

Prof. Gary E. Keck for helpful synthetic advice.

**Registry No.** I, 85908-78-7; II, 85893-68-1; ruthenium trichloride, 10049-08-8; 2,3,4-trimethyl-1,3-pentadiene, 85893-67-0; 2,4-dimethyl-1,3-pentadiene, 1000-86-8.

**Supplementary Material Available:** A listing of non-hydrogen atom anisotropic thermal parameters (Table II), the hydrogen atom parameters (Table III), least-squares plane data (Table V), and the structure amplitude table (22 pages). Ordering information is given on any current masthead page.

## Preparation of 3,3',4,4'-Tetramethyl-1,1'-biphospholyl and Its Reactions with Iron and Cobalt Carbonyls. Synthesis and X-ray Crystal Structure of a Phospholyl Complex with a Chain of Four Cobalt Atoms

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Received January 31, 1983

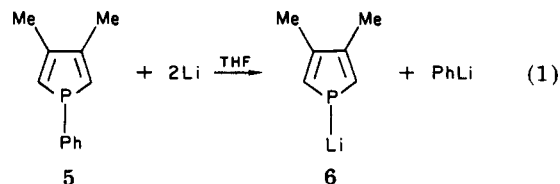
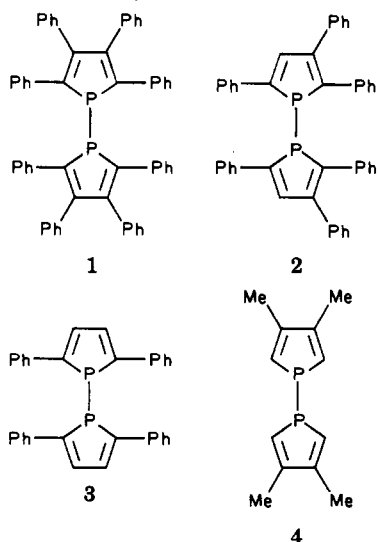
3,3',4,4'-Tetramethyl-1,1'-biphospholyl (L-L) has been prepared by reaction of iodine with (3,4-dimethylphospholyl)lithium (L-Li) in the presence of  $\text{AlPh}_3$ . It reacts with  $\text{Fe}_2(\text{CO})_9$  to yield a mixture of  $\text{L}_2\text{Fe}_2(\text{CO})_6$ ,  $\text{L}_2\text{Fe}_3(\text{CO})_9$ , and  $\text{L}_2\text{Fe}_4(\text{CO})_{12}$ . The first compound is a classical phosphido-bridged species in which L acts as a three-electron donor through its phosphorus atom. The  $\eta^4$  complexation by  $\text{Fe}(\text{CO})_5$  of the dienic system of one of the phospholyl units in  $\text{L}_2\text{Fe}_2(\text{CO})_6$  produces the second complex. In the third compound, both phospholyls act as (4 + 3)-electron donors. The reaction of L-L with  $\text{Co}_2(\text{CO})_8$  yields  $\text{L}_2\text{Co}_4(\text{CO})_8$  which has been shown by X-ray crystal structure analysis to contain a chain of four cobalt atoms sandwiched between two phospholyl units again acting as (4 + 3)-electron donors.

1,1'-Biphospholyls are especially interesting molecules for three main reasons: (a) They are convenient sources for a wide range of unknown phospholes with P substituents such as alkoxy, amino, halo, etc.... (b) They offer the opportunity to study a fulvalene-like interaction between two  $6\pi$ -electron phosphole rings. (c) They can be used as generators of phospholyl radicals through thermal or UV-induced homolytic cleavage of the phosphorus-phosphorus bond. Up to now, only three such species were known 1-3.<sup>2-4</sup> Unfortunately, in all cases, the substitution

drastically alters the properties of the phosphole rings since the phenyl groups conjugate with the diene systems and hinder the phosphorus lone pairs. We report hereafter on the synthesis of 4 which is the first discovered fully representative 1,1'-biphospholyl and on its very peculiar coordinating behavior toward iron and cobalt carbonyls.

### Results and Discussion

**Synthesis and Coordination Chemistry of 4.** The only easily available starting material for the synthesis of 4 is the 3,4-dimethylphospholyl anion 6 obtained by lithium cleavage of the phosphorus-phenyl bond<sup>5</sup> in 1-phenyl-3,4-dimethylphosphole (eq 1). However, the

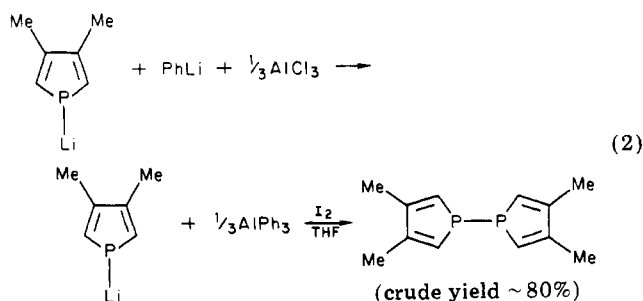


treatment of the crude mixture of 6 and phenyllithium by phosgene in strict analogy with the successful synthesis of 3<sup>4</sup> does not produce the expected biphospholyl. Similarly, the reaction of this mixture with iodine produces mainly 5 through cross-coupling of 6 and phenyllithium and yields only minute amounts of 4. On the other hand, if phenyllithium is first "neutralized" by a stoichiometric amount of aluminum chloride, then the synthesis of 4 succeeds (eq 2). Iodine is the most convenient oxidizing agent for that purpose; however, other positive halogen sources such as bromophenylacetylene, ethyl bromo-

