71332-21-3; III, R = C_2H_5, 71332-23-5; III, R = n-C_3H_7, 75132-80-8; III, R = n-C_4H_9, 75132-82-0; III, R = i-C_3H_7, 75155-05-4; III, R = t-C_4H_9, 75155-06-5; IV, R = CH_3, 77589-25-4; IV, R = C_2H_5, 77589-26-5; IV, R = n-C_3H_7, 77589-27-6; IV, R = n-C_4H_9, 77611-13-3; IV, R = i-C_3H_7, 77589-28-7; IV, R = t-C_4H_9, 77589-29-8; V, R = CH_3, 77589-30-1; V, R = C_2H_5, 77589-31-2; V, R = n-C_3H_7, 77589-32-3; V, R = n-C_4H_9, 77589-33-4; V, R = i-C_3H_7, 77589-34-5; V, R = t-C_4H_9, 77589-35-6; VI, R′ = OCH_3, R = CH_3, 77589-36-7; VI, R′ = OC_6H_5, R = CH_3, 77589-37-8; VI, R′ = n-BuNH, R = CH_3, 77589-38-9; VI, R′ = t-BuNH, R = CH_3, 77589-39-0; Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2; $NaOCH_3$, 124-41-4; $NaOC_6H_5$, 139-02-6; n-$BuNH_2$, 109-73-9; t-$BuNH_2$, 75-64-9.

Supplementary Material Available: Haloalkylphosphazene infrared data (Table II) and NMR data (Table III) (8 pages). Ordering information is given on any current masthead page.

Contribution from Laboratoire CNRS-SNPE, 94320 Thiais, France,
and Laboratoire de Cristallochimie, Institut Le Bel, Université Louis Pasteur, 67070 Strasbourg Cedex, France

Bimetallic Sandwiches Based upon Phosphole Ligands

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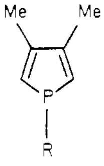
The reaction of a phosphole (L) with a σ,π complex $L'Fe_2(CO)_n$ (L′ = another phosphole; n = 6 or 7) gives the metallic sandwich $L[Fe_2(CO)_4]L'$. A heterobimetallic sandwich is also obtained when $L'FeMo(CO)_8$ is the starting compound. The X-ray crystal structure of the complex with L = L′ = 1-phenyl-3,4-dimethylphosphole has been determined. Crystal data: monoclinic, $C2/c$, with a = 14.334 (1) Å, b = 12.375 (1) Å, c = 16.470 (1) Å, β = 112.62 (1)°. The two phosphole rings adopt a head to tail disposition and are strongly folded. Very large ^{31}P–^{31}P NMR coupling suggests a direct through-space interaction between the nonbonded phosphorus and iron atoms.

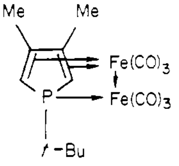
The fact that phospholes (L) can act as six-electron ligands by complexation of their phosphorus atoms and of their dienic systems with two different metal atoms was suspected as early as 1961[2] and was fully demonstrated more recently when the X-ray crystal structure of one $LMn_2(CO)_7$ complex[3] was established.[4] It has also been shown in our laboratory that the formation of a bond between the two complexed metals was dependent on the bulkiness of the phosphole P substituent.[5] Thus, when heated with triiron dodecacarbonyl, 1-phenyl-3,4-dimethylphosphole (**1**) gave an $LFe_2(CO)_7$ complex with no Fe–Fe bond whereas 1-*tert*-butyl-3,4-dimethylphosphole (**2**) gave a metal–metal bonded $LFe_2(CO)_6$ species. This intriguing observation was the starting point of a more exhaustive investigation of the reactions of iron carbonyls with phospholes, which led to the discovery of new types of bimetallic sandwiches described herein.

Results and Discussion

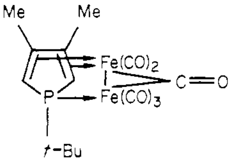
Synthesis. All our work has been carried out with phospholes **1** and **2**. At first we reinvestigated the reaction of **2** with $Fe_3(CO)_{12}$. In our previous work,[5] this reaction was performed at 110 °C in boiling toluene and gave predominantly the Fe–Fe bonded species **3**. Since no band could be ascribed to a bridging carbonyl in the IR spectrum of **3**, we proposed the structure **3A** for this complex. However, in view of the structural results of Weiss[6] on ferrole **4**, which had a semibridging carbonyl as shown despite the absence of ν(CO) absorptions in the bridging carbonyl region of the IR spectrum, the correct structure might be **3B**. Unfortunately the room-temperature ^{13}C NMR spectrum of **3** ($CDCl_3$, Me_4Si) did not allow us to choose between the two formulations since all the ^{13}CO resonances appeared equivalent on the NMR time scale [δ(CO) = 213.63; J(C–P) = 5.8 Hz] contrary to what happens for ferrole **4**.[7] During this reinvestigation we also detected another complex to which we ascribed the structure **6** [identical with that of the main product (**5**) of the reaction of **1** with $Fe_3(CO)_{12}$] on the basis of the C, H, and Fe analysis, the IR spectrum (very similar to that of **5**), and the ^{31}P NMR spectrum [^{31}P δ(**6**) = 113.9, very close to the calculated value for **6**; see ref 5]. This complex was only a byproduct (maximum yield 10%) and disappeared completely if the reaction was run at 150 °C in boiling xylene. Thus it seemed that **6** decomposed to give **3** in boiling xylene, and we tried to extend this reaction to **5**. When heated at 150 °C in xylene for 24 h, **5** gave indeed a new complex but with the unexpected formula **7**. In view of this formula, which was fully established



