obtained by using other reducing agents, such as potassium or an excess of $Li[HBEt_3]$, with only minor differences in their IR or ^{31}P NRM spectra, surely due to slightly different ion-pair effects.[9] Removal of solvents from a filtered solution yields compound **1** as a very air-sensitive green powder, which readily decomposes upon manipulation, attempts of crystallization, etc. Attempts to exchange the cation (Na^+ by $AsPh_4^+$, $N(PPh_3)_2^+$, etc.) so as to give a more stable salt were also unsuccessful. As expected, anion **1** is readily protonated (by $[NH_4]PF_6$) to regenerate the starting dihydride.

Chart 2



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3a (R= Ph)
3b (R= OMe)

Spectroscopic data in solution for **1** are indicative of a highly symmetric structure for this anion, close to that of the starting dihydride (Chart 1). For example, the IR spectrum shows four strong ν_{st}(CO) bands (Table 1), and its ^{31}P spectrum denotes a single environment for both phosphorus atoms of the bridging ligand, as found for the dihydride precursor. All this is consistent with a C_{2v} symmetry for the anion. Furthermore, the absence of additional bands in the IR spectrum and the low sensitivity of the latter to the nature of the cation (Li^+, Na^+, K^+) indicate that anion−cation interactions for **1** are rather weak in tetrahydrofuran solutions. This in turn is consistent with the very low C−O stretching frequencies exhibited by **1**, with an average value (1833 cm^{-1}) some 140 cm^{-1} lower than the corresponding figure for the neutral precursor (1975 cm^{-1}).

Oxidation of Tetrahydrofuran Solutions of Compound 1. When 2 equiv of $[FeCp_2]PF_6$ is added to a tetrahydrofuran solution of **1** at − 80 °C, an immediate color change from green to orange is observed, and within a few minutes the IR spectrum of the solution shows almost complete formation of the new heptacarbonyl complex $[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CO})(CO)_6(\mu\text{-dppm})]$ (**2**). The structure of **2** (Chart 2) is firmly supported by spectroscopic data (Table 1 and Experimental Section). Thus, the IR spectrum of **1** shows five strong ν(CO) bands in the terminal carbonyl region, with a pattern similar to that of other dimetallic complexes having two *fac*-$Mn(CO)_3$ oscillators in a low-symmetry environment. In addition, there is a low-frequency ν(CO) band at 1709 cm^{-1}, which suggests the presence of a four-electron-donor μ-η^1:η^2 bridging carbonyl ligand, as found in the prototypal $[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CO})(CO)_4(\mu\text{-dppm})_2]$.[10] The latter complex was found to be fluxional in solution, the NMR data being compatible with the restricted exchange process depicted in Figure 1.[11] That process creates a pseudo mirror plane containing the phosphorus and manganese atoms and seems to be present also in compound **2**. Thus, the ^{13}C NMR spectrum of **2** at

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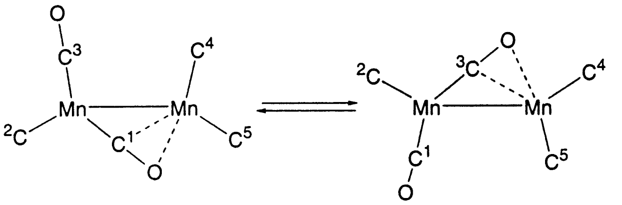


Figure 1. Fluxional process proposed for [Mn$_2$(μ-η^1:η^2-CO)(CO)$_4$(μ-dppm)$_2$][11] (only the plane containing the manganese and carbonyl atoms is shown).

238 K exhibits seven CO resonances in the range 240−215 ppm, in agreement with the static structure. At room temperature, however, three resonances remain unchanged, while the other four have coalesced pairwise. This is consistent with the rearrangement depicted in Figure 1, which also implies (in the fast exchange limit) the equivalence of the methylenic protons of the dppm ligand, as observed in the room-temperature ^{1}H NMR spectrum of **2**.

Compound **2** has a low thermal stability. Solutions of **2** slowly transform (even at −20 °C) into [Mn$_2$(CO)$_8$(μ-dppm)].[10a,12] This corresponds to an intermediate behavior between the stable pentacarbonyl [Mn$_2$(μ-η^1:η^2-CO)(CO)$_4$(μ-dppm)$_2$] and the enneacarbonyl complex [Mn$_2$(μ-η^1:η^2-CO)(CO)$_8$], the latter being a very unstable species detected during different photolysis studies carried out on [Mn$_2$(CO)$_{10}$].[13]

The formation of heptacarbonyl **2** from **1** requires some decomposition so as to liberate the extra carbon monoxide needed at some stage of the process. In fact, IR monitoring of the reaction mixture denotes the presence of at least an intermediate species for which stretching C−O bands at 1999 and 1689 cm^{-1} can be assigned (others being obscured by those of **2**). This species rapidly disappears at room temperature or by removal of tetrahydrofuran (THF) from the cold reaction mixture and dissolution of the residue in toluene. It is thus sensible to assume that the mentioned intermediate could be the hexacarbonylic solvate [Mn$_2$(μ-η^1:η^2-CO)(CO)$_5$(THF)(μ-dppm)]. To check this hypothesis, we studied the oxidation reactions of **2** in the presence of PPh$_3$ or P(OMe)$_3$, two P-donor ligands with different electronic and steric properties.

Oxidation of 1 in the Presence of PR$_3$ (R = Ph, OMe). Anion **1** reacts with 2 equiv [FeCp$_2$]PF$_6$ in the presence of stoichiometric amounts of PR$_3$ to give in good yields the corresponding hexacarbonyl complexes [Mn$_2$(μ-η^1:η^2-CO)(CO)$_5$(PR$_3$)(μ-dppm)] (**3a, b**) (**a**, R = Ph; **b**, R=OMe).

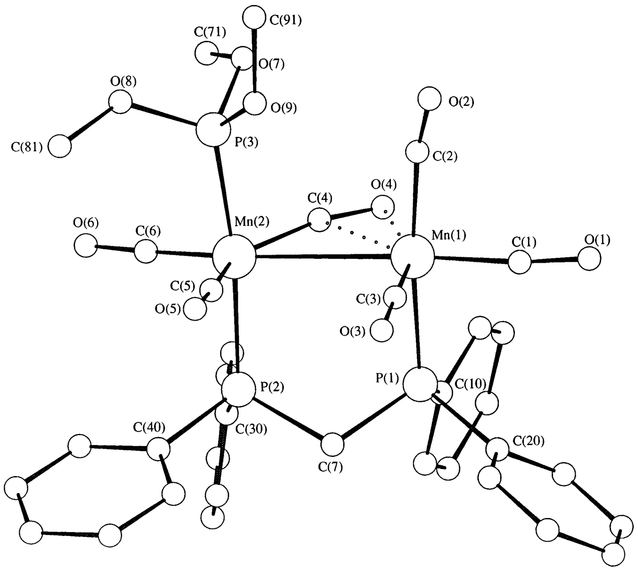
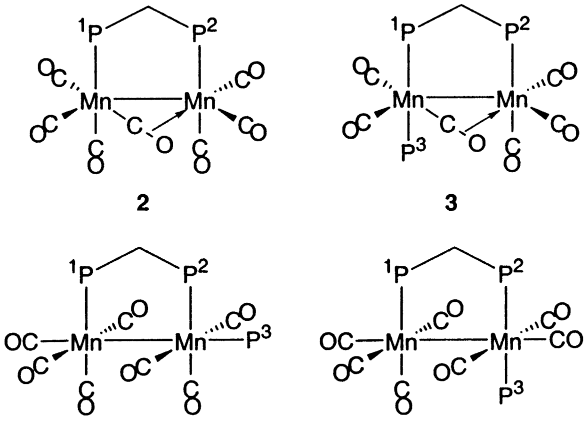


Figure 2. CAMERON drawing of the molecular structure of [Mn$_2$(μ-η^1:η^2-CO)(CO)$_5${P(OMe)$_3$}(μ-dppm)] (**3b**). Ellipsoids represent 30% probability.