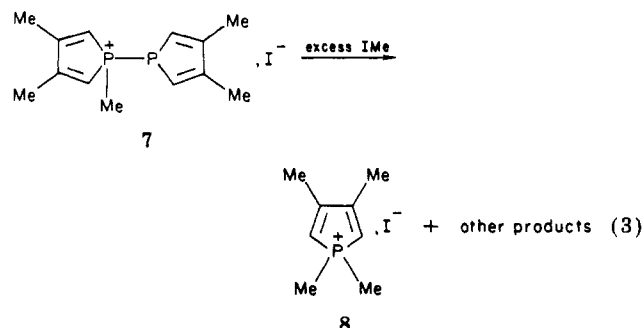
(1) (a) Laboratoire CNRS-SNPE. (b) Institut Le Bel.  
 (2) E. W. Abel and C. Towers, *J. Chem. Soc., Dalton Trans.*, 814 (1979); E. W. Abel, N. Clark, and C. Towers, *ibid.*, 1552 (1979).  
 (3) C. Charrier, H. Bonnard, and F. Mathey, *J. Org. Chem.*, **47**, 2376 (1982).  
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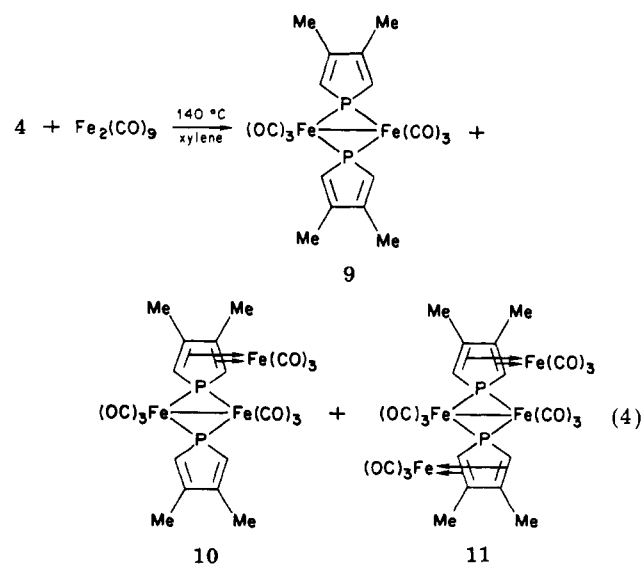
(6) L. D. Quin, S. G. Borleske, and J. F. Engel, *J. Org. Chem.*, **38**, 1954 (1973).



malonate, and *N*-bromosuccinimide may be used. The biphospholyl thus obtained has been characterized by  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{13}\text{C}$  NMR spectroscopy. The recorded data are unexceptional and need no special comment. The biphospholyl **4** is extremely sensitive toward oxygen. It reacts rapidly with methyl iodide to give first the monophosphonium salt **7** ( $\delta(^{31}\text{P})$  -53.5 and +64.5 ( $^1J(\text{P-P}) = 280$  Hz)) and then two cleavage products ( $\delta(^{31}\text{P})$  +35 and +40 ppm), one of which is very probably the phospholium salt **8**<sup>6</sup> (eq 3). However, until now, we have mainly studied



the coordination chemistry of **4**. Our first investigations have been focused on the reactions of **4** with iron and cobalt carbonyls. Thus, the reaction of **4** with  $\text{Fe}_2(\text{CO})_9$  in refluxing xylene yields three main complexes **9**–**11** (eq 4).

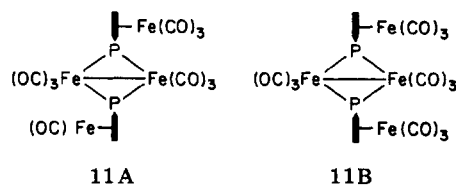


Complex **9** results from the expected cleavage of the phosphorus–phosphorus bond which has been previously observed with simple diphosphines.<sup>7</sup> That the diene systems of the two phosphole rings do not participate in the complexation of iron atoms is obvious from inspection

of the  $^1\text{H}$  NMR spectrum of **9**. Indeed, the  $^{31}\text{P}$ -decoupled spectrum shows two broad singlets at 6.4 and 6.75 ppm ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) corresponding to the two inequivalent vinylic protons of each phosphole ring. Their occurrence at low field excludes  $\pi$  complexation of the dienic systems. Their inequivalency is the expected consequence of the folding of the  $\text{Fe}_2\text{P}_2$  ring around the  $\text{Fe}\cdots\text{Fe}$  axis. The only curious feature of this otherwise classical complex lies in the shielding of the phosphorus atom ( $\delta(^{31}\text{P}(\mathbf{9}))$  +90 in  $\text{CDCl}_3$ ). Other complexes of the same type show  $^{31}\text{P}$  resonances at much lower field; for example,  $\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)_2$  resonates at +142.8 ppm.<sup>8</sup> According to the work of Carty,<sup>8</sup> this observation suggests a large  $\text{Fe-P-Fe}$  angle and an abnormally long  $\text{Fe}\cdots\text{Fe}$  distance for such a complex. The large  $\text{Fe-P-Fe}$  angle is perhaps a consequence of the inclusion of phosphorus in the strained 3,4-dimethylphosphole ring.

