Reaction of Bulky Monosubstituted Phosphorus(III) Halides with Disodium Tetracarbonylferrate. Steric and Electronic Factors in the Synthesis of Fe(CO)$_4$ Complexes of Diphosphene and Phosphinidene Ligands

Ruth A. Bartlett, H. V. Rasika Dias, Kathy M. Flynn, Marilyn M. Olmstead, and Philip P. Power*[1]

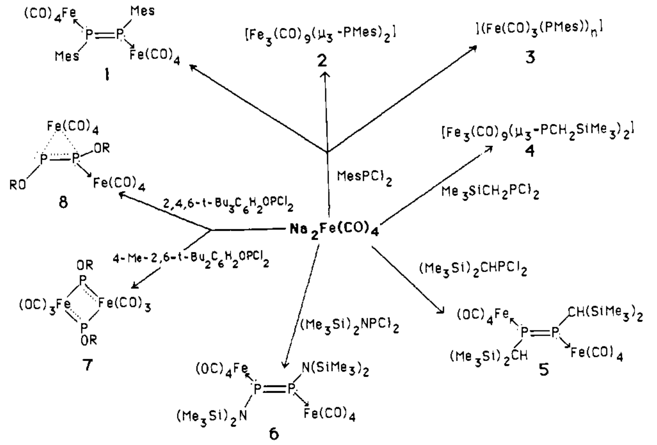
Contribution from the Department of Chemistry, University of California, Davis, California 95616. *Received December 30, 1986*

Abstract: Reaction of $Na_2Fe(CO)_4$ with a bulky monosubstituted phosphorus(III) halide $RPCl_2$ where R = Mes (2,4,6-$Me_3C_6H_2$), CH_2SiMe_3, $CH(SiMe_3)_2$, $N(SiMe_3)_2$, $-OC_6H_2$-2,6-*t*-Bu_2-4-Me, or $-OC_6H_2$-2,4,6-*t*-Bu_3 yields products in which the phosphorus center behaves as either a diphosphene or a bridging phosphinidene group. The type of product depends on the substituent used. The synthesis of two precursor ligands, 2,4,6-*t*-$Bu_3C_6H_2OPCl_2$ and 4-Me-2,6-*t*-$Bu_2C_6H_2OPCl_2$, and eight iron carbonyl complexes involving various diphosphene and phosphinidene ligand are described and discussed in the context of the corresponding chromium carbonyl complexes. The complexes are $[\{Fe(CO)_4\}_2$-*trans*-$(PMes)_2]$ (**1**), $[Fe_3(CO)_9(\mu_3\text{-}PMes)_2]\cdot THF$ (**2**), $[\{Fe(CO)_3(PMes)\}_n]$ (**3**), $[Fe_3(CO)_9(\mu_3\text{-}PCH_2SiMe_3)_2]$ (**4**), $[\{Fe(CO)_4\}_2$-*trans*-$\{PCH(SiMe_3)_2\}_2]$ (**5**), $[\{Fe(CO)_4\}_2$-*trans*-$\{PN(SiMe_3)_2\}_2]$ (**6**), $[\{Fe(CO)_3(POC_6H_2$-2,6-*t*-Bu_2-4-$Me)\}_2]$ (**7**), and $[Fe(CO)_4\{\mu\text{-}Fe(CO)_4\}\{POC_6H_2$-2,4,6-*t*-$Bu_3\}_2]$ (**8**). X-ray data at 130 K are as follows. **1**: $C_{26}H_{22}Fe_2P_2O_8$, a = 7.980 (2) Å, b = 10.882 (3) Å, c = 17.125 (4) Å, α = 78.49 (2)°, β = 86.14 (2)°, γ = 82.74 (2)°, triclinic, space group $P\bar{1}$, Z = 2, R = 0.040 for 4431 unique observed data. **2**: $C_{27}H_{22}Fe_3P_2O_{10}\cdot C_4H_8O$, a = 8.358 (3) Å, b = 15.712 (8) Å, c = 25.184 (9) Å, orthorhombic, space group $C2cm$, Z = 4, R = 0.046 for 1169 unique observed data. The structures of **5**–**8** have been briefly described in preliminary communications. The structures of both **7** and **8** are the only two of that type so far described. Complex **5** was the first example of a transition-metal diphosphene complex having an unsupported PP double bond. Compounds **1** and **6** are further examples. A major difference between the reactions of $Na_2Fe(CO)_4$ and $Na_2Cr(CO)_5$ with $RPCl_2$ compounds is the generally cleaner nature of the products obtained for $Na_2Fe(CO)_4$. A significant feature of the reactions involving iron is the isolation of clusters involving Fe–Fe bonds with less bulky substituents. With chromium complexes, P–P rather than Cr–Cr bonds are obtained when the smaller substituents are used. Details of the syntheses and spectroscopic characterization of the precursors 2,4,6-*t*-$Bu_3C_6H_2OPCl_2$ and 4-Me-2,6-*t*-$Bu_2C_6H_2OPCl_2$ are also given.

Interest in multiple bonding between heavier main-group elements has greatly intensified over the past five years.[2] The major emphasis has involved the kinetic stabilization of species which have unsupported double bonds such as RP=PR[2] or $R_2Si{=}SiR_2$[2,3] and the study of their spectroscopic and chemical properties. In the case of the main group V elements the discovery of 2,4,6-*t*-$Bu_3C_6H_2P{=}PC_6H_2$-2,4,6-*t*-Bu_3 by Yoshifuji[4] and co-workers has heralded an extensive array of publications by many research groups which have detailed the interesting physical and chemical characteristics of the P=P moiety and its heavier congeners.