Table 2. ^{31}P{^{1}H } NMR Data for New Compounds[a]



2 **3**

5(C) **5(T)**

	δ/ppm			J(PP)/Hz		
compd	P^1	P^2	P^3	*J*(1,2)	*J*(1,3)	*J*(2,3)
1[b]	60.7 (s)					
2	68.2 (d)	51.8 (d)		91		
3a	78.5 (dd)	49.0 (dd)	74.1 (s, br)	88	3	9
3b	75.1 (dd)	50.7 (dd)	194.2 (s, br)	92	30	12
4a[c]	55.8	54.4		66		
4b[c]	52.5	51.4		61		
5a (*C*)[d]	58.5 (d)	52.7 (dd)	75.4 (d)	77		24
5a (*T*)[d]	57.7 (d)	72.8 (d)	70.6 (s, br)	83		
5b (*C*)[d]	60.4 (d)	58.3 (dd)	191.0 (d)	80		58
5b (*T*)[d]	60.3 (dd)	68.7 (dd)	183.9 (dd)	88	9	40
6	51.4	48.3		94		

[a] Measured at 121.5 MHz, in CD$_2$Cl$_2$ solution at room temperature, unless otherwise stated. Phosphorus atoms are labeled (P1 to P3) according to the figure shown, except for compounds **4** and **6**, where labeling is arbitrary. [b] In tetrahydrofuran: C$_6$D$_6$ solution (9:1). [c] AB multiplet. [d] 213 K.

The structure of **3b**·C$_7$H$_8$ has been solved through an X-ray study and is depicted in Figure 2, while Table 3 lists the most relevant bond distances and angles. The structure is closely related to those previously found for the pentacarbonyl complexes [Mn$_2$(μ-η^1:η^2-CO)(CO)$_4$(μ-R$_2$PCH$_2$PR$_2$)$_2$] (R = Ph,[10] Cy[14]) after replacing in the latter a diphosphine ligand by CO and P(OMe)$_3$. Bond distances and angles within the almost planar Mn$_2$(μ-η^1:η^2-CO)(CO)$_4$ moiety in **3b** are similar to those found for the bis(diphosphine) derivatives. Because of the low accuracy of our structural determination, the small differences in the bond lengths observed for the bridging carbonyl [Mn(1)−C(4) longer and Mn(1)−O(4) shorter with respect to the referenced compounds] are probably

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

Mn(1)−Mn(2)	2.981(8)	Mn(1)−P(1)	2.33(1)
Mn(1)−C(1)	1.80(4)	Mn(1)−C(2)	1.87(5)
Mn(1)−C(3)	1.70(5)	Mn(1)−C(4)	2.23(3)
Mn(2)−P(2)	2.28(1)	Mn(2)−P(3)	2.20(1)
Mn(2)−C(4)	1.84(4)	Mn(2)−C(5)	1.81(4)
Mn(2)−C(6)	1.66(3)	Mn(1)−O(4)	2.12(3)
P(1)−Mn(1)−C(2)	175.0(14)	P(2)−Mn(2)−P(3)	172.6(5)
C(3)−Mn(1)−P(1)	91.0(15)	C(3)−Mn(1)−C(1)	94.8(19)
C(3)−Mn(1)−Mn(2)	88.4(14)	C(5)−Mn(2)−P(2)	87.7(12)
C(5)−Mn(2)−C(6)	106.5(16)	C(5)−Mn(2)−C(4)	141.5(15)
C(5)−Mn(2)−Mn(1)	93.9(11)	Mn(2)−C(4)−O(4)	163.5(33)

not significant. However, the intermetallic separation in **3b** [2.981(8) Å], while compatible with the formulation of a single Mn−Mn bond, is significantly longer than the corresponding figure in the bis(diphosphine) analogues (ca. 2.93 Å)[10,14] and even longer than that for [Mn$_2$(CO)$_{10}$] [2.904(1)].[15] The large intermetallic separation in **3b** cannot be obviously attributed to the presence of a single dppm bridge in the molecule. This is more obvious when comparing its structure with that of the isoelectronic [Mn$_2$(μ-η^1:η^2-C=CH^{t}Bu)(CO)$_6$(μ-dppm)], a molecule displaying a Mn−Mn bond length as short as 2.800(5) Å.[16] Thus, there seems to be a genuine lengthening effect of the 4e-donor bridging CO on the Mn−Mn bond. The associated effect of this lengthening is an increase of the distance between the bridgehead carbon and the Mn atom to which it is π-bonded and a decrease in the oxygen−metal distance. In terms of the structural classification of the linear semibridging carbonyls proposed by Crabtree and Lavin,[17] the (μ-η^1:η^2-CO) ligand in the above dimanganese complexes, rather than representing an entirely differentiated type of coordination for CO ligands (class IV),[17] might instead be viewed as examples of an intermediate situation between class I (strong O−M interaction, 4e-donors) and class II (weak O−M interaction, 2e-donors) linear semibridging carbonyls.

IR and ^{31}P NMR data in solution for compounds **3** are consistent with the solid-state structure found for **3b.** For example, the IR spectra exhibit five strong bands in the terminal ν_{st}(CO) region and a weak absorption at ca. 1670 cm^{-1}, which can be assigned to the μ-η^1:η^2-CO ligand. As expected, the ^{31}P spectra of **3** exhibit separated resonances for the inequivalent P atoms of dppm. However, the two-bond couplings between dppm and PR$_3$ (J_{13} in Table 2) are unusually low (3 or 30 Hz) for mutually *trans* P atoms (cf. a value of 110 Hz has been calculated for [Mn$_2$(μ-η^1:η^2-CO)(CO)$_4$(μ-dppm)$_2$]).[18] We will address this point later on.

The ^{13}C and ^{1}H NMR spectra of compound **3b** (see Experimental Section) give clear indication of fluxional behavior in solution. Although we have not studied this in detail, we note that the room-temperature ^{1}H NMR spectrum displays just a single triplet for the methylenic hydrogens of the bridging dppm, which is inconsistent with the static structure of the molecule. By lowering the temperature, however, this resonance broadens and eventually transforms into a poorly resolved ABMX multiplet. The ^{13}C spectra are also temperature-dependent. At 213 K, the spectrum exhibits in the carbonyl region three doublets of doublets and three doublets, which is consistent with the static structure. At 293 K, however, just two resonances remain sharp (one dd and one d), while the other four resonances are very broad. All this is consistent with the fluxional process depicted in Figure 1 and allows us to identify the chemical shift of the bridging CO as either 235.7 or 231.8 ppm on the basis of the multiplicity and temperature-dependence of these two resonances.

Compounds **3** are structural models for the intermediate species detected during the formation of heptacarbonyl complex **2** (see above). Indeed, the bands that can be clearly assigned to that intermediate (1999 and 1689 cm^{-1}) are very close to those observed for **3**. Thus we assume that this intermediate is isostructural to complexes **3**, with THF in the former occupying the position of PR$_3$ in the latter.

Whatever the exact nature of the intermediate resulting from the removal of two electrons in dianion **1**, that species effectively behaves as a source for the highly unsaturated, 30-electron [Mn$_2$(CO)$_6$(μ-dppm)] fragment. To explore the synthetic potential of this system, we studied the oxidation reactions of **1** in the presence of ligands able to act as 4e-donor bridging groups, such as nitriles or 1-alkynes.