As proven by analytical and mass spectral data, complex **10** is obtained by adding one  $\text{Fe}(\text{CO})_3$  unit to complex **9**. The  $^{31}\text{P}$ -decoupled  $^1\text{H}$  NMR spectrum of **10** shows two inequivalent phosphole rings as evidenced by the presence of two sets of  $\text{CH}_3$  and  $\text{CH}$  resonances. One phosphole is complexed only at phosphorus (vinylic protons at 6.16 and 6.58 ppm) and the other is also  $\pi$  complexed through its dienic system (vinylic protons at 2.65 and 3.13 ppm). The formula is thus unambiguously established. The  $^{31}\text{P}$  NMR spectrum shows an AB system:  $\delta_A$  +95.4,  $\delta_B$  +202,  $J_{AB} = 131.8$  Hz. It is interesting to note that the A resonance corresponding to the  $\pi$ -uncomplexed phosphole ring is very close to the resonance observed for complex **9**. This suggests that the geometry of the  $\text{Fe}_2\text{P}_2$  ring is not affected by the  $\pi$  complexation of one phosphole ring. The coupling between the two inequivalent phosphorus atoms of **10** is rather large. In  $\text{Fe}_2(\text{CO})_6(\mu\text{-PMe}_2)_2$  the P–P coupling has been estimated around 85 Hz.<sup>9</sup> This observation suggests a rather short P $\cdots$ P distance in **10** and probably also in **9**. This proposal supports the former suggestion of a long  $\text{Fe}\cdots\text{Fe}$  distance in these complexes.

The elemental analysis and the mass spectrum of complex **11** show that it is built by adding one more  $\text{Fe}(\text{CO})_3$  unit to complex **10**. Here, the two phosphole rings are  $\pi$  complexed and the vinylic protons appear to 2.44 and 3.0 ppm in the  $^1\text{H}$  NMR spectrum. The phosphorus resonance ( $\delta(^{31}\text{P}(\mathbf{11}))$  199.8) lies very close to the B resonance of complex **10**. Its uniqueness demonstrates that **11** is not a mixture of two diastereoisomers, **11A** and **11B**. The



choice between the two possible formulas is only tentative. Indeed,  $^{13}\text{C}$  NMR fails to detect the inequivalency between the two  $\text{Fe}(\text{CO})_3\text{P}_2$  groups of complex **10** and, thus, is unable to discriminate between formula **11A** and **11B**. We prefer formula **11A** for steric reasons.

Up to now, only one complex in which a phospholyl ring acted as a (4 + 3)-electron donor was described in the literature<sup>10</sup> and it appeared as quite exceptional. The easy synthesis of **10** and **11** demonstrates clearly that, in fact,

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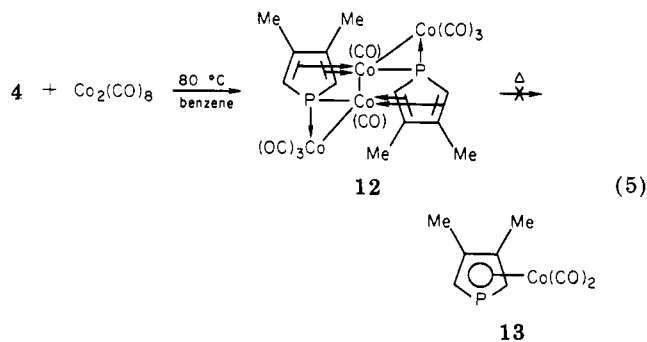
**Table II.** Bond Lengths (Å) and Bond Angles (deg) with Their Estimated Standard Deviations

Bond Lengths			
Co1-Co1'	2.787 (1)	Co2-C13	1.764 (6)
Co1-Co2	2.635 (1)	P-C1	1.776 (5)
Co1-P'	2.275 (1)	P-C4	1.754 (5)
Co1-P	2.357 (1)	C1-C2	1.397 (7)
Co1-C1	2.073 (5)	C3-C4	1.428 (7)
Co1-C2	2.115 (5)	C2-C3	1.428 (7)
Co1-C3	2.088 (5)	C2-C5	1.492 (7)
Co1-C4	2.097 (5)	C3-C6	1.498 (8)
Co2-P'	2.107 (1)	C7-O8	1.145 (7)
Co1-C11	1.753 (5)	C9-O10	1.148 (8)
Co2-C7	1.770 (6)	C11-O12	1.143 (6)
Co2-C9	1.773 (7)	C13-O14	1.143 (7)