Work on such compounds in this laboratory stemmed from attempts to synthesize transition-metal complexes having a terminal metal phosphinidene ligand, M=PX. The existence of this interesting moiety, which has not yet been isolated in a stable form under ambient conditions, has been demonstrated by Mathey in trapping experiments.[5] In addition, a very large number of publications beginning in 1975[6,7] had focussed on compounds of the type $(L_nM)_2EX$ and $[L_nMEXEXML_n)(\mu\text{-}ML_n)]$ (E = P, As, Sb, or Bi) and related species which contained planar bridging phosphinidene ligands (also As, Sb, or Bi analogues) and (E–E) multiple bonds bridged by organometallic fragments.[8] We reasoned that if the substituent on phosphorus were sufficiently large terminal rather than bridging phosphinidene complexes would be isolated. Accordingly, beginning in early 1982, a series of reactions between $Na_2Fe(CO)_4$[9-12] or $Na_2Cr(CO)_5$[10,11] and

Scheme I. Summary of the Products Derived from the Reaction of $Na_2Fe(CO)_4$ with Various Monosubstituted Phosphorus(III) Halides



---

[1] A. P. Sloan Foundation Fellow 1985–1987.

[2] Cowley, A. H. *Polyhedron* **1984**, *3*, 389. Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 384. Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1.

[3] West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

[4] Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

[5] Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 4484. Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488. Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

[6] Huttner, G. *Pure Appl. Chem.* **1986**, *24*.

[7] Huttner, G.; Müller, H.-D.; Frank, A.; Lorentz, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 705. The first example of a similar arsinidene species was reported shortly beforehand. Huttner, G.; Schmid, H. G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 430.

[8] For example: Lang, H.; Huttner, G.; Sigwarth, B.; Wever, U.; Zsolnai, L.; Jibril, I.; Orama, O. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 191. See also: Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 924 for a very useful general review of the role of the low coordinate heavier main group 5 species as transition-metal ligands.

[9] Flynn, K. M.; Olmstead, M. M.; Power, P. P.; *J. Am. Chem. Soc.* **1983**, *105*, 2085.

[10] Flynn, K. M .; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am, Chem. Soc.* **1983**, *105*, 7460.

0002-7863/87/1509-5699$01.50/0

$RPCl_2$ (R = large alkyl, aryl, amide, or aryloxide group) were investigated (see Scheme I). In no case was the expected terminal phosphinidene product isolated. Instead, hitherto unreported complexes which, in many cases, possessed unsupported (E–E) double bonds were obtained. The predominance of these compounds, exemplified by the facile synthesis and characterization[9] of the new organometallic diphosphene complex *trans*-$[(OC)_4Fe\{(Me_3Si)_2CHP{=}PCH(SiMe_3)_2\}Fe(CO)_4]$ (**5**), is due in large measure (electronic factors also play a role) to the large size of the organic phosphorus substituent. A further example involving the *trans*-PhP=PPh ligand bonded to two $Cr(CO)_5$ fragments was published shortly thereafter.[13] The P–P bond length in **5** was essentially the same as those found[4] in the Yoshifuji compound (2.034 (2) Å) and the dialkyldiphosphene *trans*-$(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (2.014 (6) Å) of Cowley,[14] showing that this parameter underwent little change upon coordination of the transition-metal fragment through the phosphorus lone pair. The complex is also notable because of its air, moisture, and thermal stability. The appearance of P–P double-bonded compounds as the major fraction is in contrast to the products isolated when less bulky starting materials such as $MePCl_2$ or PCl_3 itself are used. However, with heavier main group V congeners, even large groups such as $CH(SiMe_3)_2$ have so far proved unsuccessful in preventing the formation of bridging species as in $[Fe(CO)_4\{\eta^2\text{-}(Me_3Si)_2CHSbSbCH(SiMe_3)_2\}]$ or $[Fe_2\{\mu\text{-}SbCH(SiMe_3)_2\}(CO)_8]$.[15]

In this paper we describe in fuller detail the products obtained from the reaction between $Na_2Fe(CO)_4$ and $RPCl_2$ as shown in Scheme I. Some details of these reactions have been given in four[9-12] preliminary reports. The results described in this paper are complimentary to, but significantly different from, those arising from the corresponding reaction between $RPCl_2$ and $Na_2Cr(CO)_5$ which will be described in a separate publication.[16]

Experimental Section

General Procedures. All experiments were performed by using either modified Schlenk techniques under N_2 or a vacuum atmosphere HE43-2 drybox under Argon. Solvents were freshly distilled under N_2 from Na/K alloy–benzophenone–ketyl and degassed twice immediately before use.

Physical Measurements. ^{31}P NMR spectra were recorded in C_6H_6 on a Nicolet NT-200 spectrometer operating at 81 MHz. All ^{31}P spectra were referenced to external 85% H_3PO_4 and recorded with 2-W proton decoupling unless otherwise noted. IR spectra were measured on a Perkin-Elmer 180 or on IBM IR/32 or IR/98 instruments. All products gave satisfactory C and H analysis.

Reagents. The reagents $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane (Alfa), 2,4,6-*t*-$Bu_3C_6H_2OH$ (Aldrich), and 4-Me-2,6-*t*-$Bu_2C_6H_2OH$ (Aldrich) were all used as received. The compounds $MesPCl_2$,[17] $Me_3SiCH_2PCl_2$,[18] $(Me_3Si)_2CHPCl_2$,[19] and $(Me_3Si)_2NPCl_2$[19] were prepared according to literature methods.