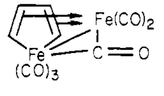
1, R = Ph
2, R = *t*-Bu



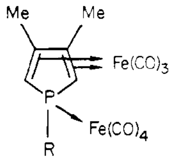
3A



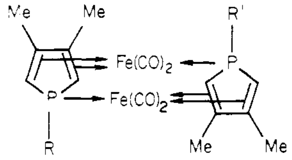
3B



4



5, R = Ph
6, R = *t*-Bu



7, R = R′ = Ph
8, R = R′ = *t*-Bu
9, R = Ph, R′ = *t*-Bu

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(1) (a) Laboratoire CNRS-SNPE. (b) Institut Le Bel.
(2) E. H. Braye, W. Hubel, and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961).
(3) F. Mathey, *J. Organomet. Chem.*, **93**, 377 (1975).
(4) J. M. Rosalky, B. Metz, F. Mathey, and R. Weiss, *Inorg. Chem.*, **16**, 3307 (1977).
(5) F. Mathey and G. Muller, *J. Organomet. Chem.*, **136**, 241 (1977).
(6) G. Dettlaf and E. Weiss, *J. Organomet. Chem.*, **108**, 213 (1976).
(7) P. Hübener and E. Weiss, *J. Organomet. Chem.*, **129**, 105 (1977).

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)	*B*(eqv)
Fe	0.12030 (4)	0.49027 (4)	0.11000 (3)	3.47 (2)	2.51 (2)	2.20 (2)	0.52 (2)	1.06 (1)	−0.22 (2)	2.73 (1)
P	−0.02555 (7)	0.38115 (7)	−0.02582 (5)	3.58 (3)	2.36 (3)	2.26 (3)	0.38 (3)	1.27 (2)	−0.21 (3)	2.69 (2)
O1	0.3192 (2)	0.5764 (3)	0.1382 (2)	5.0 (1)	7.1 (2)	6.5 (1)	−1.4 (1)	3.0 (1)	−1.8 (1)	5.95 (9)
O2	0.1224 (2)	0.5642 (3)	0.2787 (2)	7.3 (1)	6.3 (2)	3.2 (1)	−0.2 (1)	2.34 (9)	−1.6 (1)	5.51 (8)
C1	0.0023 (3)	0.3809 (3)	0.0900 (2)	4.5 (1)	2.4 (1)	2.7 (1)	0.0 (1)	1.7 (1)	−0.4 (1)	3.10 (8)
C2	0.0988 (3)	0.3316 (3)	0.1374 (2)	5.4 (2)	2.8 (2)	2.5 (1)	0.9 (1)	1.4 (1)	0.1 (1)	3.59 (9)
C3	0.1604 (3)	0.3361 (3)	0.0876 (2)	4.2 (2)	2.7 (2)	3.1 (1)	0.8 (1)	1.2 (1)	−0.4 (1)	3.40 (9)
C4	0.1078 (3)	0.3877 (3)	0.0047 (2)	3.8 (1)	2.6 (1)	2.7 (1)	0.3 (1)	1.6 (1)	−0.3 (1)	2.94 (8)
C5	0.1288 (4)	0.2787 (4)	0.2259 (3)	8.1 (2)	4.3 (2)	3.2 (2)	1.2 (2)	2.0 (1)	0.9 (2)	5.2 (1)
C6	0.2658 (3)	0.2912 (4)	0.1160 (3)	5.4 (2)	5.1 (2)	4.3 (2)	2.7 (2)	1.0 (1)	−0.4 (2)	5.2 (1)
C7	−0.0652 (3)	0.2430 (3)	−0.0652 (2)	3.8 (1)	2.4 (1)	2.9 (1)	0.2 (1)	0.9 (1)	−0.2 (1)	3.15 (8)
C8	−0.0360 (3)	0.1956 (4)	−0.1268 (3)	5.1 (2)	4.1 (2)	5.5 (2)	−0.6 (2)	2.4 (1)	−1.5 (2)	4.8 (1)
C9	−0.0633 (4)	0.0907 (4)	−0.1541 (3)	6.8 (2)	5.3 (2)	6.9 (2)	−0.3 (2)	3.1 (2)	−3.3 (2)	6.2 (1)
C10	−0.1203 (4)	0.0327 (4)	−0.1205 (3)	9.1 (3)	3.6 (2)	6.7 (3)	−0.8 (2)	2.5 (2)	−1.7 (2)	6.6 (2)
C11	−0.1517 (5)	0.0793 (4)	−0.0609 (4)	12.3 (3)	5.1 (2)	8.1 (2)	−3.8 (2)	5.9 (2)	−2.0 (2)	7.9 (2)
C12	−0.1229 (4)	0.1841 (4)	0.0325 (3)	10.3 (2)	4.3 (2)	6.0 (2)	−2.3 (2)	5.4 (1)	−1.6 (2)	6.2 (1)
C13	0.2405 (3)	0.5452 (3)	0.1266 (2)	4.2 (1)	3.9 (2)	3.5 (1)	0.2 (1)	1.6 (1)	−0.8 (1)	3.81 (9)
C14	0.1220 (3)	0.5377 (3)	0.2118 (2)	4.1 (2)	3.4 (2)	3.0 (1)	0.4 (1)	1.1 (1)	−0.3 (1)	3.57 (9)