Bond Angles			
Co1-Co1'-Co2'	104.45 (4)	P-C1-C2	114.0 (3)
Co1'-P-Co2'	73.82 (5)	P-C4-C3	113.2 (3)
Co1'-Co2'-P	56.01 (4)	C1-C2-C3	111.3 (4)
C1-P-Co1'	110.9 (2)	C4-C3-C2	111.9 (4)
C4-P-Co1'	107.2 (2)	C1-C2-C5	123.5 (5)
C1-P-Co2'	132.7 (2)	C4-C3-C6	123.7 (5)
C4-P-Co2'	136.3 (2)	C3-C2-C5	125.0 (5)
C1-P-C4	88.7 (2)	C2-C3-C6	124.2 (5)

3,4-dimethylphospholyl has a high propensity to form such complexes. The study of the reaction of **4** with cobalt carbonyl again illustrates this astonishing property. Our incentive for such a study was to compare the behavior of **3** and **4** toward  $\text{Co}_2(\text{CO})_8$ . In the first case, a ( $\eta^5$ -phospholyl)dicarbonylcobalt had been obtained as the sole tractable product.<sup>4</sup> We wished to check if the replacement of a 2,5-diphenyl by a 3,4-dimethyl substitution would alter the course of the reaction. This is indeed the case to an unpredictable extent. In fact, in refluxing benzene, **4** reacts with  $\text{Co}_2(\text{CO})_8$  to give a 75% yield of a single complex, **12**, in which the 3,4-dimethylphospholyl ring acts again as a (4 + 3)-electron donor (eq 5).



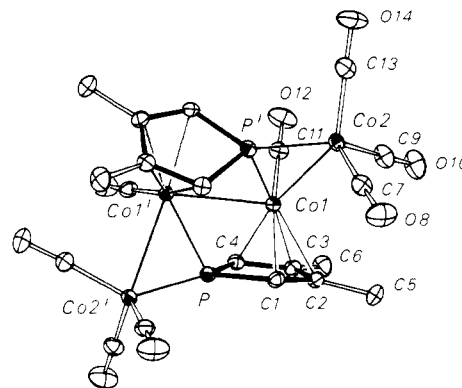
Every attempt to convert **12** into the corresponding  $\eta^5$ -phospholyl complex **13** failed (thermolysis in boiling xylene or in vacuo up to 250 °C). The elemental analysis and the mass spectrum indicated that **12** contained two phospholyl units and four cobalt atoms. The unique  $^{31}\text{P}$  resonance at +56 ppm demonstrated that the two phospholyl units were equivalent. However, the  $^1\text{H}$  NMR spectrum comprised two sets of methyl resonances at 1.95 and 2.05 ppm and two sets of CH resonances at 1.07 and 3.55 ppm, showing a strong inequivalency between the two sides of each phospholyl ring. Thus, in order to establish the precise disposition of the four cobalt atoms and to understand the origin of the observed inequivalency within each ring, we decided to perform a X-ray crystal structure analysis of **12**.

**X-ray Crystal Structure of Complex 12.** Atomic positional parameters, with corresponding esd's estimated from the least-squares inverse matrix, are presented in Table I. Bond lengths and bond angles appear in Table

**Table III.** Least Squares Planes

	distance, <sup>a</sup> Å	equation <sup>b</sup>
P11	C1° -0.008 (5)	-0.0517x + 0.3465y - 0.9366z +
	C2° 0.015 (5)	0.7165 = 0
	C3° -0.015 (5)	
	C4° 0.008 (5)	
	P 0.160 (1)	
	Co1 -1.661 (1)	
P12	P° 0:000 (1)	-0.1781x + 0.3427y - 0.9224z +
	C1° 0.000 (5)	0.5394 = 0
	C4° 0.000 (5)	

<sup>a</sup> Atoms with the deg sign are used in computing equation. <sup>b</sup> Orthogonal reference system according to D. M. Blow, *Acta Crystallogr.*, 13, 168 (1960).

**Figure 1.** ORTEP drawing of the dimer showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity. Ellipsoids are scaled to enclose 50% of the electronic density.

II. Table III gives selected mean planes. Observed and calculated structure factor amplitudes and thermal parameters are available as supplementary material.<sup>11</sup> Figure 1 shows molecule **12** together with the atom numbering scheme. Molecule **12** is a dimer of  $\text{Co}_2(\text{CO})_4(\text{PC}_6\text{H}_8)$  moieties lying on a crystallographic twofold axis.

The four metallic atoms form a bent chain with Co-Co bond length of 2.635 (1) and 2.787 (1) Å, giving the complex a twofold axis which is coincident with the crystallographic twofold axis in the space group ( $C_2/c$ ); these bonds are longer than those found in tetrahedral  $\text{Co}_4$  moieties (2.49–2.32 Å<sup>12-14</sup>) or in  $\text{Co}_2$  phosphorus  $\mu$ -bridged species (2.56<sup>15</sup> and 2.57 Å<sup>16</sup>). As far as we know, this is the first time that a complex with an open chain of four cobalt atoms has been structurally characterized.