2,4,6-*t*-$Bu_3C_6H_2OPCl_2$. 2,4,6-*t*-$Bu_3C_6H_2OLi$ was prepared from 2,4,6-*t*-$Bu_3C_6H_5OH$ and *n*-BuLi as reported earlier.[20] The PCl_3 (30 mmol) in Et_2O (50 mL) was added dropwise at 0 °C to an Et_2O (100 mL) solution of 2,4,6-*t*-$Bu_3C_6H_5OLi$ (25 mmol). This was allowed to warm up to room temperature and stirred overnight. The Et_2O was removed under reduced pressure, and the residue was extracted with *n*-hexane, filtered, and cooled at −20 °C. White crystals were isolated from the hexane solution and recrystallized from *n*-hexane: yield 90%; ^{31}P NMR δ 202.7; mp 68–72 °C.

4-Me-2,6-*t*-Bu_2-$C_6H_2OPCl_2$. This was prepared from 4-Me-2,6-*t*-$Bu_2C_6H_2OLi$ and PCl_3 in a procedure similar to that described above: yield 90%; ^{31}P δ 202; mp 44–46 °C.

Preparation of $[\{Fe(CO)_4\}_2$-*trans*-$\{PMes\}_2]$ (1), $[Fe_3(CO)_9(\mu_3\text{-}PMes)_2]\cdot THF$ (2), and $[\{Fe(CO)_3(PMes)\}_n]$ (3). $MesPCl_2$ (0.442 g, 2 mmol) in Et_2O (50 mL) was added dropwise to $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane (0.629 g, 2 mmol) in Et_2O (100 mL) at 0 °C. The resulting solution was stirred overnight at room temperature. The solvent was removed in vacuo, and the products were separated by column chromatography (silica gel/*n*-hexane) and crystallized in *n*-hexane at −20 °C to obtain [*trans*-$\{Fe(CO)_4(PMes)\}_2]$ (**1**) (dark red crystals; 35% yield; mp 103 °C; ^{31}P NMR δ 335.5; IR (Nujol) 1973, 1992, 2048, 2075 cm^{-1}), $[Fe_3(CO)_9(\mu_3\text{-}PMes)_2]\cdot THF$ (**2**) (red crystals; 10% yield; mp >255 °C; ^{31}P NMR δ 306.1; IR (Nujol) 1951, 1984, 2004, 2026, 2038, 2068 cm^{-1}), and yellow crystals of $[\{Fe(CO)_3(PMes)\}_n]$ (**3**) (15%, yield; ^{31}P NMR δ 48; IR (Nujol) 1965, 1975, 1994, 2020, 2059 cm^{-1}).

$[Fe_3(CO)_9(\mu_3\text{-}PCH_2SiMe_3)_2]$ (4). $Me_3SiCH_2PCl_2$ (1.79 g, 9.5 mmol) in Et_2O (50 mL) was added dropwise to $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane (3.29 g, 9.5 mmol) in THF (100 mL) at 0 °C. The solution was stirred overnight (at room temperature), and the solvents were removed under reduced pressure. The red-colored product was separated by column chromatography (silica gel/*n*-hexane) The crystals were not suitable for X-ray diffraction: 35% yield; ^{31}P NMR δ 331.4; IR (Nujol) 1945, 1982, 2014, 2035, 2049 cm^{-1}.

$[\{Fe(CO)_4\}_2$-*trans*-$\{PCH(SiMe_3)_2\}_2]$ (5). Solid addition of $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane (1.2 g, 3.8 mmol) to a solution of $(Me_3Si)_2CHPCl_2$ (1.0 g, 3.8 mmol) in Et_2O (30 mL) at 0 °C resulted in a red solution. Stirring was continued for 12 h at room temperature, and the volatiles were removed under reduced pressure. The residue was extracted into *n*-hexane (20 mL), filtered, and cooled to −20 °C. Dark red brown crystals of **5** were obtained: 1.4 g, 50% yield; mp 145–147 °C; ^{31}P NMR δ 384.6; IR (Nujol) 1962, 1988, 2013, 2053 cm^{-1}.

$[\{Fe(CO)_4\}_2$-*trans*-$\{PN(SiMe_3)_2\}_2]$ (6). Solid $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane (1.0 g, 3 mmol) was added to a THF (100 mL) solution of $(SiMe_3)_2NPCl_2$ (0.78 g, 3 mmol) at room temperature and stirred overnight. After the solvent was removed under reduced pressure, the crude product was extracted into *n*-hexane (20 mL), filtered, and cooled to −20 °C to obtain orange red crystals of **6** in 45% yield: mp 134–136 °C; ^{31}P NMR δ 403.9; IR (Nujol) 1957, 1966, 1982, 2046 cm^{-1}.

$[\{Fe(CO)_3(POC_6H_2\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}Me)\}_2]$ (7). Solid $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane (1.0 g, 3 mmol) was added to a THF (50 mL) solution of 4-Me-2,6-*t*-$Bu_2C_6H_2OPCl_2$ (0.94 g, 3 mmol) at 0 °C. The resulting solution was stirred overnight at room temperature. The volatiles were removed under reduced pressure, and the residue was dissolved in *n*-hexane, filtered, and cooled to −20 °C. Red brown crystals of **7** were obtained in 35% yield: mp 191–193 °C; ^{31}P NMR δ 564; IR (Nujol) 1967, 1994, 2014, 2028, 2041, 2052 cm^{-1}.