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

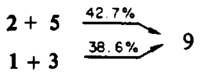
by X-ray analysis (see below), we devised an optimized synthesis of **7** by reaction of the free phosphole **1** with **5**:

$$\mathbf{1} + \mathbf{5} \xrightarrow[24\ \mathrm{h}]{150\ ^\circ\mathrm{C,\ xylene}} \mathbf{7} \quad \text{(yield 47\%)}$$

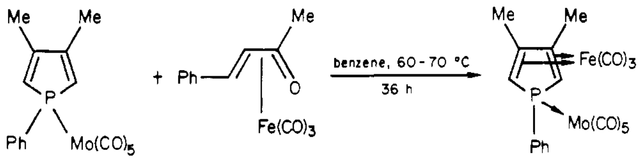
This scheme was extended to the synthesis of **8**:

$$\mathbf{2} + \mathbf{3} \rightarrow \mathbf{8} \quad \text{(yield 46\%)}$$

In this case it must be noted that the Fe–Fe bond of **3** was cleaved during the reaction. We were also able to prepare the mixed complex **9** either by reaction of **2** with **5** or by reaction of **1** with **3**:



At this point, this type of reaction already appeared to be quite general. It was nevertheless obviously interesting to extend further its scope by trying to incorporate two different metals between the two phospholes. For that purpose we started from the LMo(CO)$_5$ complex **10**.[8] Reaction with (benzylideneacetone)tricarbonyliron gave the bimetallic complex **11**:

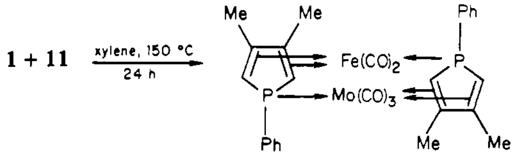


10

11

yield 59%

This complex was in turn reacted with the free phosphole **1** to give the bimetallic sandwich **12** in a surprisingly high yield:



12

yield 92%

The preferential coordination of the molybdenum atom with the dienic system of the second phosphole nucleus is rather unusual. Generally molybdenum has a much higher tendency to coordinate with trivalent phosphorus than with dienes. In this case the presence of two nonequivalent phosphorus atoms and two nonequivalent dienic systems in the NMR spectra is definitive proof of the proposed structure.

Table II. Contacts between Molecules

A···B	dist, Å	equiv position for atom B
H8[a]···H61	2.76	$^1/_2 - x$, $^1/_2 - y$, z
H9···H9	2.48	$\bar{x}$, y, $^1/_2 - z$
H10···H52	2.43	$\bar{x}$, $\bar{y}$, $\bar{z}$
H1···H4	2.62	$\bar{x}$, $1 - y$, $\bar{z}$
H51···H51	2.21	$\bar{x}$, y, $^1/_2 - z$
H52···O1	2.68	$^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$
H52···H10	2.43	$\bar{x}$, $\bar{y}$, $\bar{z}$
H61···H61	2.56	$^1/_2 - x$, $^1/_2 - y$, $\bar{z}$
H63···O2	2.58	$^1/_2 - x$, $^1/_2 - y$, $\bar{z}$

[a] The labels of hydrogen atoms are derived from those of the corresponding carbon atoms, the first digit indicating the carbon number and the second the hydrogen number for methylene and methyl groups.

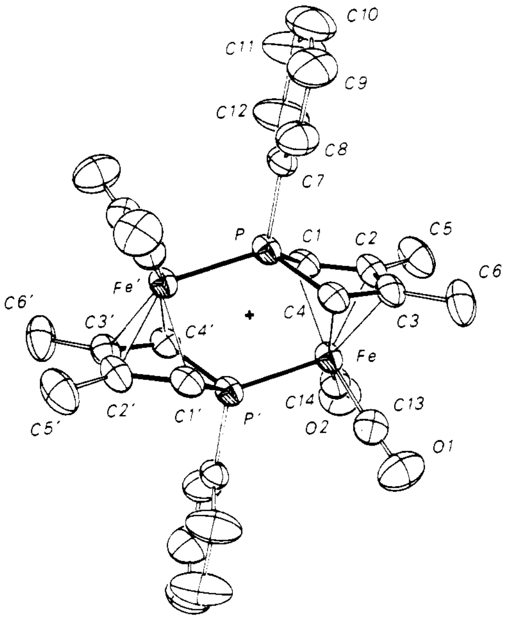


Figure 1. ORTEP[22] plot of the dimer L$_2$Fe$_2$(CO)$_4$ without hydrogen atoms and with the labeling scheme used in this paper. Atoms are represented by their ellipsoids of thermal motion scaled to enclose 50% of the electron density.