Oxidation of 1 in the Presence of Terminal Alkyne or Nitrile Ligands. Although the title ligands are rather poor donors (when compared with PR$_3$), they are active enough when used in excess so as to compete with solvent during oxidation of **1**, thus yielding the corresponding derivatives in good yield.

In the case of RCCH (R = Ph, ^{t}Bu), the products are the corresponding vinylidene complexes [Mn$_2$(μ-η^1:η^2-CCHR)(CO)$_6$(μ-dppm)], and these are obtained in quite good yields (80−85%). We note that these compounds could be obtained previously from RCCH and either [Mn$_2$(μ-H)$_2$(CO)$_6$(μ-dppm)] (slow thermal reaction) or [Mn$_2$(CO)$_8$(μ-dppm)] (slow photochemical reaction), but yields were in general much lower (ca. 30%).[16] Therefore, the present procedure is more convenient from a synthetic point of view.

The oxidation of **1** in the presence of excess nitrile NCR (R = ^{t}Bu, Ph) gives the corresponding derivatives [Mn$_2$(μ-η^1:η^2-NCR)(CO)$_6$(μ-dppm)] (**4a**,**b**). Similar compounds have been obtained from dihydride [Mn$_2$(μ-H)$_2$(CO)$_6$(μ-dppm)] and NCR (R = Me, Et, Pr).[19] In fact, spectroscopic data for the latter nitrile derivatives are very similar to those of **4** (Tables 1 and 2), so they all must have the same structure (Chart 3), confirmed for R = Me through an X-ray study.[19]

There are several points of interest in the formation of compounds **4**. In the first place, neither **4a** nor **4b** can be obtained through the reaction of dihydride [Mn$_2$(μ-H)$_2$(CO)$_6$(μ-dppm)] with the corresponding nitrile. Actually, NC^{t}Bu failed to react at all, even at 330 K, whereas NCPh gave the hydridoalkylideneimido complex [Mn$_2$(μ-H)(μ-NCHPh)(CO)$_6$(μ-dppm)].[19] Thus, oxidation of **1** in the presence of NCR is the only synthetic way currently available for compounds **4a**,**b**. The failure of NC^{t}Bu to react with the dimanganese dihydride must

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(15) Churchill, M. R.; Amoh, K. N.; Wassermann, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

(16) García-Alonso, F. J.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Organometallics* **1992**, *11*, 370.

(17) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* **1986**, *25*, 805.

(18) Caulton, K. G.; Adair, P. *J. Organomet. Chem.* **1976**, *114*, C11.

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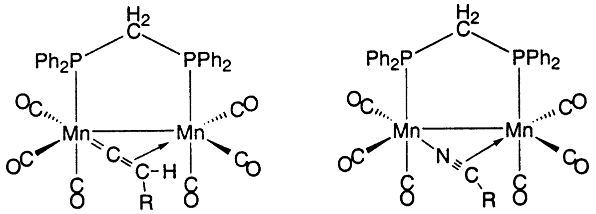
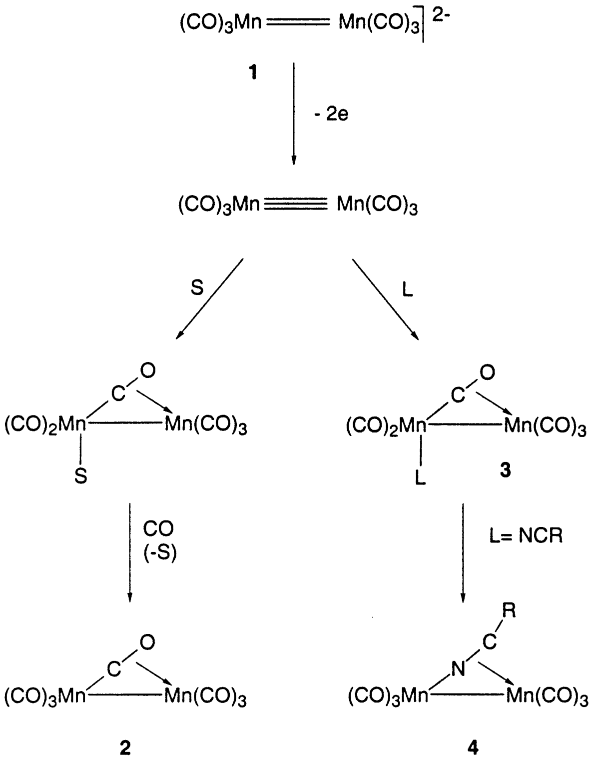
Chart 3



4a (R= ^{t}Bu)
4b (R= Ph)

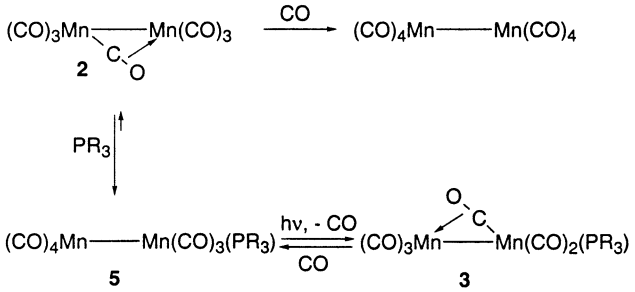
Scheme 1. Proposed Reaction Pathways for the Oxidation Reactions of Dianion 1 [Mn−Mn = $Mn_2(\mu$-dppm); S = Tetrahydrofuran]



have therefore a kinetic origin, as we have found that compound **4a** is in fact very stable. For example, it does not react with CO or PPh_3 at room temperature, thus indicating that the μ-η^1:η^2-nitrile ligand is tightly bound to the dimanganese center, in contrast to the μ-η^1:η^2-carbonyl ligand present in compounds **2** or **3**. In agreement with this, we note that an intermediate species can be detected during the formation of **4a**. IR bands clearly assignable to that intermediate species appear at 1998 and 1707 cm^{-1}, which suggests a structure similar to that of compounds **3**. We trust this intermediate has a terminal nitrile and bridging μ-η^1:η^2-CO group and evolves at room temperature to the thermodynamic product **4a**, with terminal CO and bridging nitrile ligands.

By considering all the results discussed so far, a unified picture emerges for the processes occurring during oxidation of dianion **1** (Scheme 1). Removal of two electron from **1** gives a highly unsaturated species, $[Mn_2(CO)_6(\mu\text{-dppm})]$, which rapidly reacts with a molecule of solvent S or ligand L (if available) to give a CO-bridged species $[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CO})(CO)_5X(\mu\text{-dppm})]$ (X = S, L). For S = tetrahydrofuran, this hexacarbonyl intermediate is thermally unstable and partially decomposes, the liberated CO completing its transformation into the heptacarbonyl **2**. In the presence of L, the corresponding hexacarbonyl structure is stable only for L = PR_3 (cf. compounds **3**). For L = nitrile, further isomerization to give the bridged nitrile products **4** rapidly occurs at room temperature. Finally, for L = 1-alkyne, the intermediate structure must have a lifetime long enough so as to allow for the isomerization of the terminally bound alkyne into a terminally bonded vinylidene group, which displaces CO from the bridging position afterward to yield the more stable μ-η^1:η^2-vinylidene derivative. We note that this last proposal is in full agreement with the data obtained from the reactions of $[Mn_2(\mu\text{-H})_2(CO)_6(\mu\text{-dppm})]$ with 1-alkynes.[16]

Scheme 2. Reactions of (μ-η^1:η^2-CO) Complexes with CO or PR_3 [Mn−Mn = $Mn_2(\mu$-dppm)]