$[Fe(CO)_4\{\mu\text{-}Fe(CO)_4\}\{POC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3\}_2]$ (8). 2,4,6-*t*-$Bu_3C_6H_2OPCl_2$ (1.08 g, 3 mmol) was dissolved in Et_2O (50 mL), and solid $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane (1.0 g, 3 mmol) was added at 0 °C. The solution was stirred overnight. The solvent was removed under reduced pressure, and the residue was extracted into n-hexane, filtered, and cooled to −20 °C. Orange-red crystals of **8** were obtained in 40% yield: mp 190–191 °C; ^{31}P NMR δ 233.8 (d), 193.4 (d), J_{PP} = 532 Hz; IR (Nujol) 1956, 1966, 1971, 1986, 1991, 2002, 2022, 2026, 2038, 2048, 2059, 2103 cm^{-1}.

X-ray Crystallographic Studies. All X-ray data were collected with a Syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 device, Mo Kα radiation, and a graphite monochromator. Calculations were carried out on a Data General Eclipse using SHELXTL, version 4, programs. Scattering factors and corrections for anomalous scattering were from ref 21. Absorption corrections were made by using the program XABS.[22]

Red parallelepiped crystals of **1** were obtained as described and coated with a hydrocarbon oil upon removal from the Schlenk tube to prevent reaction with the air. A suitable crystal was selected, attached to a glass fiber on a mounting pin, and placed in the low-temperature N_2 stream. Triclinic lattice constants were determined by least-squares fit of 22

---

(11) Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7750.

(12) Flynn, K. M.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Organometallics* **1986**, *5*, 813.

(13) Borm, J.; Zsolnai, L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 977.

(14) Cowley, A. H.; Kilduff, J. E.; Newman, G. H.; Pakulski, M. *J. Am. Chem. Soc.* **1982**, *104*, 5820. Cowley, A. L.; Kilduff, J. E.; Norman, N. C.; Atwood, J. L.; Pakulski, M.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 4845.

(15) Cowley, A. H.; Norman, N. C.; Pakulski, M.; Bricker, D. L.; Russell, D. H. *J. Am. Chem. Soc.* **1985**, *107*, 8211.

(16) Bartlett, R. A.; Dias, H. V. R.; Flynn, K. M.; Hope, H.; Murray, B.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.*, preceding paper in this issue.

(17) The reported synthesis for $MesPCl_2$ by: Oshikawa, T.; Yamashita, M. *Chem. Ind.* (*London*) **1955**, 126 was used with slight modifications. MesLi was prepared from *n*-BuLi and MesBr in Et_2O/hexane. After overnight stirring the solid MesLi was filtered off and suspended in Et_2O and 15% excess PCl_3 in Et_2O was added at −20 °C. The mixture was worked up as described to obtain 70% yield of $MesPCl_2$.

(18) Seyferth, D.; Freyer, W. *J. Org. Chem.* **1961**, *26* 2604.

(19) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428.

(20) Cetinkaya, B.; Gumrukcu, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2086.

(21) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1976; Vol. IV.

(22) Hope, H.; Moezzi, B. Program XABS obtains an absorption tensor from $F_o - F_c$ differences. University of California, Davis, 1986.

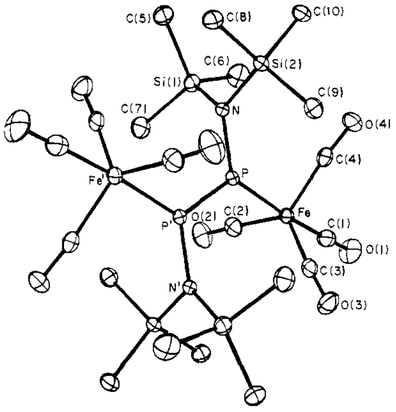


Figure 1. Computer-generated thermal ellipsoid plot of **6** (thermal ellipsoids at 30% probability level). Important bond distances (Å) and angles (deg): PP' = 2.053 (1), FeP = 2.232 (1), PN = 1.682 (2), FeC_{av} = 1.794, CO_{av} = 1.146, Si(1)N = 1.791 (3), Si(2)N = 1.793 (3), SiC_{av} = 1.861, FePN = 120.9 (1), NPP' = 110.2 (1), FePP' = 128.7 (1), PNSi(1) = 118.7 (2), PNSi(2) = 118.9 (1), Si(1)NSi(2) = 120.2 (1). Angle between Si_2N and FePN planes = 75°.

accurately centered reflections with $30° < 2\theta < 48°$. The structure was solved by Patterson method in the space group $P\bar{1}$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included by using a riding model with C–H of 0.96 Å and $U_{iso}(H) = 1.2U^*_{iso}(C)$, where U^*_{iso} is the equivalent isotropic thermal parameter.

Red crystals of **2** were obtained as described and handled in a similar manner as **1**. The orthorhombic cell constants were determined by least-squares fit of 12 centered reflections with $25° < 2\theta < 40°$. Intensity data was collected with C centering and the space group determined to be *C2cm*, a *cba* permutation of *Ama*2, No. 40. The structure was solved by a combination of Patterson and direct methods. The Fe atoms were refined anisotropically. A disordered lattice THF was modeled with two equally probable positions for one of the carbons. These are labeled C(17) and C(18), resulting in two possible THF molecules, O(7)–C(16)–C(17')–C(18')–C(16') and O(7)–C(16)–C(18)–C(17)–C(16'). Hydrogens were added to all appropriate carbons with the exception of the disordered THF by the riding model described above. The handedness was shown to be correct by the program ABSCON.[23] Further details of data collection and refinement for **1** and **2** are in Table I (supplementary material).