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(8) C. Santini, J. Fischer, F. Mathey, and A. Mitschler, *J. Am. Chem. Soc.*, **102**, 5809 (1980).

Table III. Least-Squares Mean Planes[a]

plane	equation	dev from plane, Å
PL1	$0.8531x + 0.0002y - 0.5218z = 0$	P 0.033 (1), Fe 0.005 (1), P′ −0.031 (1) C1 −1.170 (4), C4 1.256 (4) C2 −0.624 (4), C3 0.795 (4) C5 −1.437 (5), C6 1.704 (5) C7 0.072 (4) C8 1.251 (5), C12 −1.068 (5) C9 1.281 (5), C11 −1.043 (7) C10 0.136 (5) C13 1.253 (4), C14 −1.332 (4) O1 2.061 (3), O2 −2.219 (3)
PL2	$-0.2220x - 0.8845y - 0.4102z - 4.6102 = 0$	C1 −0.001 (3), C2 0.002 (4) C3 −0.002 (4), C4 0.001 (3) P 0.644 (1), Fe −1.671 (1)
PL3	$-0.0451x + 0.9990y - 0.0066z + 4.7236 = 0$	P, C1, C4 in plane Fe 1.280 (1)

[a] The reference system used was described by D. M. Blow, *Acta Crystallogr.*, **13**, 168 (1960).

Table IV. Selected Bond Length (Å) and Angles (Deg) with Their Esd's

Fe–P	2.757 (1)		C2–C5	1.503 (5)	1.504 (3)
Fe–P′[a]	2.202 (1)		C3–C6	1.505 (5)	
Fe–C1	2.091 (4)	2.080 (2)	C7–C8	1.370 (5)	1.367 (3)
Fe–C2	2.064 (4)		C8–C9	1.381 (6)	
Fe–C3	2.067 (3)		C9–C10	1.355 (7)	
Fe–C4	2.100 (3)		C10–C11	1.356 (7)	
P–C1	1.791 (3)	1.786 (2)	C11–C12	1.386 (7)	
P–C4	1.781 (4)		C12–C7	1.358 (6)	
P–C7	1.839 (4)		Fe–C13	1.772 (5)	1.769 (3)
C1–C2	1.436 (5)	1.429 (3)	Fe–C14	1.767 (4)	
C2–C3	1.420 (5)		C13–O1	1.138 (5)	1.143 (3)
C3–C4	1.431 (5)		C14–O2	1.148 (5)	

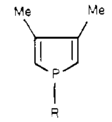
C13–Fe–P′	134.5 (1)	P–C1–C2	110.7 (2)
C14–Fe–P′	131.4 (1)	P–C4–C3	111.3 (2)
C13–Fe–C14	93.9 (2)	C1–C2–C3	110.6 (3)
Fe′–P–C7	114.6 (1)	C4–C3–C2	110.5 (3)
Fe′–P–C1	120.1 (1)	C1–C2–C5	124.7 (4)
Fe′–P–C4	118.7 (1)	C4–C3–C6	125.4 (3)
C7–P–C1	106.6 (1)	Fe–P–Fe′	104.39 (4)
C7–P–C4	107.1 (1)	P–Fe–P′	75.61 (4)
C1–P–C4	85.6 (1)		

[a] Fe′ and P′ refer to equivalent Fe and P atoms derived from the originals by a center of symmetry of the unit cell.

Table V. Structural Comparisons of the Phosphole Rings in Various Complexes

	P–C, Å				
products[a]	mean intracyclic	exocyclic	C–P–C, deg	ring folding, deg	ref
1-benzylphosphole	1.783	1.858	90.7	9.6	11
$L_2Fe_2(CO)_4$ (R = Ph)	1.786	1.839	85.6	29.4	this work
$LMn_2(CO)_7$ (R = *t*-Bu)	1.778	1.858	87.7	11.8	4
cis-L_2PdCl_2 (R = Ph)	1.795	1.815	92.7	~0	0

[a] The structure for L is as follows:



Crystal Structure of Complex 7. Table I gives the coordinates $B(i,j)$ and B(eqv) with their estimated standard deviations for all nonhydrogen atoms.

The crystal structure of $L_2Fe_2(CO)_4$ **7** consists of discrete molecules only linked by van der Waals contacts and hydrogen bonds; the molecular contacts are listed in Table II. One discrete $L_2Fe_2(CO)_4$ group is in fact a dimer of $LFe(CO)_2$ moieties related by a crystallographic center of symmetry as shown in Figure 1. Table III gives the least-squares mean planes of interest. Together with the inversion center, the whole dimer possesses a pseudo mirror plane containing the inversion center, the two iron atoms, and the two phosphorus atoms as shown by the distances of all atoms to mean plane PL1 in Table III.

Table IV gives selected bond lengths and bond angles with averages and estimated standard deviations.