Chemical Behavior of the μ-η^1:η^2-CO Bridged Compound 2. The prototypal $[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CO})(CO)_4(\mu\text{-dppm})_2]$ has been shown to be quite reactive toward a variety of reagents including CO,[20] RNC,[21] diazomethane,[22] or even weaker electron donors such as SO_2 or CS_2.[22a] In all cases, the incoming molecule destroys the π interaction between the bridging CO and the second metal atom (eq 1), although further rearrangements are possible.

$$[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CO})(CO)_4(\mu\text{-dppm})_2] + L \rightarrow [Mn_2(CO)_5L(\mu\text{-dppm})] \quad (1)$$

When L = CO, eq 1 also represents a carbonylation/decarbonylation equilibrium which has been previously studied for several bridging diphosphines. From that study it was concluded that steric factors were dominant, with the bulkier diphosphine ligands favoring the pentacarbonyl structure.[20b] On this basis, the bridging CO ligands in compounds **2** and **3** are expected to be much more reactive than the above bis-dppm-bridged compounds. To explore this, we studied the reactions of **2** or **3** with CO, PR_3 (R = Ph, OMe), and $CH(SiMe_3)N_2$. The results of the reactions with simple two-electron donor ligands are summarized in Scheme 2. As stated above, compound **2** slowly decomposes to give $[Mn_2(CO)_8(\mu\text{-dppm})]$, and, expectedly, this transformation occurs instantaneously in the presence of CO. Hexacarbonyls **3a**,**b** are more stable complexes, but are also readily carbonylated in the presence of CO to yield the

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(20) (a) Aspinall, H. C.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 724. (b) Wolf, T. E.; Klemann, L. P. *Organometallics* **1982**, *1*, 1667.

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(22) (a) Turney, T. W. *Inorg. Chim. Acta* **1982**, *64*, L141. (b) Ferguson, G.; Laws, W. J.; Parvez, M.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 276.

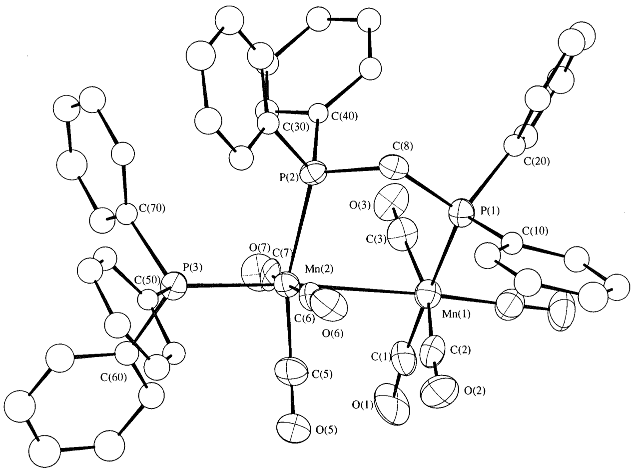


Figure 3. CAMERON drawing of the molecular structure of $[Mn_2(CO)_7(PPh_3)(\mu\text{-dppm})]$ (**5a**). Ellipsoids represent 30% probability.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound 5a

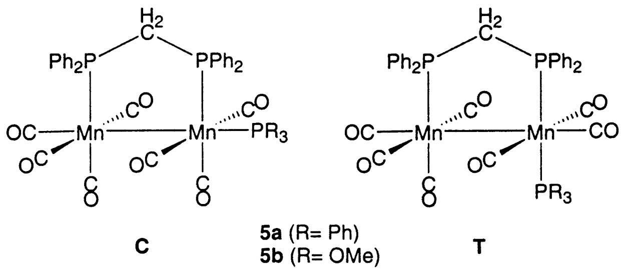
Mn(1)−Mn(2)	3.005(3)	Mn(1)−P(1)	2.280(5)
Mn(1)−C(1)	1.73(2)	Mn(1)−C(2)	1.82(2)
Mn(1)−C(3)	1.85(2)	Mn(1)−C(4)	1.76(2)
Mn(2)−P(2)	2.345(5)	Mn(2)−P(3)	2.285(4)
Mn(2)−C(5)	1.77(2)	Mn(2)−C(6)	1.78(2)
Mn(2)−C(7)	1.85(2)		
C(4)−Mn(1)−Mn(2)	176.6(6)	C(4)−Mn(1)−P(1)	91.2(6)
C(2)−Mn(1)−C(3)	166.0(7)	C(1)−Mn(1)−P(1)	176.7(6)
C(6)−Mn(2)−C(7)	173.5(7)	C(5)−Mn(2)−P(2)	162.0(6)
P(3)−Mn(2)−Mn(1)	168.5(2)	P(3)−Mn(2)−P(2)	102.0(2)

corresponding heptacarbonyls $[Mn_2(CO)_7(PR_3)(\mu\text{-dppm})]$ (**5a**,**b**). A further proof of the stabilizing effect of PR_3 (relative to CO) on the (μ-η^1:η^2-CO) structures is the fact that compounds **5a**,**b** can be converted back to **3a**,**b** through UV photolysis at −10 °C, whereas $[Mn_2(CO)_8(\mu\text{-dppm})]$ fails to yield **2** in that way.

The high reactivity of **2** is illustrated through its facile reaction with PR_3 (R = Ph, OMe) under ambient conditions. As expected, the products are the heptacarbonyls **5a**,**b**, and this is in fact the preferred preparative method for these new compounds.

Structure and Solution Dynamics of Compounds 5. Both **5a** and **5b** exist in solution as an equilibrium mixture of two isomers, which we have labeled *C* and *T* (Table 2). The structure of the major (*C*) isomer for **5a** has been solved through an X-ray study and is depicted in Figure 3, while Table 4 lists the most relevant bond distances and angles. As expected, the structure can be derived from that of $[Mn_2(CO)_{10}]$ by replacing two equatorial carbonyls by the dppm bridge and one axial carbonyl by PPh_3. The intermetallic distance 3.005(3) Å is longer than that in $[Mn_2(CO)_{10}]$ (2.9038(3) Å)[15] but comparable to that in $[Mn_2(CO)_6(\mu\text{-dppm})_2]$ (3.010(3) Å)[23] or $[Mn_2(CO)_8(\mu\text{-}Ph_2AsCH_2AsPh_2)]$ (2.962(3) Å).[24] As found for the above dimanganese compounds, the bridging ligand constrains the staggering of both coordination octahedra, so that the torsion angle defined by P(2)−Mn(2)−Mn(1)−P(1) in compound **5a** is ca. 30°, rather than the optimum value (45°) for minimum repulsion between both metal fragments. The presence of two relatively bulky phosphorus ligands around Mn(2) seems to impose some steric pressure on the structure, as deduced from the bending of these ligands away from each other [P(2)−Mn(2)−P(3) = 102.0(2)°]. This might be related with the observation that, in solution at room temperature, compound **5a** (but not **5b**) reversibly dissociates PPh_3 to a small extent (Scheme 2). This dissociation process is favored upon increasing the temperature, and it is fully suppressed below 0 °C, as shown by IR and NMR data.

Chart 4



As stated above, compounds **5** exist in solution as a mixture of two isomers. In both isomers the methylenic protons of dppm are chemically equivalent, as deduced from ^{1}H NMR data (see Experimental Section). Therefore, we conclude that the PR_3 ligand must be contained in the averaged plane defined by the dppm bridge and manganese atoms. This leaves out just two possibilities, labeled *C* and *T* to indicate the position of PR_3 (*cis* or *trans*) relative to dppm (Chart 4). Isomer *C* is that one found in the crystal for **5a**. The equilibrium ratio *C*/*T* for compounds **5** was found to be somewhat dependent on temperature or solvent, but we have not studied this dependence in detail. In addition, isomers *T* were found to be fluxional in solution, whereas isomers *C* remained rigid on the NMR time scale.