Results and Discussion

Much of the work carried out in this laboratory on the interactions between carbonylmetelate salts and monosubstituted phosphorus(III) halides has focused on the readily available dianions $[Fe(CO)_4]^{2-}$ and $[Cr(CO)_5]^{2-}$. The concentration upon mononuclear dianions arose from the original intention to avoid the occurrence of bridged or metal–metal bonded species. This approach, in combination with the use of bulky substitutents on phosphorus, has been for the most part successful in the case of both the iron and chromium compounds. The carbonylmetalate fragment functions as a reducing agent giving rise to metal complexes involving a combination of $M(CO)_n$ and $:\ddot{P}R$ moieties in various proportions. These may take the form of phosphinidene $[\{M(CO)_n\}_2PR]$, diphosphene $[\{M(CO)_n\}_x(RP{=}PR)_y]$, cyclopolyphosphine $[\{M(CO)_n\}_x\text{-}cyclo\text{-}(PR)_y]$, or cluster complexes. The metal carbonyl fragment serves in effect as a trapping agent for the $:\ddot{P}R$ phosphinidene ligand. In some cases hydrogen may also be abstracted from the solvent to give phosphane complexes.[16] The types of complex obtained are summarized in Scheme I.

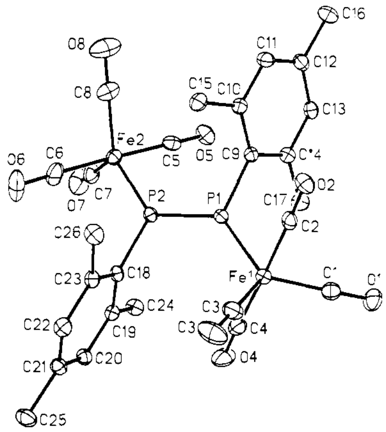


Figure 2. Computer-generated thermal ellipsoid plot of **1** (thermal ellipsoids at 30% probability level). Important bond distances (Å) and angles (deg): P(1)P(2) = 2.029 (1), P(1)Fe(1) = 2.186 (1), P(2)Fe(2) = 2.192 (1), P(1)C(9) = 1.821 (3), P(2)C(18) = 1.823 (3), FeC_{av} = 1.803, CO_{av} = 1.141, Fe(1)P(1)C(9) = 121.7 (1), Fe(1)P(1)P(2) = 132.9 (1), C(9)P(1)P(2) = 105.4 (1), Fe(2)P(2)C(18) = 122.7 (1), Fe(2)P(2)P(1) = 131.5 (1), C(18)P(2)P(1) = 105.4 (1).

The complex $[\{Fe(CO)_4\}_2\text{-}trans\text{-}\{PCH(SiMe_3)_2\}_2]$ (**5**) was the major product to be isolated from the $RPCl_2/Na_2Fe(CO)_4$ reaction system, and some structural details have been reported.[9] The compound was the first reported example of a transition-metal complex having an unsupported phosphorus–phosphorus double bond. This was quickly followed by the synthesis of the isoelectronic (and structurally very similar) amido-substituted complex $[\{Fe(CO)_4\}_2\text{-}trans\text{-}\{PN(SiMe_3)_2\}_2]$ (**6**),[16] which is illustrated in Figure 1. These reactions are notable for the cleanness of the products. In each case the diphosphene is the only major species obtained when the reaction mixtures are examined by using chromatography (silica gel with hexane eluant) or ^{31}P NMR. This result differs from the corresponding reaction of $Na_2Cr(CO)_5$ with $(Me_3Si)_2NPCl_2$ which gives moderate yields of three major products and that with $(Me_3Si)_2CHPCl_2$ which gives two products. The salient features of the structures of both **5** and **6** are the central planar array of iron, phosphorus, and its substituent carbon or nitrogen atoms. The PP distances are 2.039 (1) Å for **5** and slightly longer 2.053 (1) Å for the nitrogen-substituted **6**. The longer distance in **6** is similar to the trend found in the $Cr(CO)_5$ system. Here, the range has been extended to include an aryloxide substituent which has an even longer PP bond than the amide. The PP bond lengths are fully consistent as P–P double bonding and are, in fact, very close to the values observed in free diphosphenes. For example, the free diphosphene $(Me_3Si)_2NP{=}PN(SiMe_3)_2$ has been isolated by Niecke and co-workers[24] and makes for an interesting comparison to **5** where it is coordinated to two $Fe(CO)_4$ fragments. In the free ligand the PP distance is 2.034 Å which is shorter than that seen in **6** (2.053 (1) Å). The PN distance in the free ligand, 1.769 Å, is considerably longer than the corresponding distance, 1.682 (2) Å, in complex **6**. This shortening is probably due to reduction in phosphorus–nitrogen lone-pair repulsion on coordination of the diphosphene to the metal. The ^{31}P NMR peaks of **5** and **6** appear as singlets at 384.6 and 403.9 ppm downfield which are typical for bulky diphosphene complexes of transition metals. A further notable feature of **5** is its stability. A sample showed no significant change over a period of 3 years on storage in the air. In the context of product **6** the reaction between $Na_2Fe(CO)_4$ and the bulky amino chlorophosphanes R_2NPCl_2 (NR_2 = $N(i\text{-}Pr)_2$, $N(C_6H_{11})_2$, or 2,2,6,6-tetramethylpiperidine) gives the interesting carbonyl bis(dialkylamino)phosphido complexes $[\{(R_2N)_2P\}_2COFe_2(CO)_6]$, but no diphosphene products were reported.[25]