As expected from the  $^1\text{H}$  NMR data, the phosphole ring acts as a (4 + 3)-electron donor giving via the diene system four electrons to Co1 and via the phosphorus atom two electrons to Co2' and one electron to Co1'. Such a situation was already found in  $\text{Mn}_3(\text{C}_{17}\text{H}_8\text{O}_{11}\text{P})^{10}$  (**14**) where the phosphole ring gives four electrons to Mn(2), one electron to Mn(1), and two electrons to Mn(3), the three metal atoms forming also a bent chain.

The geometry of the phosphole ring in **12** is comparable to that found in **14**. The carbon ring atoms are coplanar within experimental error as seen by the distances of these atoms to P11 in Table III. Co1 is out of P11 by -1.661 (1)

(11) See the paragraph at the end of the paper concerning the supplementary material.

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(13) F. H. Carré, F. A. Cotton, and B. A. Frenz, *Inorg. Chem.*, 15, 380 (1976).

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(16) C. F. Campana, A. Vizi-Orosz, G. Palyi, L. Markó, and L. F. Dahl, *Inorg. Chem.*, 18, 3054 (1979).

Å and P by 0.160 (1) Å leading to a folding angle of 7.3° around the C1–C4 axis. These values lead to a Co1–P distance of 2.357 (1) Å showing the tendency of 12 to yield the  $\pi$ -aromatic complex 13. At the temperature where such a process can take place, however, complex 13 is probably too unstable and cannot be isolated. The Co1–C ring bond distances range from 2.073 (5) to 2.115 (5) Å. The two P–C intracyclic bond distances are not significantly different and are in the range of those found in other  $\eta^4$ -phospholes.<sup>17</sup> The three intracyclic C–C bond distances are also equivalent and comparable to those found in other structures. The inequivalency of the two sides of each phosphole ring stems from the presence of one carbonyl group on each of the two central cobalt atoms. It is rather astonishing that the mere vicinity of a carbonyl group suffices to displace the CH resonance by more than 2 ppm downfield.

The two P–Co1' and P–Co2' bond lengths are logically different due to different bonding modes; the same effect was also observed in 14.

The Co–C carbonyl bond length range from 1.735 (5) to 1.773 (7) Å; they are not significantly different from each other and have values close to those observed for other terminal carbonyls.<sup>14</sup> The Co–C carbonyl–O carbonyl bond angles are close to 180° and the C=O bond lengths of the carbonyl groups are normal.

### Experimental Section

NMR spectra (chemical shifts in parts per million from internal Me<sub>4</sub>Si for <sup>1</sup>H and <sup>13</sup>C and from external H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P;  $\delta$  positive for downfield shifts in all cases) were recorded on a Bruker WP 80 instrument respectively at 80.13, 20.15, and 32.44 MHz. Mass spectra (electronic impact desorption (EID) or chemical ionization desorption (CID)) were recorded on a Nermag R10-10 spectrometer by Mr Charré (SNPE). All reactions were carried out under argon. Chromatographic separations were performed on deoxygenated silica gel columns (70–230 mesh Riedel de Haën).

**3,3',4,4'-Tetramethyl-1,1'-biphospholyl (4).** To a solution of 3.76 g ( $2 \times 10^{-2}$  mol) of 1-phenyl-3,4-dimethylphosphole in 50 mL of dry THF cooled by a water bath was added 0.56 g ( $8 \times 10^{-2}$  mol) of Li wire. After 4 h of stirring, the excess of lithium was removed and 0.9 g ( $6.6 \times 10^{-3}$  mol) of anhydrous AlCl<sub>3</sub> was rapidly added at –10 °C. After 0.5 h at room temperature a solution of 2.65 g ( $2.1 \times 10^{-2}$  mol) of iodine in 10 mL of THF was added to the mixture. The solvent was then distilled, and 100 mL of hexane, 5 mL of water, and anhydrous sodium sulfate were added successively to the residue with vigorous stirring. The solution was then decanted or filtered on sintered glass and the solid washed two or three times with hexane. Vacuum distillation of the solvent gave a yellow oil which solidified: yield 1.8 g (80%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.11 (m, 12 H, CH<sub>3</sub>), 6.38 (m, 4 H, =CH); <sup>31</sup>P (CDCl<sub>3</sub>)  $\delta$  –25.3; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  18.8 (CH<sub>3</sub>), 129.0 (secondary vinylic carbons), 150.6 (tertiary vinylic carbons). Due to the great oxygen sensitivity of this compound, a satisfactory analysis could not be obtained.

**Iron Carbonyl Complexes 9–11.** A mixture of 1.1 g ( $5 \times 10^{-3}$  mol) of tetramethylbiphospholyl 4 and 5.8 g ( $1.5 \times 10^{-2}$  mol) of diiron nonacarbonyl was refluxed for 1 h in xylene. After vacuum distillation of the solvent, the residue was chromatographed on 100 g of silica gel with a mixture of hexane and successively 2%, 10%, and 50% of toluene. Three complexes were recovered.

