bond distances and angles in Table V.

All computation used the SHELXTL program system (version 5.1), Nicolet Corp., Madison, WI. Atomic coordinates and selected bond distances and angles are given in Tables IV and V, respectively.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support, and Degussa AG for generous gifts of chemicals. We also thank U. Neumann and R. Schedl for the elemental analyses, Dr. G. Lange for the mass spectra, and Dr. W. Buchner and C. P. Kneis for NMR measurements.

Registry No. **2**, 12354-85-7; **3**, 67841-74-1; **4**, 87882-77-7; **5**, 112654-36-1; **6**, 87897-87-8; **7**, 87897-88-9; **8**, 112654-37-2; **9**, 87882-79-9; **10**, 87882-78-8; **11**, 112654-38-3; **13**, 87882-88-0; **14**, 112654-39-4; **15**, 112654-40-7; **16**, 112654-41-8; **17**, 112654-42-9; **18**, 112680-31-6; **19**, 112654-43-0; $[C_5He_5Rh(PMe_2H)_2]$, 86224-84-2; $[C_5H_5Rh(CO)I_2]$, 12192-49-3; $[C_5H_5Co(CO)I_2]$, 12012-77-0; $[C_6H_6RuCl_2]_2$, 37366-09-9; $[C_5Me_5Ir(PMe_2H)Cl_2]$, 112654-44-1; $[C_5Me_5IrCl_2]_2$, 12354-84-6; Rh, 7440-16-6; Co, 7440-48-4.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages); a listing of structure factors (30 pages). Ordering information is given on any current masthead page.

Phosphido-Bridged Diiron Complexes from Low-Coordinate Phosphorus Compounds

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Received August 24, 1987

The (methylene)phosphido-bridged diiron complex $[\mu\text{-}(Me_3Si)_2C{=}P](\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (**2**) was prepared by the reaction of $Li[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ (**1**) with $(Me_3Si)_2C{=}PCl$, and the structure was determined by X-ray diffraction. Treatment of **1** with $(Me_3Si)_2NP{=}C(H)SiMe_3$ (**3**) yielded two new phosphido-bridged complexes, $\{\mu\text{-}[Me_3Si(H)N][(Me_3Si)_2CH]P\}(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (**4**) and $\{\mu\text{-}[(Me_3Si)_2N][Me_3SiCH_2]P\}(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (**5**). While the major product of **1** and **3** was **4**, complex **5** was the major product when **3** was treated with $Et_3NH[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$. Characterization of these new complexes by ^1H, ^{31}P, and ^{13}C NMR spectroscopy, elemental analysis, and IR spectroscopy is discussed.

Introduction

Low-coordinate phosphorus compounds, $RP{=}NR'$ and $RP{=}CR'_2$, are interesting ligands because there are several sites for bonding to transition metals, i.e., through the phosphorus lone pair[1] as is typical for ordinary phosphines, R_3P, through the $P{=}E$ π system[2] as is typical for alkenes, through direct σ P–M bonds,[3] or through combinations of these.[4] Another type of phosphine bonding mode is that found in phosphido-bridged systems where the phosphorus is essentially bonded to the two metals through both a simple σ covalent bond and a coordinate covalent bond involving the phosphorus lone pair.[5] The only examples of this type of bonding mode for low-coordinate phosphorus are $\{[\mu\text{-}P{=}C(SiMe_3)_2]_2Fe_2(CO)_6\}$ which has been prepared by treatment of $(Me_3Si)_2C{=}PCl$ with $Na_2Fe(CO)_4$[6] and $\{(\mu\text{-}P{=}ML_n)_2Fe_2(CO)_6\}$ $[ML_n = Cr(CO)_5, Cp(CO)_2Mn]$ which has been prepared from $Fe_2(CO)_9$ and $L_nM\text{-}PX_3$.[7] In this paper we report the preparation and X-ray crystallographic structure of another low-coordinate phosphido-bridged diiron complex as well as the preparation of two sterically hindered phosphido-bridged complexes that are derived from a low-coordinate (methylene)phosphine.