The reaction between $Na_2Fe(CO)_4$ and $MesPCl_2$ provides a contrast to the clear-cut nature of the product in the case of **5** or **6**. In this case three significant products are obtained on chromatographic separation. The first involves the *trans*-diphosphene complex **1** as dark red purple crystals in 35% yield. This has structural features (Figure 2) similar to **5** and **6** with a PP distance of 2.029 (1) Å. The second product obtained is

---

(23) Hope, H.; De La Camp, U. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1972**, *A28*, 201.

(24) Niecke, E.; Rüger, R.; Lysek, M.; Pohl, S.; Schoeller, W. *Angew. Chem., Int. Ed. Engl.*

(25) King, R. B.; Wu, F.-J., Sadanani, N. D.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 4449.

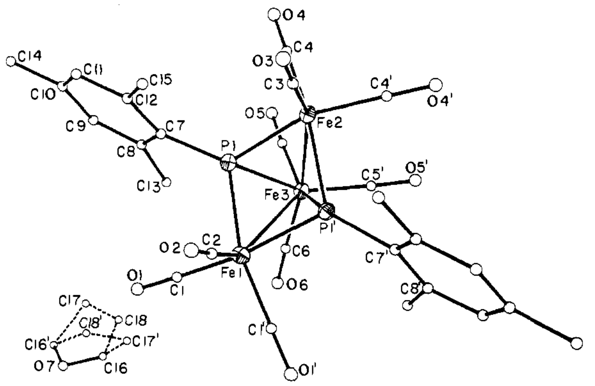


Figure 3. Computer-generated thermal ellipsoid plot of **2** (thermal ellipsoids at 40% probability for P and Fe, isotropic atoms given arbitrary fixed radius circles). Important bond distances (Å) and angles (deg): Fe(1)P(1) = 2.221 (3), Fe(2)P(1) = 2.240 (3), Fe(3)P(1) = 2.241 (3), Fe(1)Fe(3) = 2.721 (2), Fe(2)Fe(3) = 2.632 (3), Fe(1)···Fe(2) = 3.566 (3), P···P′ = 2.653 (3), P(1)C(7) = 1.833 (8), FeC_{av} = 1.791, CO_{av} = 1.142, Fe(1)P(1)Fe(2) = 106.2 (1), P(1)Fe(1)P(1)′ = 73.4 (1), P(1)-Fe(2)P(1)′ = 72.6 (1), Fe(1)Fe(3)Fe(2) = 83.5 (1), P(1)Fe(3)P(1′) = 72.6 (1), C(7)P(1)Fe(2) = 128.2 (3), Fe(3)P(1)C(7) = 130.8 (4), C(7)P(1)Fe(1) = 123.6 (4).

the cluster species $[Fe_3(CO)_9(\mu_3\text{-}PMes)_2]$ (**2**) in a 10% yield. The compound (Figure 3) has the same nido framework geometry as other Fe_3X_2 systems (X = S, Se, NR, AsR).[26] The cluster may also be considered as a complex between the planar basal $\{Fe(CO)_3PMes\}_2$ fragment (isoelectronic to cyclobutadiene) and $Fe(CO)_3$ (see later discussion of **7**). There is, however, no asymmetry in the Fe–P distances in the Fe(1)P(1)Fe(2)P(1′) moiety as seen in the case of **7**. Also the average basal Fe–P bond, ca. 2.23 Å, is, as expected, almost 0.1 Å longer than the average Fe–P distance found in **7**. The third fraction, compound **3**, is an orange-yellow crystalline substance and has a ^{31}P NMR that consists of a singlet at +48 ppm and an elemental analysis corresponding to the formula $[\{Fe(CO)_3PMes\}_n]$. It is very likely the mesityl-substituted analogue of the tetrahedrane isolobe $[\{Fe(CO)_3(P\text{-}t\text{-}Bu)\}_2]$ of Vahrenkamp and co-workers.[27] In the reaction between $Me_3SiCH_2PCl_2$ and $Na_2Fe(CO)_4$ only one isolable product is obtained although other ^{31}P resonances are seen in the crude reaction mixture. This has been assigned the same structure as **2** on the basis of IR, ^{31}P NMR, and analytical data. The smaller size of the Me_3SiCH_2 group relative to Mes may contribute to the lack of any nonaggregated products such as diphosphenes or phosphinidene complexes among the products.

The reaction between $Na_2Fe(CO)_4$ and $ROPCl_2$ (R = $-C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3$ or $-C_6H_2\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}Me$) results in two major products depicted by **7** and **8**. When the $-OC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3$ substituent is used, complex **8** crystallizes first, but a complex like **7** is also detectable (^{31}P NMR δ 564) in solution. If the $-OC_6H_2\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}Me$ group is used, complex **7** is crystallized first and a species similar to **8** remains in solution. Complexes of type **8** may be converted into complexes of type **7** by gently heating with the elimination of 2 equiv of CO in the process. However, this reaction is not reversible under ambient conditions.