The most significant features of this structure are as follows: (a) The Fe⋯Fe distance (3.933 Å) is very long, which precludes any kind of direct interaction between the two iron atoms. (b) The P⋯Fe distance (2.757 Å) is rather short compared with the length of the true P—Fe′ bond (2.202 Å);[9] this distance is well inside the sum of the van der Waals radii (P ≃1.85 Å; Fe ≃1.70 Å) and may allow direct interactions between these two atoms.[10a] (c) The folding of the phosphole nuclei around the C1–C4 and C1′–C4′ axes is impressive; some comparative data are given in Table V. On the basis of other literature data on monometallic π complexes of phospholes,[10b] it seems that this folding is a direct consequence of the π complexation of the diene portion of the phosphole rings, resulting in the short P⋯Fe distance already mentioned.

In spite of such folding the intracyclic P–C bonds remain significantly shorter than that of the exocyclic P–C bonds as in free phospholes. In fact, the comparison with the data for the $LMn_2(CO)_7$ structure seems to indicate that this P–C bond shortening is completely insensitive to the variations of the phosphole folding in the σ,π complexes. This observation suggests that the shortening is not due to some cyclic delocalization within the ring as in free phospholes but is just another consequence of the π complexation of the dienic system, which probably increases the electronegativity of the ring carbons and induces some polarity in the P–C bonds together with a slight strengthening (see ref 13 for a discussion of the factors influencing the strength of the heteropolar bonds with phosphorus.

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(9) E. A. Koerner von Gustorf, T. W. Grevels, and J. Fischler, "The Organic Chemistry of Iron", Vol. 1, Academic Press, New York, 1978, Chapter 1.

(10) (a) This point has been made by one of the reviewers. (b) K. Yasufuku, A. Amada, K. Aoki, and H. Yamazaki, *J. Am. Chem. Soc.*, **102**, 4363 (1980); M. J. Barrow, A. A. Freer, W. Harrison, G. A. Sim, D. W. Taylor, and F. B. Wilson, *J. Chem. Soc., Dalton Trans.*, 197 (1975).

(11) P. Coggon and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 1888 (1973).

(12) J. J. MacDougall, J. H. Nelson, F. Mathey, and J. J. Mayerle, *Inorg. Chem.*, **19**, 709 (1980).

(13) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry", Academic Press, New York, 1965, p 11; for a more recent discussion see also J. Emsley and D. Hall, "The Chemistry of Phosphorus", Harper and Row, London, 1976.

Spectral Data. These data are extensively given in the Experimental Section; however we wish here to cast some light upon two special spectral features of complexes **7**–**9** and **12**. In complexes **9** and **12**, which possess two dissimilar phosphorus atoms, a large ^{31}P$\cdots$^{31}P NMR coupling is observed (respectively 152.4 and 206.3 Hz). At this point three facts must be remembered: (a) In complex **7**, the arrangement of the phosphorus atoms around the metal atoms is approximately cis (P–Fe–P′ = 75.61°). (b) ^{2}J(P–P) cis couplings as large as 685 Hz have been already observed in some transition-metal complexes.[14] (c) A direct through-space interaction between P and Fe atoms is possible in complex **7**.

Thus one possible explanation of the large couplings observed here would be to consider them as pseudo-^{2}J(P–P) cis couplings $P\cdots\text{Fe}{-}P'$; this would also explain the spectral features of the *t*-Bu–P and cyclic CH–P proton resonances in complexes **7** and **8** (pseudotriplets; X part of $X_nAA'X'_n$ spectrum).[15]

Experimental Section

General Comments. NMR spectra (in CDCl$_3$) [chemical shifts in ppm from internal Me$_4$Si for ^{1}H and from 85% H$_3$PO$_4$ (external reference) for ^{31}P; δ positive for downfield shifts in all cases] were recorded for the proton resonances on a Perkin-Elmer R12 at 60 MHz and for the phosphorus resonances on a Bruker WH-90 at 36.447 MHz. IR spectra (in hexane) were recorded on a Perkin-Elmer Model 457 and mass spectra on a VG-micromass 70-70F spectrometer at 70 eV (Service Central de Microanalyse, Lyon). Elemental analyses were performed by Service Central de Microanalyse de l'Ircha, Vert-le-Petit. All reactions were carried out under argon. Chromatographic separations were performed on silica gel columns (70–230 mesh, Merck). 1-Phenyl-3,4-dimethylphosphole (DMP),[16] 1-*tert*-butyl-3,4-dimethylphosphole (TBP),[17] (DMP)Fe$_2$(CO)$_7$,[5] (TBP)-Fe$_2$(CO)$_6$,[5] (DMP)Mo(CO)$_5$,[8] and (benzylideneacetone)tricarbonyliron[18] ((BDA)Fe(CO)$_3$) ((BDA)Fe(CO)$_3$) were synthesized according to the literature.