Results and Discussion

A novel diiron complex with the metal atoms bridged by one [bis(trimethylsilyl)methylene]phosphido moiety, $P{=}C(SiMe_3)_2$, and by the bulky *tert*-butylthio group, *t*-

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(1) See for example: (a) Eshtiagh-Hosseini, H.; Kroto, H. W.; Nixon, J. F.; Maah, M. J.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1981**, 199. (b) Appel, R.; Casser, C.; Immenkeppel, M.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 895. (c) Neilson, R. H.; Thoma, R. J.; Vickovic, I.; Watson, W. H. *Organometallics* **1984**, *3*, 1132. (d) Scherer, O. J.; Konrad, R.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1982**, *115*, 414.

(2) See for example: (a) Al-Reysayes, S.; Klein, S. I.; Kroto, H. W.; Meidine, M. F.; Nixon, J. F.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 930. (b) Cowley, A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H.-M. *J. Am. Chem. Soc.* **1984**, *106*, 7015. (c) Appel, R.; Casser, C.; Knoch, F. *J. Organomet. Chem.* **1986**, *293*, 213. (d) Akpan, C. A.; Meidine, M. F.; Nixon, J. F.; Yoshifugi, M.; Toyota, K.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1985**, 946.

(3) See, for example: (a) Gudat, D.; Niecke, E.; Arif, A. M.; Cowley, A. H.; Quashie, S. *Organometallics* **1986**, *5*, 593. (b) Weber, L.; Reizig, K.; Frebel, M. Boese, R.; Polk, M. *J. Organomet. Chem.* **1986**, *306*, 105.

(4) See, for example: (a) Holand, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1984**, *106*, 826. (b) Kraaijkamp, J. G.; von Koten, G.; van der Knaap, T. A.; Bickelhaupt, F.; Stam, C. H. *Organometallics* **1987**, *6*, 2014. (c) Knoll, F.; Huttner, G.; Wasiucionek, M.; Zsolnai, L. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 739. (d) Scherer, O. J.; Walter, R.; Sheldrick, W. E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 115.

(5) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 40 and references cited therein.

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(7) Lang, H.; Zsolnai, L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 976.

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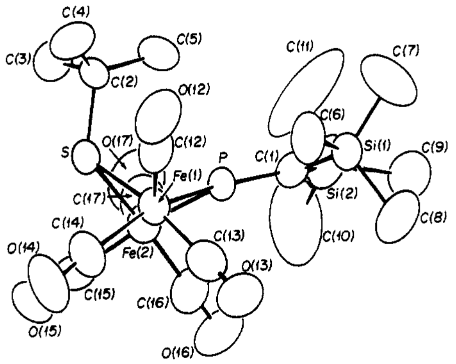
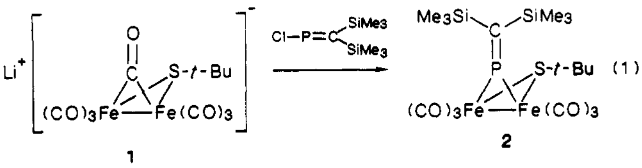


Figure 1. Perspective drawing of [μ-(Me$_3$Si)$_2$C=P](μ-*t*-BuS)-Fe$_2$(CO)$_6$ (2) showing the numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

BuS, was prepared in high yield by treatment of readily available Li[(μ-*t*-BuS)(μ-CO)Fe$_2$(CO)$_6$][8] with (Me$_3$Si)$_2$C=PCl.[9] This reaction proceeded with elimination of the bridging carbonyl group to afford high yields of a red crystalline compound identified as the new (methylene)phosphido-bridged species 2 (eq 1) and nonisolable quantities of its isomer (<5% by ^{31}P NMR; δ 475). NMR spectroscopic analysis of 2 was particularly helpful in establishing the bridging structure. The downfield chemical shift (δ 490) in the ^{31}P NMR spectrum is typical of both low-coordinate phosphorus compounds[10] and μ-phosphido-bridged Fe–Fe-bonded systems.[11] Furthermore, the ^{13}C NMR shows a downfield doublet for the P=C carbon at δ 171.5 and a large P=C coupling constant (J_{PC} = 42.4 Hz) which confirm the sp^2 nature of the carbon attached to phosphorus. The composition of 2 was also confirmed by a straightforward ^{1}H NMR spectrum, by elemental analysis, and by the mass spectrum which contained a peak for the parent ion at *m/z* 558 followed by signals for the sequential loss of six carbon monoxide units.