The structure of complex **7** (Figure 4) features the interesting Fe_2P_2 core with unequal Fe–P bond lengths 2.202 (1) and 2.112 (1) Å prompting an isolobal comparison with cyclobutadiene. Moreover, this complex should, in theory at least, be capable of behaving as a donor in much the same way. We have been unable to detect any donor property in **7** which is, of course, quite sterically hindered. However, the isolobal comparison remains valid as exemplified by the donor behavior of the $\{Fe(CO)_3PMes\}_2$ in **2**. Complex **2** is probably formed as a consequence of the reduced

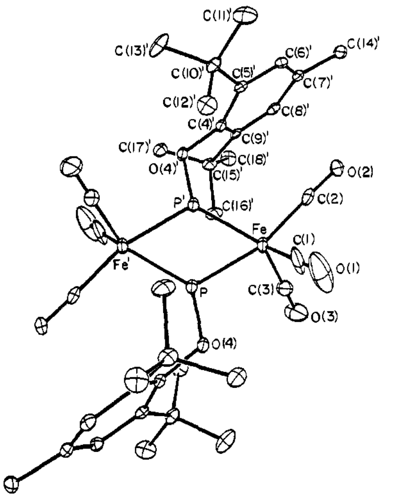


Figure 4. Computer-generated thermal ellipsoid plot of **7** reproduced from ref 12 (thermal ellipsoids at 30% probability level). Bond distances (Å) and angles (deg) relevant to this discussion: FeP = 2.202 (1), FeP′ = 2.112 (1), FePFe′ = 113.5 (1), PFeP′ = 66.5 (1), FePO(4) = 113.6 (1).

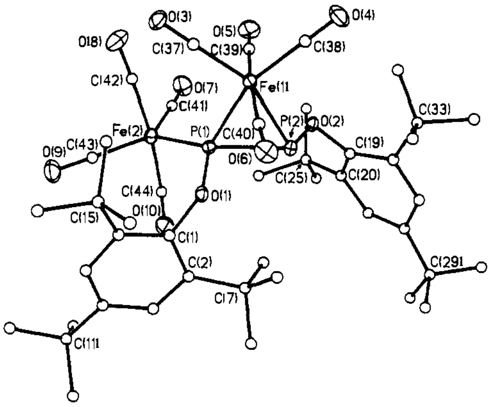


Figure 5. Computer-generated thermal ellipsoid plot of **8** (40% probability level thermal ellipsoids, isotropic atoms at arbitrary fixed radius circles). Bond distances and angles (deg) relevant to this discussion: P(1)P(2) = 2.184 (2), P(1)Fe(2) = 2.226 (2), P(1)Fe(1) = 2.347 (2), P(2)Fe(1) = 2.362 (2), P(1)Fe(1)P(2) = 55.3 (1), Fe(1)P(1)P(2) = 62.7 (1), Fe(1)P(2)P(1) = 62.0 (1).

steric requirements of the mesityl group compared to the large aryloxide substituents.[28]

The structure of **8** (Figure 5) remains unique and to our knowledge has not been described in any other system. The AB patterns observed in the ^{31}P NMR originally led us to assign its structure as a diphosphene coordinated to one $Fe(CO)_4$ fragment similar to the chromium species $[Cr(CO)_5\text{-}\textit{trans}\text{-}\{PCH(SiMe_3)_2\}_2]$. However, the X-ray structure showed it to have the diphosphene ROP=POR coordinated sideways to one $Fe(CO)_4$ and end-on to another $Fe(CO)_4$ fragment with concomitant lengthening of the PP bond from ca. 2.05 to 2.184 (2) Å. The odd structure may be due in part to enhancement of the π-orbital electron density by back-donation from OR. This results in side-on bonding, the earliest type of coordination known for diphosphenes.[29] The coordination of one (but not two as seen in other systems)[8] further

---

(26) Treichel, P. M.; Dean, W. K.; Douglas, W. M. *Inorg. Chem.* **1982**, *11*, 1609. Doedens, R. J. *Inorg. Chem.* **1969**, *8*, 570. Huttner, G.; Mohr, G.; Frank, A.; Schubert, U. *Inorg. Chem.* **1976**, *118*, 673. Jacob, M.; Weiss, F. *J. Organomet. Chem.* **1977**, *131* 263.

(27) Vahrenkamp, H.; Wolters, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 154.

(28) Johnson, M. D. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: New York, 1982; Chapter 31, Vol. 4, 460.

(29) Green, J. C.; Green, M. L. H.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1974**, 212. Cammilo, E.; Loda, A.; Prout, Y.; Daran, J.-C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *33B*, 2608. Elanes, P. S.; Leverett, P.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1971**, 747. Schäfer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1358. Deppisch, B.; Schäfer, H. *Acta Crystallogr. Sect. B: Struct. Crystallogr., Cryst. Chem.* **1982**, *38B*, 748. Chatt, J.; Hitchcock, P. F., Pidcock, A.; Warrens, C. P.; Dixon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 932.

metal carbonyl moiety in the end on fashion is probably a result of steric factors.

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Tables of crystal data, atom coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates (11 pages); listings of structure factors (34 pages). Ordering information is given on any current masthead page.