General Procedure. (1-*tert*-Butyl-3,4-dimethylphosphole)heptacarbonyldiiron (6). The reaction was performed as described in ref 5. The two complexes **3** and **6** were separated by chromatography (eluant 80:20 hexane–benzene): R_f(**3**) 0.6, R_f(**6**) 0.3; yield ~10%; yellow crystals (hexane); mp 98 °C. Anal. Calcd for C$_{17}$H$_{17}$Fe$_2$O$_7$P: C, 42..89; H, 3.60; Fe, 23.46. Found: C, 43.49; H, 3.99; Fe, 23.29. IR: ν(CO) 2062, 2042, 2007, 1991 br, 1968 sh, 1956 br, vs, 1937 cm^{-1}. ^{1}H NMR: δ 0.68 (d, $^{3}J_{PH}$ = 13.6 Hz, 9 H, *t*-Bu), 1.56 (s, 6 H, Me), 2.40 (d, $^{2}J_{PH}$ = 24.0 Hz, 2 H, ═CH). ^{31}P NMR: δ +113.9.

Bis[μ-(1-phenyl-3,4-dimethylphosphole)]-bis(dicarbonyliron) (7). (DMP)Fe$_2$(CO)$_7$ (1.49 g, 3 × 10^{-3} mol), DMP (0.6 g, 3.19 × 10^{-3} mol), and xylene (50 mL) placed in a 100-mL Erlenmeyer flask were heated at reflux with stirring under argon for 24 h. After the solution was cooled to room temperature, the black precipitate that formed was removed by filtration, the solvent evaporated, and the crude complex purified by chromatography (eluant 80:20 hexane–benzene) affording 0.85 g (47%) of **7** (R_f 0.41): yellow crystals (benzene); mp 278 °C dec. Anal. Calcd for C$_{28}$H$_{26}$Fe$_2$O$_4$P$_2$: C, 56.03; H, 4.37; Fe, 18.66. Found: C, 56.34; H, 4.40; Fe, 17.67. IR: ν(CO) 1975, 1915 cm^{-1}. ^{1}H NMR: δ 2.25 (s, Me), 2.49 (pseudotriplet, $^{2}J_{PH} \simeq$ 27 Hz, ═CH), 7.12 and 7.22 (m, *o*-H, *m*-H). ^{31}P NMR: δ +63.5. Mass spectrum (120 °C): *m/e* 600 (16%) [M], 572 (45%) [M – CO], 488 (32%) [M – 4CO], 334 (100%) [M – 4CO – 2Ph],

Bis[μ-(*tert*-butyl-3,4-dimethylphosphole)]-bis(dicarbonyliron) (8). Yellow crystals were prepared from (TBP)Fe$_2$(CO)$_6$ (0.52 g, 1.16 × 10^{-3} mol) and TBP (0.16 g, 10^{-3} mol): yield 0.3 g, 46%; R_f 0.78; mp 240.8 °C dec. Anal. Calcd for C$_{24}$H$_{34}$Fe$_2$O$_4$P$_2$: C, 51.45; H, 6.11; Fe, 19.93. Found: C, 52.21; H, 6.30; Fe, 19.56. IR: ν(CO) 1975 and 1927 cm^{-1}. ^{1}H NMR: δ 0.925 (pseudotriplet, $^{3}J_{PH}$ = 12.6 Hz, *t*-Bu), 2.06 (pseudotriplet, $^{2}J_{PH}$ = 25.3 Hz, ═CH), 2.18 (s, Me). ^{31}P NMR: δ +97.92. Mass spectrum (140 °C): *m/e* 560 (~0%) [M], 503 (100%) [M – *t*-Bu], 447 (28%) [M – *t*-Bu – 2CO], 419 (57%) [M – *t*-Bu – 3CO], 391 (46%) [M – *t*-Bu – 4CO], 334 (94%) [M – 2*t*-Bu – 4CO], 278 (85%) [bis(3,4-dimethylphosphollyl)iron], 168 (0%) [TBP].

μ-(1-Phenyl-3,4-dimethylphosphole)-μ-(1-*tert*-butyl-3,4-dimethylphosphole)-bis(dicarbonyliron) (9). The compound was first prepared from (DMP)Fe$_2$(CO)$_7$ (0.48 g, 0.96 × 10^{-3} mol) and TBP (0.18 g, 1.07 × 10^{-3} mol): yield 0.24 g, 42.7% R_f 0.6; mp (4:1 MeOH–C$_6$H$_6$) 224.2 °C. Yellow crystals of **7** (0.1 g, 17.2%; R_f 0.4) were also obtained. The second preparation used (TBP)Fe$_2$(CO)$_6$ (1.0 g, 2.2 × 10^{-3} mol) and DMP (0.4 g, 2.12 × 10^{-3} mol): yield 0.5 g, 38.6% of **9**. Anal. Calcd for C$_{26}$H$_{30}$Fe$_2$O$_4$P$_2$: C, 53.82; H, 5.21; Fe, 19.2; P, 10.67. Found: C, 53.88; H, 5.40; Fe, 19.03; P, 10.35. IR: ν(CO) 1993 m, 1982 s, 1936 s, 1931 s cm^{-1}. ^{1}H NMR: δ 0.86 (d, $^{3}J_{PH}$ = 12 Hz, *t*-Bu), 2.06 (d, $^{2}J_{PH}$ = 25.5 Hz, ═CH), 2.11 (d, $^{4}J_{PH}$ = 2.2 Hz, Me), 2.16 (d, $^{4}J_{PH}$ = 2.3 Hz, Me), 2.36 (d, $^{2}J_{PH}$ = 25.0 Hz, ═CH), 7.08 (m, *o*-H), 7.18 (m, *m*-H). ^{31}P NMR (AB system): δ_A 97.74, δ_B 64.32, J_{AB} = 152.59 Hz. Mass spectrum (140 °C): *m/e* 552 (≃0%) [M – CO], 524 (23%) [M – 2CO], 523 (79%) [M – *t*-Bu], 468 (9%) [M – 4CO], 467 (26%) [M – *t*-Bu – 2CO], 439 (29%) [M – *t*-Bu – 3CO], 412 (26%) [M – 4CO – Fe], 411 (100%) [M – *t*-Bu – 4CO], 278 (15%) [bis(3,4-dimethylphosphollyl)iron].