The assignment of ^{31}P resonances (Table 2) has been made on the basis of the expected trends in chemical shifts: (a) Isomers *C* and *T* should display similar chemical shifts for P^1 (P trans to CO), with a value close to that for $[Mn_2(CO)_8(\mu\text{-dppm})]$ (59.7 dppm). (b) Isomer *T* should have a second dppm resonance P^2 (*trans* to PR_3) with a higher chemical shift, close to the value of 70.2 ppm reported for $[Mn_2(CO)_6(\mu\text{-dppm})_2]$.[18] The above assignments imply that the coupling constant between P^2 and P^3 in the *cis* isomers exceeds by some 20 Hz the value for the corresponding *trans* isomers. We recall here that an unusually low value for *trans*-$^2J_{PP}$ coupling was also found for compounds **3**. Although the usual trend for $^2J_{PP}$ in octahedral geometry is $|J_{trans}| > |J_{cis}|$, there are cases where the reverse holds, mainly because $^2J_{cis}$ tends to be negative while $^2J_{trans}$ is usually positive.[25]

The assignment just discussed is fully consistent with the dynamic behavior exhibited by these isomers in solution, as deduced from the ^{13}C NMR data. By recalling the fluxional behavior of $[Mn_2(CO)_6(\mu\text{-dppm})_2]$[11] we would expect that a similar CO scrambling process should be possible in isomer *T*, but not for *C* because of

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(24) Hoskins, B. F.; Steen, R. J. *Aust. J. Chem.* **1983**, *36*, 683.

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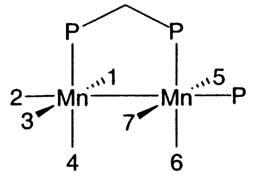
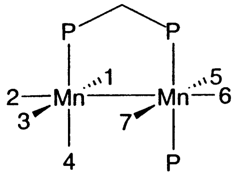
Table 5. $^{13}C\{^1H\}$ NMR Data[a] for Compounds 5



5(C)



5(T)

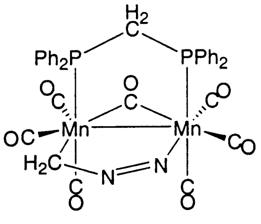
		δ/213 K		δ/293 K	
isomer	resonance	**5a**	**5b**	**5a**	**5b**
C	5 + 7	233.9	231.1	233.9	231.5
C	6	229.9	225.8	229.6	226.4
C	1 + 3	228.6	228.7	228.5	229.0
C	4	225.1	224.9	224.7	225.0
C	2	222.2	221.9	222.1	222.4
T	5 + 7	236.1	232.7	229.0[b]	228.5[b]
T	1 + 3	227.4	227.4	229.0[b]	228.5[b]
T	6	227.4	224.9	229.0[b]	228.5[b]
T	4	224.8	223.2	224.7	223.4
T	2	222.3	221.9	229.0[b]	228.5[b]

[a] Measured in CD_2Cl_2 solutions; chemical shifts are only given for CO resonances. Carbonyl ligands have been labeled (1−7) according to the figures shown. [b] Very broad resonance.

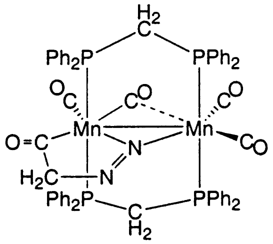
the presence of the PR_3 ligand in the plane perpendicular to the dppm bridge, where the carbonyl scrambling should take place. Indeed, isomer *C* behaves as a rigid molecule from 213 to 293 K, exhibiting the expected five ^{13}C carbonyl resonances (ca. 2:2:1:1:1 intensity). For isomer *T*, however, the five carbonyl resonances observed at low temperatures broaden on warming up and at 293 K are observed as two broad resonances (ca. 6:1 intensity). This is consistent with the "merry-go-round" mechanism proposed for $[Mn_2(CO)_6(\mu\text{-dppm})_2]$, whereby the resonance not involved in the dynamic process can be safely assigned to the carbonyl *trans* to phosphorus in isomer *T* (position 4, see Table 5). Starting from this assignment and proceeding through the expected analogies in chemical shifts, all carbonyl resonances can be assigned as shown in Table 5.

Diazomethane Derivative of Compound 2. The high reactivity of compound **2** (compared with the related pentacarbonyl $[Mn_2(\mu\text{-}\eta^1{:}\eta^2\text{-CO})(CO)_4(\mu\text{-dppm})_2]$) is also illustrated through its rapid reaction with $CH(SiMe_3)N_2$, a stable but less reactive derivative of diazomethane. This reaction takes place in a few minutes, in contrast to the reaction of $[Mn_2(\mu\text{-}\eta^1{:}\eta^2\text{-CO})(CO)_4(\mu\text{-dppm})_2]$ with diazomethane, reported to be completed in about 24 h.[22b] Surprisingly, however, no $SiMe_3$ group is incorporated into the major product isolated from the reaction of **2** with $CH(SiMe_3)N_2$, which instead can be formulated as the diazomethane complex $[Mn_2(\mu\text{-}\eta^1{:}\kappa^1\text{-}CH_2N_2)(\mu\text{-CO})(CO)_6(\mu\text{-dppm})]$ (**6**). Monitoring of the above reaction by IR and ^{31}P NMR spectroscopy suggests that a species similar to **6** might be formed initially (perhaps containing a $CH(SiMe_3)N_2$ ligand), but this intermediate is rapidly decomposed (presumably through hydrolysis) upon manipulation or any attempts of isolation (crystallization, chromatography, etc.) to give **6** and other unidentified products. There are precedents of the use of $CH(SiMe_3)N_2$ as a synthetic equivalent of diazomethane, the $CH(SiMe_3)$ group being transformed into CH_2 through hydrolysis during workup.[26]

Chart 5



6



$[Mn_2(CO)_4\{\mu\text{-}C(O)CH_2N_2\}(\mu\text{-dppm})_2]$

Spectroscopic and microanalytical data for **6** give full support to its formulation as a diazomethane complex, although some details of the structure cannot be deduced without uncertainty. In light of our data we propose for **6** the structure depicted in Chart 5, containing a diazomethane molecule bridging the manganese atoms through C and N and behaving as a two-electron donor group. However, we cannot exclude completely for **6** a structure related to that found for $[Mn_2\{C(O)CH_2N_2\}(CO)_4(\mu\text{-dppm})_2]$,[22b] where the diazomethane molecule bridges the manganese atoms through a single N atom, while the methylenic end couples to a carbonyl, yielding a bonded acyl group (Chart 5). We favor the first formulation on the basis of different pieces of evidence. First, the IR spectrum of **6** exhibits five ν_{st}(CO) bands between 2032 and 1922 cm^{-1}, with a pattern characteristic of many hexacarbonylic dimanganese compounds of general formula $[Mn_2(\mu\text{-X})(\mu\text{-Y})(CO)_6(\mu\text{-dppm})]$ (X, Y being one to three electron-donor ligands). In addition, there is also a weak band substantially shifted to lower wavenumbers (1871 cm^{-1}), thus suggesting the presence of a bridging or semibridging carbonyl ligand, and a weak band at 1653 cm^{-1} which could be assigned to the N−N stretch.[22] In agreement with the IR data, the ^{13}C NMR spectrum of **6** exhibits six different resonances in the terminal carbonyl region and a seventh one at 279 ppm. We note here, however, that the high chemical shift of the latter could be itself consistent with the presence of either a bridging carbonyl or an acyl group.[27] Unfortunately, in the absence of ^{13}C data on related complexes, the chemical shift of the methylenic group of the diazo fragment (116 ppm) cannot be used as a diagnostic for its attachment to either C or Mn atoms. The ^1H NMR spectrum of **6**, however, suggests that the CH_2N_2 group also binds the metal through its C atom. This is because the methylenic protons exhibit a coupling to phosphorus (4 Hz) that can be reasonably identified as a $^3J_{PH}$ figure while would appear as too large for a four-bond coupling constant.