Preparation and Physical Properties of Trinuclear Oxo-Centered Manganese Complexes of the General Formulation $[Mn_3O(O_2CR)_6L_3]^{0,+}$ (R = Me or Ph; L = a Neutral Donor Group) and the Crystal Structures of $[Mn_3O(O_2CMe)_6(pyr)_3](pyr)$ and $[Mn_3O(O_2CPh)_6(pyr)_2(H_2O)]\cdot 0.5MeCN$

John B. Vincent,[†] Hsiu-Rong Chang,[§] Kirsten Folting,[‡] John C. Huffman,[‡] George Christou,*[†] and David N. Hendrickson*[§]

Contribution from the Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, and the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. *Received October 15, 1986*

Abstract: The reaction of N-*n*-Bu_4MnO_4 with appropriate reagents in nonaqueous solvents leads to the high-yield formation of trinuclear oxo-centered Mn complexes of general formulation $[Mn_3O(O_2CR)_6L_3]^{z+}$ (**1**, R = Me, L = pyr, z = 1; **2**, R = Me, L = pyr, z = 0, monopyridine solvate; **3**, R = Me, L = pyr, z = 0, unsolvated; **4**, R = Ph, L_3 = $(pyr)_2(H_2O)$, z = 0; **5**, R = Me, L = HIm, z = 1; pyr = pyridine, HIm = imidazole). The crystal structures of complexes **2** and **4** have been determined. Complex **2** crystallizes in rhombohedral space group R32 with (at −50 °C) $a = b = 17.552$ (6) Å, $c = 10.918$ (3) Å, $\gamma = 120.00$ (1)°, and $Z = 3$. A total of 1546 unique data with $F > 3\sigma(F)$ were refined to conventional values of R and R_w of 5.77 and 5.86%, respectively. Complex **4** crystallizes in monoclinic space group $P2_1$ with (at −156 °C) $a = 15.058$ (10) Å, $b = 23.600$ (17) Å, $c = 14.959$ (10) Å, $\beta = 91.01$ (3)°, and $Z = 2$. A total of 7174 unique data with $F > 3\sigma$ (F) were refined to values of R and R_w of 8.64 and 8.43%, respectively. Both **2** and **4** possess an oxo-centered Mn_3O unit characteristic of "basic carboxylates" with peripheral ligation provided by bridging carboxylate and terminal pyr (or H_2O) groups. Each Mn is distorted octahedral, and consideration of overall charge of the trinuclear units necessitates a mixed-valence $Mn^{II}Mn_2^{III}$ description. In **2**, the presence of a C_3 axis through the central O and perpendicular to the Mn_3O unit necessitates the Mn centers to be crystallographically equivalent, suggesting rapid *intra*molecular electron transfer or electronic delocalization. In contrast, **4** possesses no imposed symmetry elements and is in a trapped-valence situation in accord with its mixed-ligand nature, since two Mn centers have a terminal pyr group while the third Mn has a terminal H_2O molecule. The latter metal center is assigned as the Mn^{II} ion based on its longer metal–ligand distances. Variable temperature solid state magnetic susceptibility studies have been performed on **1–4** in the temperature range of ∼6 to ∼340 K. Satisfactory fits to the observed susceptibility data have been obtained by assuming isotropic magnetic exchange interactions and employing the appropriate spin Hamiltonians and derived susceptibility equations. All Mn centers are shown to be in high-spin electronic configurations and to be antiferromagnetically coupled. The derived exchange parameters are all relatively small in magnitude, $|J| < 11$ cm^{-1}. In addition, it is found that the antiferromagnetic exchange interactions are smaller for the Mn_3O units than those for isostructural Fe_3O systems, and a rationalization is proposed. Since phase transitions had previously been characterized by heat capacity measurements on $[Fe_3O(O_2CMe)_6(pyr)_3](pyr)$, isostructural complex **2** was investigated by differential scanning calorimetry (DSC) in the temperature range 153–303 K. An exothermic thermal effect is clearly evident with a peak at 184.7 K in the cooling curve (the other mixed-valence Mn_3O systems showed no thermal effects in their DSC thermograms). The origin of this thermal effect and comparisons with the corresponding behavior of the Fe complex are described.

Interest in trinuclear μ_3-oxo-bridged manganese complexes of general composition $[Mn_3O(O_2CR)_6L_3]$ draws from three quarters. First, there is a need to characterize polynuclear manganese complexes as models for the water oxidation center of photosynthetic electron transport chains. A cluster of two to four manganese ions is known to catalyze the oxidation of two H_2O molecules to give one O_2 molecule.[1] Second, a comparison of the *intra*molecular electron transfer characteristics of mixed-valence Mn_3O complexes with those of the reasonably well-characterized Fe_3O analogues would be instructional. The electronic coupling between Mn ions in the Mn_3O complexes should be weaker than that found for the mixed-valence Fe_3O complexes. Third, the magnetic exchange interaction characteristics of the mixed-valence Mn_3O complexes need to be compared to those of the Fe_3O analogues.

Trinuclear μ_3-oxo-bridged iron acetate complexes have been studied in great detail,[2-7] whereas analogous mixed-valence

---

[†] Indiana University, Department of Chemistry.

[‡] Indiana University, Molecular Structure Center.

[§] University of Illinois.

(1) (a) Amesz, J. *Biochim. Biophys. Acta* **1983**, *726*, 1. (b) Govindjee; Kambara, T.; Coleman, W. *Photochem. Photobiol.* **1985**, *42*, 187. (c) Dismukes, G. C. *Photochem. Photobiol.* **1986**, *43*, 99.

(2) (a) Oh, S. M.; Hendrickson, D. N.; Hassett, K. L.; Davis, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 7984. (b) Oh, S. M.; Hendrickson, D. N.; Hassett, K. L.; Davis, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 8009.