**Complex 9:** dark orange crystals; yield 0.25 g (10%); mp 242 °C dec; <sup>1</sup>H NMR  $\delta$  2.17 (br s, 12 H, CH<sub>3</sub>), 6.40 (m, 2 H, =CH), 6.75 (m, 2 H, =CH); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  92.5; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  17.7 and 18.4 (CH<sub>3</sub>), 131.5 and 131.8 (secondary vinylic carbons), 151.2 and 152.4 (tertiary vinylic carbons), 211.5 (m, CO); IR (decalin)  $\nu$ (CO) 2055, 2028, 2018, 1985, 1975, 1962, 1945 cm<sup>–1</sup>; mass spectrum (EID, 70 eV, 200 °C)  $m/e$  (relative intensity) 502 (M, 10), 418 (M – 3CO, 15), 390 (M – 4CO, 8), 362 (M – 5CO, 20), 334

(M – 6CO, 100), 278 (M – Fe(CO)<sub>6</sub>, 60). Anal. Calcd for C<sub>18</sub>H<sub>16</sub>Fe<sub>2</sub>O<sub>9</sub>P<sub>2</sub>: C, 43.07; H, 3.21; Fe, 22.25; P, 12.34. Found: C, 43.01; H, 3.40; Fe, 22.45; P, 11.80.

**Complex 10:** orange crystals; yield 0.25 g (8%); mp 153 °C dec; <sup>1</sup>H NMR  $\pi$ -complexed ring  $\delta$  2.14 and 2.10 (s, 3 + 3 H, CH<sub>3</sub>), 2.65 (dd, <sup>4</sup>J<sub>HH</sub> = 2.9 Hz, <sup>2</sup>J<sub>HP</sub> = 38.8 Hz, 1 H) and 3.13 (dd, <sup>4</sup>J<sub>HH</sub> = 2.9 Hz, <sup>2</sup>J<sub>HP</sub> = 37.3 Hz, 1 H, =CH),  $\pi$ -uncomplexed ring  $\delta$  2.40 and 2.44 (s, 3 + 3 H, CH<sub>3</sub>), 6.16 (d, <sup>2</sup>J<sub>HP</sub> = 40.5 Hz, 1 H), 6.58 (d, <sup>2</sup>J<sub>HP</sub> = 40.5 Hz, 1 H, =CH); <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>)  $\delta$  95.4 and 202.0 ( $J_{PP}$  = 131.8 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  15.6 and 15.7 (CH<sub>3</sub>,  $\pi$ -complexed ring), 17.6 and 18.3 (CH<sub>3</sub>,  $\pi$ -uncomplexed ring), 53.7 and 54.1 (=CH,  $\pi$ -complexed ring), 107.0 and 107.3 (=CCH<sub>3</sub>,  $\pi$ -complexed ring), 130.5 and 132.4 (=CH,  $\pi$ -uncomplexed ring), 151.0 and 152.1 (=CCH<sub>3</sub>,  $\pi$ -uncomplexed ring), 208.2 and 212.4 (CO); IR (decalin)  $\nu$ (CO) 2065, 2040, 2015, 1992, 1983, 1975, 1950 cm<sup>–1</sup>; mass spectrum (EID, 70 eV, 200 °C),  $m/e$  (relative intensity) 642 (M, 5), 474 (M – 6CO, 45), 446 (M – 7CO, 100), 278 (M – Fe<sub>2</sub>(CO)<sub>9</sub>, 50). Anal. Calcd for C<sub>21</sub>H<sub>16</sub>Fe<sub>3</sub>O<sub>9</sub>P<sub>2</sub>: C, 39.29; H, 2.51; Fe, 26.11; P, 9.37. Found: C, 39.14; H, 2.43; Fe, 26.09; P, 9.37.

**Complex 11:** orange crystals; yield 0.6 g (15%); mp 215 °C dec; <sup>1</sup>H NMR  $\delta$  2.42 (s, 12 H, CH<sub>3</sub>), 2.44 (m partially masked by Me signal) and 3.0 (m, <sup>4</sup>J<sub>HH</sub> = 2.7 Hz, 2 H, =CH); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  199.8; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  15.6 and 15.9 (Me); 53.6 and 54.2 (secondary vinylic carbons), 107.1 and 107.7 (tertiary vinylic carbons), 208.1 and 213.5 (CO); IR (decalin)  $\nu$ (CO) 2060, 2033, 2010, 1998, 1990, 1977, 1958 cm<sup>–1</sup>; mass spectrum (EID, 70 eV, 200 °C),  $m/e$  782 (M, 3), 642 (M – Fe(CO)<sub>3</sub>, 40), 558 (M – Fe(CO)<sub>6</sub>, 100), 474 (M – Fe(CO)<sub>9</sub>, 75), 446 (M – Fe(CO)<sub>10</sub>, 75), 278 (M – Fe<sub>2</sub>(CO)<sub>12</sub>, 35). Anal. Calcd for C<sub>24</sub>H<sub>16</sub>Fe<sub>4</sub>O<sub>12</sub>P<sub>2</sub>: C, 36.87; H, 2.08; Fe, 28.58; P, 7.92. Found: C, 36.94; H, 1.99; Fe, 28.25; P, 7.96.