[η^4-(1-Phenyl-3,4-dimethylphosphole)tricarbonyliron)-*P*]pentacarbonylmolybdenum (11). (BDA)Fe(CO)$_3$ (0.83 g, 2.90 × 10^{-3} mol) and (DMP)Mo(CO)$_5$ (1.02 g, 2.40 × 10^{-3} mol) were heated in benzene (90 mL) at 60–70 °C with stirring under argon for 36 h. After the mixture was cooled to room temperature, the solvent was evaporated and the brown oily residue was chromatographed (eluant hexane), affording 0.35 g of unreacted (DMP)Mo(CO)$_5$ (R_f = 0.34) and then 0.53 g (yield 59.4%) of **11** (R_f 0.17); bright yellow crystals mp (hexane) 129 °C. Anal. Calcd for C$_{20}$H$_{13}$FeMoO$_8$P: C, 42.58; H, 2.32; Fe, 9.90; Mo, 17.0; P, 5.49. Found: C, 42.36; H, 2.21; Fe, 9.81; Mo, 16.90; P, 5.46. IR: ν(CO) 2070 w, 2050 s, 2000 s, 1987 s, br, 1946 vs, br cm^{-1}. ^{1}H NMR: δ 2.46 (s, Me), 2.7 (d, $^{2}J_{PH}$ = 19.6 Hz, ═CH), 7.16 (m, *o*-H), 7.3 (m, *m*-H). ^{31}P NMR: δ +134.15. Mass spectrum (140 °C; ^{98}Mo): *m/e* 566 (14%) [M], 342 (100%) [M – 8CO], 286 (95) [M – 8CO – Fe].

Bis[μ-(1-phenyl-3,4-dimethylphosphole)]-(dicarbonyliron)(tricarbonylmolybdenum) (12). **11** (0.53 g, 0.93 × 10^{-3} mol) and DMP (0.176 g, 0.94 × 10^{-3} mol) (20 mL) were heated in xylene at reflux with stirring under argon for 24 h. After evaporation of solvent and chromatography (R_f 0.5) 0.58 g (92%) of **12** was obtained: yellow-orange crystals; mp 220 °C dec. Anal. Calcd for C$_{29}$H$_{26}$FeMoO$_5$P$_2$: C, 52.12; H, 3.92; Fe, 8.35; Mo, 14.35. Found: C, 51.98; H, 3.86; Fe, 8.40; Mo, 14.90. IR: ν(CO) 1982 s, 1930 s, 1915 m, 1897 s cm^{-1}. ^{1}H NMR: δ 2.19 (s, Me), 2.24 (s, Me), 2.48 (d, $^{2}J_{PH}$ = 27.7 Hz, ═CH), 3.41 (d, $^{2}J_{PH}$ = 27.1 Hz, ═CH), 7.22 (m, Ph), 7.25 (m, Ph). ^{31}P NMR (AB system): δ_A 35.35, δ_B 74.16, J_{AB} = 206.3 Hz. Mass spectrum (140 °C, ^{98}Mo): *m/e* 670 (13%) [M], 642 (66%) [M – CO], 586 (35%) [M – 3CO], 558 (52%) [M – 4CO], 530 (100%) [M – 5CO].

X-ray Data Collecting and Processing. Suitable single crystals of **7** were obtained by slow evaporation at room temperature of chlorobenzene solutions.

Preliminary precession photographs and a systematic search in reciprocal space using a Enraf-Nonius CAD-4F automatic diffractometer show that crystals of **7** belong to the monoclinic system and that the space group is $C2/c$ or Cc.

The unit-cell dimensions and their standard deviations were obtained and refined at room temperature with Cu Kα radiation (λ = 1.5418 Å) by using the standard Enraf-Nonius software. The experimental density was measured by flotation in aqueous KI solution. Final results: Fe$_2$P$_2$O$_4$C$_{28}$H$_{26}$, mol wt 600, a = 14.334 (1) Å, b = 12.375 (1) Å, c = 16.470 (1) Å, β = 112.62 (1)°, V = 2697 Å^3, d_{obsd} = 1.46 ± 0.03 g cm^{-3}, Z = 4, d_{calcd} = 1.478 g cm^{-3}, $C2/c$ or Cc, μ = 101.7 cm^{-1}.

An octahedral crystal 0.38 × 0.42 × 0.48 mm was sealed in a Lindemann glass capillary and mounted on a rotation-free goniometer head. All quantitative data were obtained from a CAD-4F four-circle diffractometer, controlled by a PDP8/A computer, using filtered radiation and standard software.