Concluding Remarks. The oxidation reactions of **1** represent a useful synthetic route to dimanganese compounds having four-electron $\eta^1{:}\eta^2$ ligands (CO, NCR, CCHR) not accessible through more conventional thermal or photochemical reactions. The new $\eta^1{:}\eta^2$-bridged complexes $[Mn_2(\mu\text{-}\eta^1{:}\eta^2\text{-CO})(CO)_5L(\mu\text{-dppm})]$ (L = CO, PPh_3, $P(OMe)_3$) are species more reactive than the pentacarbonyls $[Mn_2(\mu\text{-}\eta^1{:}\eta^2\text{-CO})(CO)_4(\mu\text{-}R_2PCH_2PR_2)_2]$. The relative stability of the singly bridged dppm complexes follows the order PR_3 > CO and $P(OMe)_3$ > PPh_3.

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(26) Chan, K. S.; Wulff, W. D. J. *Am. Chem. Soc.* **1986**, *108*, 5229.

(27) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, U.K., 1981.

The latter suggests, in contrast to previous conclusions,[20b] that π acid phosphorus-donor ligands increase the stability of the μ-η^1:η^2-CO complexes when steric effects are not to be considered.

Experimental Section

General Considerations. All manipulations and reactions were carried out using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen. Solvents were purified according to standard literature procedures[28] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 60−65 °C. Compounds [Mn_2(μ-$H)_2(CO)_6$(μ-dppm)],[16] [$FeCp_2$]PF_6,[29] and $Ph_2PCH_2PPh_2$[30] were prepared according to literature procedures. Other reagents were obtained from the usual commercial suppliers and used without further purification. Filtrations were carried out using diatomaceous earth, and alumina for column chromatography was deactivated by appropriate addition of water to the commercial material (Aldrich, neutral, activity I). NMR spectra were recorded at 300.13 MHz (^{1}H), 121.50 MHz (^{31}P{^{1}H}), and 75.47 MHz (^{13}C{^{1}H}), at room temperature unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal TMS (^{1}H, ^{13}C) or external 85% H_3PO_4 aqueous solution (^{31}P), with positive values for frequencies higher than that of the reference. Coupling constants (J) are given in hertz. ^{13}C-{^{1}H} NMR spectra were routinely recorded on solutions containing a small amount of tris(acetylacetonate)chromium-(III) as a relaxation reagent.

Preparation of Tetrahydrofuran Solutions of Na_2[Mn_2-$(CO)_6$(μ-dppm)] (1). In a typical experiment, dihydride [Mn_2(μ-$H)_2(CO)_6$(μ-dppm)] (0.035 g, 0.053 mmol) in tetrahydrofuran (10 mL) was stirred with an excess of 1% (by weight) sodium amalgam (ca. 1 mL, 5 mmol of Na) for 30 min, affording a dark green solution. The latter was filtered using a cannula and was then ready for further use. IR and ^{31}P NMR spectroscopy showed the presence of a single species in this solution, and thus a 100% yield in the formation of **1** was assumed.

Preparation of [Mn_2(μ-η^1:η^2-CO)$(CO)_6$(μ-dppm)] (2). Solid [$FeCp_2$]PF_6 (0.033 g, 0.1 mmol) was added to a solution of compound **1** (ca. 0.05 mmol) in THF (10 mL), previously cooled at −80 °C. The mixture was stirred for 5 min and the solvent then removed under vacuum from the yellow-orange resulting solution. Toluene (10 mL) was then added to the residue, and the mixture was further stirred for 5 min and filtered. Removal of solvent from the filtrate and washing of the residue with petroleum ether (3 × 5 mL, so as to remove [$FeCp_2$]) gave compound **2** as an essentially pure yellow powder (0.026 g, 75%). Although this complex could be purified by column chromatography on Florisil (Aldrich, 100−200 mesh) at −40 °C by using dichloromethane/petroleum ether (1:1) as elution solvent, all attempts to crystallize this complex resulted in its progressive decomposition (to give [$Mn_2(CO)_8$(μ-dppm)]). Anal. Calcd for $C_{32}H_{22}Mn_2O_7P_2$: C, 55.66; H, 3.21. Found: C, 55.92; H, 3.21. ^{1}H NMR (CD_2Cl_2): δ 7.6−7.0 (m, 20H, Ph), 3.45 (t, J_{PH} = 11, 2H, CH_2). ^{13}C{^{1}H} NMR [THF/C_6D_6 (9:1)]: δ 233.2 (br, 2 × CO), 226.0 (br, 2 × CO), 223.6 (d, J_{PC} = 7, CO), 222.8 (d, J_{PC} = 26, CO), 215.3 (d, J_{PC} = 29, CO), 135.0−128.5 (Ph), 39.6 (t, J_{PC} = 19, CH_2). ^{13}C NMR [THF/C_6D_6 (9:1), 228 K]: δ 239.0, 231.3, 227.5 (3 × m, 3 × CO), 223.8 (s, CO), 222.7 (d, J_{PC} = 27, CO), 220.0 (m, CO), 215.4 (d, J_{PC} = 29, CO).

Preparation of [Mn_2(μ-η^1:η^2-CO)$(CO)_5(PPh_3)$(μ-dppm)] (3a). Solid [$FeCp_2$]PF_6 (0.050 g, 0.15 mmol) was added to a THF solution (15 mL) containing compound **1** (ca. 0.075 mmol) and PPh_3 (0.021 g, 0.075 mmol) at −80 °C. The mixture was stirred at that temperature for 10 min and then allowed to reach room temperature for 1 h. Solvent was afterward removed under vacuum and the orange residue chromatographed on an alumina column (activity III, 15 cm) at −35 °C. Elution with THF/petroleum ether (1:5) gave a yellow fraction containing [$FeCp_2$]. Elution with a 1:2 mixture gave a yellow-orange fraction, which yielded, after removal of solvents under vacuum, compound **3a** as an orange powder (0.026 g, 45%). This compound can be recrystallized from toluene/petroleum ether at −20 °C. Anal. Calcd for $C_{49}H_{37}Mn_2O_6P_3$: C, 63.65; H, 4.03. Found: C, 63.71; H, 4.11. ^{1}H NMR (C_6D_6): δ 7.9−6.6 (complex, Ph, 35H), 3.33 (ABMX broad multiplet, CH_2, 2H).