**Cobalt Carbonyl Complex 12.** A solution of 1.55 g ( $7 \times 10^{-3}$  mol) of tetramethylbiphospholyl 4 and 5.9 g ( $1.54 \times 10^{-2}$  mol) of Co<sub>2</sub>(CO)<sub>8</sub> in 100 mL of benzene was refluxed for 2 h. After evaporation of the solvent, the residue was chromatographed on 70 g of silica gel in toluene giving a deep purple solution. Distillation of the toluene led to a shiny black solid: yield 3.55 g (75%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.07 (dq, 2 H, =CH) and 3.55 (dq, 2 H, =CH), 1.95 and 2.05 (2s, 12 H, CH<sub>3</sub>); <sup>31</sup>P NMR (C<sub>2</sub>D<sub>6</sub>)  $\delta$  56.0; <sup>13</sup>C NMR  $\delta$  14.6 and 15.1 (m, CH<sub>3</sub>), 82.3 (m, secondary vinylic carbons), 106.5 and 112.8 (m, tertiary vinylic carbons), 208.7 (CO); IR (Nujol)  $\nu$ (CO) 2005, 1985, 1963, 1938, 1910 cm<sup>–1</sup>; mass spectrum (CID NH<sub>3</sub><sup>+</sup>, 100 eV, 100 °C),  $m/e$  (relative intensity) 683 (M + 1, 35). Anal. Calcd for C<sub>20</sub>H<sub>16</sub>Co<sub>4</sub>O<sub>8</sub>P<sub>2</sub>: C, 35.22; H, 2.35; P, 9.08. Found: C, 35.97; H, 2.50; P, 9.06.

**X-ray Data Collection and Processing.** Suitable single crystals of 12 were obtained by slow evaporation of ethanolic solutions at room temperature. A systematic search in reciprocal space using a Philips PW 1100/16 automatic diffractometer showed that crystals of 12 belong to the monoclinic system. The unit-cell dimensions and their standard deviations were obtained and refined at room temperature with Cu K $\alpha$  radiation ( $\lambda$  = 1.5405 Å) by using 25 carefully selected reflections and the standard Philips software. Final results: Co<sub>2</sub>PO<sub>4</sub>C<sub>10</sub>H<sub>8</sub>, mol wt 341,  $a$  = 19.551 (8) Å,  $b$  = 9.505 (3) Å,  $c$  = 13.144 (5) Å,  $\beta$  = 90.75 (2)°,  $V$  = 2442 Å<sup>3</sup>,  $Z$  = 8,  $d$ (calcd) = 1.855 g cm<sup>–3</sup>,  $d$ (obsd) = 1.87  $\pm$  0.02 g cm<sup>–3</sup>,  $\mu$  = 236 cm<sup>–1</sup>,  $F(000)$  = 1352, space group  $C2/c$ .

A spherical crystal of mean diameter 0.26 mm was sealed in a Lindemann glass capillary and mounted on a rotation free goniometer head. All quantitative data were obtained from a Philips PW 1100/16 four-circle automatic diffractometer, controlled by a P852 computer, using graphite-monochromated 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 2 $\sigma$  level. The total scan width in the  $\theta/2\theta$  flying step-scan used was  $\Delta\omega$  = 0.9 + (Cu K $\alpha_{1,2}$  splitting) with a step width of 0.05° and a scan speed of 0.016° s<sup>–1</sup>. A total of 1796  $hkl$  and  $hkl$  reflections were recorded (6° <  $\theta$  < 57°). The resulting data-set was transferred to a PDP11/60 computer, and for all subsequent computations, the Enraf-Nonius SDP/V18 package was used<sup>18</sup> with the exception of a local data reduction program.

(18) B. A. Frenz, "The Enraf-Nonius CAD<sub>4</sub>-SDP" in "Computing in Crystallography", H. Schenk, R. Olthof-Hazenkamp, H. Van Koningsveld, and G. C. Bassi, Eds., Delft University Press, Delft, Holland, 1978, pp 64–71.

Three standard reflections measured every hour during the entire data collection period showed no significant trend in intensity. The raw step-scan data were converted to intensities using the Lehmann-Larsen method<sup>19</sup> and then corrected for Lorentz, polarization, and absorption factors, the latter computed by interpolation in the tabulated tables<sup>20</sup> (transmission factors between 0.25 and 0.87). A unique data set of 1326 reflections having  $I > 3\sigma(I)$  was used for determining and refining the structure.

The structure was solved by using the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in

(19) M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, **A30**, 580 (1974).

(20) "International tables for X-ray crystallography", Vol. II, Kynoch Press, Birmingham, England, 1959, p 302.

structure factor calculations by their computed coordinates (C-H = 0.95 Å) and isotropic temperature factors of 1 Å<sup>2</sup> more than the bonded C atom, but not refined. Full least-squares refinement converged to  $R(F) = 0.035$  and  $R_w(F) = 0.048$  ( $w = 1/(\sigma^2(\text{count}) + (pI)^2)$ ). The unit-weight observation was 1.04 for  $p = 0.08$ . A final difference map revealed no significant maxima.