The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width in the $\omega/2\theta$ mode used was $\Delta\omega$ = 0.9° + (Cu Kα_1,α_2 splitting). All reflections were prescanned with a scan speed of 2° min^{-1}; if $\sigma(I)/I$ of the scan was greater than 1, the reflection was flagged weak and not

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measured. The final scan speed used was such that $\sigma(I)/I$ approaches 0.33 with a maximum counting time of 90 s; 3936 hkl, $hk\bar{l}$, $h\bar{k}l$, and $h\bar{k}\bar{l}$ reflections were prescanned ($2° < \theta < 60°$).

Three standard reflections measured every hour during the entire data collection period showed no significant trend in intensity.

The resulting data set was transferred to a PDP 11/60 computer, and for all subsequent computations the Enraf-Nonius SDP/V16 package[19] was used.

Intensities were corrected for Lorentz, polarization, and absorption factors, the last being computed by numerical integration[20] (transmission factors between 0.04 and 0.25). The 3936 measurements were sorted and averaged, leading to a unique data set of 1807 reflections; 178 of these had $\sigma(I)/I > 0.4$ and were considered as unobserved. Finally, 1629 reflections were used for refining the structure.

The statistical distribution of E values in reciprocal space and the cumulative Nz test on $|F_{\text{obsd}}|$ excluded the noncentrosymmetric space group Cc. The structure was solved by a direct method using MULTAN.[21] All nonhydrogen atoms could be located in the Fourier map computed with the phases of the most probable set of MULTAN. Hydrogen atoms were introduced in structure factor calculation by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors (B_H = 6 Å^2) but not refined. The CH_3 hydrogen atoms were previously located in a difference map. The temperature factors of all converged to $R(F) = 0.038$ and $R_w(F) = 0.050$. The unit-weight observation was 1.24 with a fudge factor of 0.07. The final difference map showed no maxima greater than 0.2 e Å^{-3}. Table VI (supplementary material) gives h, k, l, F_o, and F_c times 10 for all observed structure factors.

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Registry No. **3**, 64367-53-9; **5**, R = Ph, 64367-52-8; **6**, 77611-22-4; **7**, 77611-23-5; **8**, 77611-24-6; **9**, 77611-25-7; **10**, 74363-92-1; **11**, 77611-26-8; **12**, 77629-03-9; (BDA)Fe(CO)$_3$, 38720-22-8.

Supplementary Material Available: Table VI, observed and computed structure factors for all observed reflections (7 pages). Ordering information is given on any current masthead page.

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Reexamination of the Crystal and Molecular Structure of Tricarbonyl(η^5-cyclopentadienyl)manganese(I): Structural and Spectroscopic Evidence for a Distortion of the Cyclopentadienyl Ring Framework and Its Implications on Bonding in a Molecule Possessing Cylindrical Symmetry[1]

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The crystal and molecular structure of tricarbonyl(η^5-cyclopentadienyl)manganese(I), CpMn(CO)$_3$ (Cp = η^5-C_5H_5), has been reinvestigated by three-dimensional single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/a$ with unit cell parameters a = 12.077 (3) Å, b = 7.057 (2) Å, c = 10.913 (2) Å, β = 117.68 (2)°, V_{calcd} = 823.5 Å^3, mol wt 204.06, and d_{calcd} = 1.646 g cm^{-3}. Intensity data were collected with use of Mo Kα radiation with peak-profile analysis of the 2θ scan results. A total of 2415 symmetry-independent reflections were collected, of which 1619 had $I \geq 3\sigma(I)$ and were included in the structure refinement, which converged to conventional residuals of R_1 = 0.0286 and R_2 = 0.0205. Contrary to the earlier work of Berndt and Marsh, the C_5H_5 ring appears to deviate significantly from a regular pentagon so as to approach planar C_{2v} symmetry. This result is indicative of some localized C–C bonding throughout the ring, highly unexpected for a molecule that possesses effective cylindrical symmetry about the metal atom. These results are similar to those that have been reported earlier for the isostructural CpRe(CO)$_3$ compound. Thermal motion analyses for the various molecular fragments reveal that the apparent distortion is not due to the librational motion of the ring about the molecular axis, and the corrected individual C–C bond distances in the ring range between 1.400 (3) and 1.439 (3) Å. Vibrational studies of CpMn(CO)$_3$ in solution are also reported, which support a breakdown of the fivefold symmetry of the ring outside of the crystalline environment. The implications on the bonding within the cyclopentadienyl ring in these simple molecules and other related complexes are discussed in terms of possible solid-state and electronic effects.

Introduction

Recently, there has been renewed interest in the origin and magnitudes of inter- and intramolecular rotational barriers in substituted and unsubstituted arene- and cyclopentadienyl-metal complexes[3,4] and in the nature of the metal–Cp ring bonding in the latter class of compounds.[5] Tricarbonyl(η^5-cyclopentadienyl)manganese(I), CpMn(CO)$_3$ (Cp = η^5-C_5H_5), was one of the first half-sandwich complexes

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