Preparation of [Mn_2(μ-η^1:η^2-CO)$(CO)_5${$P(OMe)_3$}(μ-dppm)] (3b). The procedure is totally analogous to that described for **3a**, except that $P(OMe)_3$ (7 μL, 0.08 mmol) was used instead of PPh_3 (reaction time 30 min), and dichloromethane/petroleum ether mixtures were used in the chromatography on alumina (activity III, 25 cm, −35 °C). Ferrocene was first eluted by using an 1:5 mixture. Further elution with a 1:3 solvent mixture gave an orange fraction, which yielded, after removal of solvents under vacuum, compound **3b** as an orange powder (0.036 g, 61%). The crystals used in the X-ray diffraction study were grown from a toluene/petroleum ether solution of the complex at −20 °C. Anal. Calcd for $C_{34}H_{31}Mn_2O_9P_3$: C, 51.93; H, 3.97. Found: C, 52.08; H, 4.01. ^{1}H NMR (CD_2Cl_2, 200.13 MHz): δ 7.6−6.9 (complex, 20H, Ph), 3.65 (d, J_{PH} = 12, 9H, OMe), 3.20 (t, J_{PH} = 11, 2H, CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 236.0, 233.5, 232.0, 220.5 (4 × m, br, 4 × CO), 227.2 (dd, J_{PC} = 38, 29, 1 × CO), 216.2 (d, J_{PC} = 34, 1 × CO), 132.5−127.6 (complex, Ph), 52.2 (d, J_{PC} = 5, OMe), 41.6 (t, J_{PC} = 16, PCH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2/213 K): δ 235.7 (dd, J_{PC} = 30, 19, CO), 233.9 (d, J_{PC} = 22, CO), 231.8 (dd, J_{PC} = 34, 23, CO), 226.8 (dd, J_{PC} = 40, 27, CO), 220.3 (d, J_{PC} = 27, CO), 215.9 (d, J_{PC} = 34, CO), 140.0−125.7 (complex, Ph), 52.4 (s, Me), 41.5 (t, J_{PC} = 16, CH_2).

Preparation of [Mn_2(μ-η^1:η^2-CCHR)$(CO)_6$(μ-dppm)] (R = Ph, ^{t}Bu). Solid [$FeCp_2$]PF_6 (0.033 g, 0.1 mmol) was added to a THF solution (10 mL) of compound **1** (ca. 0.05 mmol) and HC_2R (1 mL, excess) at − 80 °C, and the mixture was stirred and allowed to reach room temperature for 40 min. Solvent was then removed under vacuum and the red residue extracted with toluene (2 × 8 mL) and filtered. Removal of solvent from the filtrate gave a residue, which was washed with petroleum ether (5 × 5 mL) and recrystallized from toluene/petroleum ether at −20 °C to give red crystals of the title compounds (0.033 g, 85% for R = Ph; 0.030 g, 80% for R = ^{t}Bu). Spectroscopic data for these products were identical to those reported in ref 19.

Preparation of [Mn_2(μ-η^1:η^2-NC^{t}Bu)$(CO)_6$(μ-dppm)] (4a). The procedure is totally analogous to that described for **3b**, except that excess ^{t}BuCN (1 mL) was used instead of $P(OMe)_3$ (reaction time 2 h). Elution with dichloromethane/petroleum ether (1:5) gave first a yellow fraction containing ferrocene and then a yellow-orange fraction. Removal of solvents from the latter under vacuum gave compound **4a** as a yellow-orange microcrystalline powder (0.043 g, 75%). Anal. Calcd for $C_{36}H_{31}Mn_2NO_6P_2$: C, 58.00; H, 4.19; N, 1.88. Found: C, 58.34; H, 4.03; N, 1.83. ^{1}H NMR (CD_2Cl_2): δ 8.00−6.41 (m, 20H, Ph), 3.20 (dt, J_{HH} = 14, J_{PH} = 12, 1H, CH_2), 2.39 (dt, J_{HH} = 14, J_{PH} = 10, 1H, CH_2), 1.08 (s, 9H, Me).

Preparation of [Mn_2(μ-η^1:η^2-NCPh)$(CO)_6$(μ-dppm)] (4b). The procedure is totally analogous to that described for **4a**, except that excess PhCN (1 mL) was used instead of ^{t}BuCN (reaction time 30 min). An orange fraction was collected when eluting with dichloromethane/petroleum ether (1:3). Removal of solvents from this fraction under vacuum gave compound **4b** as a yellow-orange microcrystalline powder (0.038 g, 65%). Anal. Calcd for $C_{38}H_{27}Mn_2NO_6P_2$: C, 59.65; H, 3.53; N, 1.83. Found: C, 59.43; H, 3.48; N, 1.81. ^{1}H NMR (CD_2Cl_2): δ 7.92−6.38 (m, 25H, Ph), 3.24 (dt, J_{HH} = 14, J_{PH} = 12.5, 1H, CH_2), 2.39 (dt, J_{HH} = 14, J_{PH} = 9.5, 1H, CH_2).

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Preparation of $[Mn_2CO)_7(PPh_3)(\mu\text{-dppm})]$ (5a). A THF solution of compound **2** was prepared in situ from ca. 0.057 mmol of anion **1** as described above. To this solution, solid PPh_3 (0.015 g, 0.057 mmol) was added at −40 °C, and the mixture was stirred at that temperature for 15 min. Solvent was removed under vacuum and the residue chromatographed on an alumina column (activity III, 20 cm) at −40 °C. Ferrocene was first eluted by using a THF/petroleum ether (1:5) mixture, while a 1:3 mixture gave a minor yellow fraction containing a small amount of $[Mn_2(CO)_8(\mu\text{-dppm})]$. Finally, elution with a THF/petroleum ether (1:2) mixture gave an orange fraction, which yielded, after removal of solvents under vacuum, compound **5a** as a red-orange powder (0.036 g, 60%). The crystals used for the X-ray study were grown by slow diffusion of a dichloromethane solution of **5a** into a layer of petroleum ether at −20 °C. Anal. Calcd for $C_{50}H_{37}Mn_2O_7P_3$: C, 63.04; H, 3.92. Found: C, 62.65; H, 4.12. $^1H\{^{31}P\}$ NMR (CD_2Cl_2, 278 K): δ 7.55−6.72 (complex, 35H, Ph), 3.93 (s, br, 2H, CH_2, isomer *C*), 3.88 (s, br, 2H, CH_2, isomer *T*). Ratio $C/T = 2$. ^{13}C-$\{^1H, ^{31}P\}$ (100.63 MHz, CD_2Cl_2, 213 K): Isomer *C*: δ 233.9 (s, 2 × CO), 229.9 (s, CO), 228.6 (s, 2 × CO), 225.1 (s, CO), 222.2 (s, CO), 137.2−127.9 (Ph), 49.9 (s, CH_2). Isomer *T*: δ 236.1 (s, 2 x CO), 227.4 (s, 3 × CO), 224.8 (s, CO), 222.3 (s, CO), 137.2−127.9 (Ph), 47.2 (s, CH_2). $^{13}C\{^1H, ^{31}P\}$ (100.63 MHz, CD_2Cl_2, 295 K): Isomer *C*: δ 233.9 (s, 2 x CO), 229.6 (s, CO), 228.5 (s, 2 x CO), 224.7 (s, CO), 222.1 (s, CO), 51.2 (s, CH_2). Isomer *T*: δ 229.0 (br, 6x CO), 224.7 (s, br, CO), 48.0 (s, CH_2). See Table 5 for assignment of the carbonyl resonances.