**Registry No.** 4, 86272-21-1; 5, 30540-36-4; 6, 67918-40-5; 7 (charged form), 86272-22-2; 7 (uncharged form), 86272-23-3; 8, 37737-13-6; 9, 86272-18-6; 10, 86272-19-7; 11, 86272-20-0; 12, 86288-20-2; Fe<sub>2</sub>(CO)<sub>9</sub>, 15321-51-4; Co<sub>2</sub>(CO)<sub>8</sub>, 10210-68-1.

**Supplementary Material Available:** Tables of atomic coordinates and thermal parameters (Tables I and V) and a listing of observed and calculated structure factors ( $\times 10$ ) (Table IV) (8 pages). Ordering information is given on any current masthead page.

## Organometallic Nitrosyl Chemistry. 19.<sup>1</sup> Protonation vs. Oxidative Cleavage of the Isoelectronic Complexes $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{LO})_2]_2$ (M = Cr, Mn, or Fe; L = C or N; R = H or Me) by HBF<sub>4</sub>

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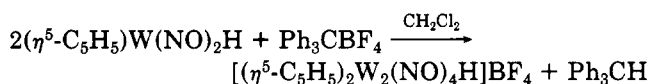
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Received February 25, 1983

Treatment of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  with an equimolar amount of HBF<sub>4</sub>·OMe<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> results in the clean formation of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4\text{H}]\text{BF}_4$  which may be isolated in good yield. In contrast, 2 equiv of the acid are required to consume completely  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]_2$ , the principal organometallic product being  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{BF}_4$ . This latter complex is not isolable, but it can be identified spectroscopically and by its derivative chemistry. Some of the workup procedures employed also afford new organometallic nitrosyl complexes of chromium such as  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{OH}]\text{BF}_4$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2(\text{OHBPh}_3)$  which have been characterized by conventional methods. Two equivalents of HBF<sub>4</sub>·OMe<sub>2</sub> also consume  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})(\text{NO})]_2$  (R = H or Me), but a complex mixture of products results. Two well-known (i.e.,  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_2(\text{NO})]^+$  and  $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Mn}_2(\text{NO})_3(\text{NO}_2)$ ) and two novel (i.e.,  $[(\eta^5\text{-C}_5\text{H}_4\text{R})_3\text{Mn}_3(\text{NO})_3\text{NH}]^+$  and  $[(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Mn}_2(\text{NO})_2(\text{CO})(\text{NH}_2)]^+$ ) types of manganese nitrosyl complexes are produced in each case, the novel cations being ultimately isolable in low yields as the BF<sub>4</sub><sup>-</sup> and BPh<sub>4</sub><sup>-</sup> salts, respectively. Cyclic voltammograms of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]_2$  recorded under identical experimental conditions reveal that the chromium dimer undergoes oxidation at a slightly more positive potential. The propensities of the  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{LO})_2]_2$  (M = Cr, Mn, or Fe; L = C or N; R = H or Me) dimers to undergo protonation or oxidative cleavage when treated with H<sup>+</sup> are thus rationalized in terms of the stabilities of the initially formed  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{LO})_2]_2\text{H}^+$  adducts. Interestingly, treatment of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{NO})]_2$  with HBF<sub>4</sub>·OMe<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> results in simple oxidation, the known  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{NO})]_2\text{BF}_4$  complex being obtainable in good yield.

### Introduction

We recently reported the preparation and characterization of the bimetallic cations  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{NO})_4\text{H}]^+$  (M = Mo or W).<sup>2</sup> Salts containing these cations were synthesized in good yields by treatment of the monomeric hydrides  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})_2\text{H}$  (M = Mo or W) with hydride-abstracting carbocations in nondonor solvents, e.g.



Unlike related carbonyl complexes, the bimetallic cations are not deprotonated by a variety of bases to afford the

as yet unknown  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})_2]_2$  (M = Mo or W) dimers. Instead, they are cleaved to the monomeric products  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})_2\text{H}$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})_2(\text{B})]^+$  (B = base) by these reagents. In the light of these observations, two questions came to mind. (1) Can the analogous  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{NO})_4\text{H}]^+$  cation be prepared by protonation of the well-known dimer  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]_2$ ? (2) Is the protonation of the neutral chromium dimer a reversible process? Our initial experiments in this regard indicated that both questions could be answered in the negative.<sup>2</sup> We have now completed a more detailed investigation of the reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]_2$  with HBF<sub>4</sub>, and in this paper we present results that permit us to answer the above questions more fully.

Of continuing interest during our work with organometallic nitrosyl compounds is how the physical and chemical properties of the nitrosyl complexes differ from

(1) Part 18: Legzdins, P.; Nurse, C. R.; Rettig, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3727.

(2) Hames, B. W.; Legzdins, P. *Organometallics* **1982**, *1*, 116.