Preparation of $[Mn_2CO)_7\{P(OMe)_3\}(\mu\text{-dppm})]$ (5b). A THF solution of compound **2** was prepared in situ from ca. 0.08 mmol of anion **1** as described above. To this solution, $P(OMe)_3$ (10 μL, 0.08 mmol) was added at −50 °C, and the mixture was stirred at that temperature for 10 min. Solvent was then removed under vacuum and the residue chromatographed on an alumina column (activity III, 15 cm) at −30 °C. Ferrocene was first eluted by using a dichloromethane/petroleum ether (1:6) mixture. Elution with a dichloromethane/petroleum ether (1:3) mixture gave a yellow-orange fraction, which yielded, after removal of solvents under vacuum, compound **5b** (46 mg, 70%) as a red-orange microcrystalline solid. Anal. Calcd for $C_{35}H_{31}Mn_2O_{10}P_3$: C, 51.62; H, 3.84. Found: C, 52.03; H, 4.02. ^1H NMR (CD_2Cl_2): Isomer *C*: δ 7.63−6.83 (complex, 20H, Ph), 3.84 (t, $J_{PH} = 10$, 2H, CH_2), 3.38 (d, $J_{PH} = 11$, 9H, OMe). Isomer *T*: δ 7.63−6.83 (complex, 20H, Ph), 3.76 (t, $J_{PH} = 10$, 2H, CH_2), 3.47 (d, $J_{PH} = 11$, 9H, OMe). Ratio $C/T = 0.5$. $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 238 K): isomer *C*: δ 231.1 (t, $J_{PC} = 20$, 2 × CO), 228.7 (d, $J_{PC} = 21$, 2 × CO), 225.8 (m, CO), 224.9 (m, CO), 221.9 (m, CO), 131.7−128.0 (Ph), 52.3 (d, $J_{PC} = 7$, OMe), 48.3 (t, $J_{PC} = 21$, CH_2). Isomer *T*: δ 232.7 (m, 2 × CO), 227.4 (d, $J_{PC} = 23$, 2 × CO), 224.9 (m, CO), 223.2 (m, CO), 221.9 (m, CO), 131.7−128.0 (Ph), 52.2 (d, $J_{PC} = 6$, OMe), 48.3 (t, $J_{PC} = 21$, CH_2). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 295 K): isomer *C*: δ 231.5 (t, $J_{PC} = 20$, 2 × CO), 229.0 (m, 2 × CO), 226.4 (m, CO), 225.0 (m, CO), 222.4 (m, CO). Isomer *T*: δ, 228.5 (br, 6 × CO), 223.4 (m, CO).

Preparation of $[Mn_2(\mu\text{-}\eta^1{:}\kappa^1\text{-}CH_2N_2)(\mu\text{-}CO)(CO)_6(\mu\text{-dppm})]$ (6). A toluene solution (10 mL) of compound **2** was prepared in situ from ca. 0.1 mmol of anion **1** as described above. To this solution, $CH(SiMe_3)N_2$ (100 μL of a 2 M solution in hexanes, ca. 0.2 mmol) was added, and the mixture was stirred at room temperature for 30 min. Solvent was then removed under vacuum and the residue chromatographed on an alumina column (activity III, 20 cm) at −30 °C. Ferrocene was first eluted by using a toluene/petroleum ether (1:4) mixture. Further elution with a 1:1 mixture gave a yellow fraction containing some $[MnH(CO)_3(dppm)]$, and elution with a 4:1 mixture gave a minor fraction containing several unidentified species. Finally, elution with pure tetrahydrofuran gave a yellow-orange fraction, which yielded, after removal of solvent under vacuum, compound **6** (0.035 g, 50%) as an orange microcrystalline powder. Anal. Calcd for $C_{33}H_{24}Mn_2N_2O_7P_2$: C, 54.13; H, 3.31; N, 3.82. Found: C, 54.56; H, 3.67; N, 3.70. ^1H NMR (CD_2Cl_2): δ 7.60−6.79 (complex, 20H, Ph), 5.49, 5.19 (ABX multiplet, $J_{HH} = 22$, $J_{PH} = 4$, 2H, CH_2N_2), 2.46 (m, 2H, PCH_2). $^1H\{^{31}P\}$ NMR (400.13 MHz, CD_2Cl_2): δ 5.49, 5.19 (AB multiplet, $J_{HH} = 22$, 2H, CH_2N_2), 2.49, 2.44 (AB multiplet, $J_{HH} = 13$, 2H, PCH_2). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 213 K): δ 279.1 (d, $J_{PC} = 20$, μ-CO), 228.1 (d, $J_{PC} = 10$, CO), 223.0 (d, $J_{PC} = 22$, CO), 222.6 (d, $J_{PC} = 20$, CO), 222.5 (d, $J_{PC} = 24$, CO), 213.7 (d, $J_{PC} = 25$, CO), 211.9 (d, $J_{PC} = 16$, CO), 135.6−128.8 (Ph), 116.0 (s, CH_2N_2), 17.0 (s, br, PCH_2).

Table 6. Experimental Data for the X-ray Diffraction Studies

	3b·C_7H_8	**5a**
mol formula	$C_{41}H_{39}Mn_2O_9P_3$	$C_{50}H_{37}Mn_2P_3O_7$
mol wt	878.53	952.61
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
radiation (λ, Å)	Mo Kα (0.71069)	
a, Å	12.091(2)	13.666(7)
b, Å	18.272(3)	18.94(1)
c, Å	18.589(4)	18.52(1)
β, deg	95.54(2)	106.21(4)
V, Å^3	4088(2)	4603(8)
Z	4	4
calcd density, gcm^{-3}	1.43	1.37
μ(Mo Kα), cm^{-1}	7.60	6.77
diffractometer	Nonius CAD4	
temperature, K	293	293
scan type	$\omega/2\theta$	$\omega/2\theta$
2θ range, deg	2−38	4−50
scan width	$0.8 + 0.345 \tan\theta$	
total no. of unique data	3273	6386
no. of unique obsd data [$I > 2.5\sigma(I)$]	707	1723
merging *R* factor	0.13	0.10
R^a	0.074	0.052
$R_w{}^b$	0.082	0.057
abs coeff corr (min., max.)	0.829, 1.195	0.90, 1.07
secondary extinction corr	205×10^{-5}	none
no. of variables	154	351

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

X-ray Structure Determination for Compounds 3b·C_7H_8 and 5a. A selected crystal was set up on an automatic diffractometer. Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 well-centered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other information are summarized in Table 6. Corrections were made for Lorentz and polarization effects. Empirical absorption correction (Difabs)[31] was applied. A secondary extinction correction was unnecessary for **5a** and was applied for **3b**.

Computations were performed by using the PC version of CRYSTALS.[32] Atomic form factors for neutral Mn, P, O, C, and (for **5a**) H were taken from ref 33. Real and imaginary parts of anomalous dispersion were taken into account. The structures were solved by direct methods (SHELXS)[34] and successive Fourier maps. Because of the few number of reflections, in the case of **5a** carbon atoms of the phenyl groups were isotropically refined, and the hydrogen atoms were theoretically located and given an overall isotropic thermal parameter. For the same reason, in the case of **3a** phenyl rings were refined as rigid groups and all atoms were isotropically refined, except the hydrogen atoms, not located nor introduced

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in calculations. In this case the unit cell also contains a toluene molecule, of which the methyl group could not be located; this molecule was also refined as a rigid group, with an overall isotropic thermal parameter.

Refinements were carried out in three blocks by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. Models reached convergence with $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ having values listed in Table 6. For **5a**, the weighting scheme was unity. For **3b**, in the last stages of refinement, each reflection was assigned a weight $w = w'[1 - ((|F_o| - |F_c|)/6\sigma(F_o))^2]^2$ with $w' = 1/\sum_{r=1,3} A_r T_r(X)$ with three coefficients 4.41, −2.88, and 3.08 for a Chebyshev series, for which $X = F_o/F_o(\max)$. Figures 2 and 3 represent CAMERON[35] views of these compounds, with ellipsoids at 30% probability. Tables of observed and calculated structure factors are available from the authors on request.

Acknowledgment. We thank the Ministerio de Educación y Ciencia and the Ministerio de Asuntos Exteriores of Spain for a grant (to X−Y. Liu), and the DGICYT of Spain (Projects PB91−0678 and PB96−0317) for financial support.

Supporting Information Available: Tables of fractional atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compounds **3b** and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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