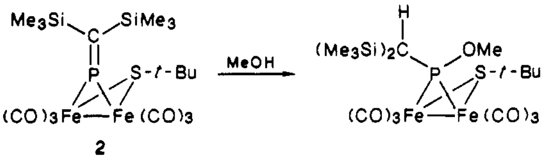


(1)

The crystallographic analysis of 2 confirms the bridging nature of the phosphorus, and Figure 1 clearly shows the "butterfly" structure of the resulting PSFe$_2$ core. This core is typical of phosphido-[5] and sulfido-bridged[12] diiron complexes. In this case, however, the angle between the planes defined by Fe(1), Fe(2), S and Fe(1), Fe(2), P, 113.2°, is somewhat larger than that in the related complexes [μ-P=C(SiMe$_3$)$_2$]$_2$Fe$_2$(CO)$_6$,[6] (μ-EtS)$_2$Fe(CO)$_3$,[13] and [(μ-Ph$_2$P)Fe(CO)$_3$]$_2$),[14] the analogous angles being 102.3°, 103°, and 100°, respectively. This angle has been opened, at least in part, to accommodate the *tert*-butyl group which is oriented toward the (methylene)phosphine.

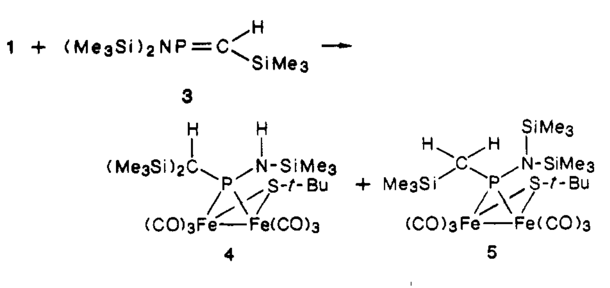
There is asymmetry in the Fe to bridging atom lengths. The Fe(1)–P and Fe(1)–S lengths are both significantly shorter than the analogous lengths from Fe(2). The P=C bond is very short, 1.621 (9) Å. Though the standard deviation is large, it is apparent that this value is shorter than the P=C bond length of 1.68–1.72 Å compiled for uncoordinated phosphaalkenes.[10] This P=C bond length in 2 is also significantly shorter than that in [μ-P=C(SiMe$_3$)$_2$]$_2$Fe$_2$(CO)$_6$ (1.650 (4) Å).[6] In concert with this is the fact that 2 adopts a slightly smaller Fe–P–Fe angle, 73.0 (1)° vs 75.0 (1)°. The length of the Fe–Fe separation in 2, 2.586 (2) Å, lies between the values for related disulfido (e.g., 2.537 Å for (μ-EtS)$_2$Fe(CO)$_3$[13]) and diphosphido (e.g., 2.666 (1) Å in [μ-P=C(SiMe$_3$)$_2$]$_2$Fe$_2$(CO)$_6$[6]) species.

The steric constraints of the bulky Me$_3$Si substituents at phosphorus and the *t*-Bu group of sulfur are demonstrated by the low reactivity of 2 with MeOH (eq 2) relative to the reaction of MeOH with less hindered (methylene)phosphines.[15] Four hours after addition of methanol to 2, the ^{31}P NMR spectrum of the reaction mixture showed only two very small signals at δ 298 and 284 in nearly equal intensities. These peaks grew gradually over 2 days with a concomitant decrease of the downfield signal at δ 490. Presumably, two isomers are formed by the addition of MeOH across the double bond. The ^{1}H NMR spectrum showed the expected signals for the P–OMe substituents on the isomers at δ 3.4 and 3.6 with typical POC coupling constants of 12.3 and 10.0 Hz, respectively.[15]



(2)

The low reactivity of 2 with methanol led to the investigation of another potential route to (methylene)phosphido-bridged complexes, particularly those which have less hindered P=C bonds. On the basis of the fact that alkyllithium reagents[16] (MeLi, *t*-BuLi) and lithium amides[17] (*i*-Pr$_2$NLi, *t*-Bu(Me$_3$Si)NLi) cause the cleavage of the P–N bond in the (methylene)phosphine (Me$_3$Si)$_2$NP=C(SiMe$_3$)H, it was anticipated that a similar P–N bond cleavage might occur with Li[μ-*t*-BuS)(μ-CO)-Fe$_2$(CO)$_6$]. Instead, the reaction took a very different pathway which produced the new phosphido-bridged diiron complex 4 and trace quantities of 5 (eq 3). Complex 4 was readily separated from 5 by frit chromatography and was obtained in high yield (62%). A plausible reaction pathway explaining the formation of 4 might involve initial



(3)

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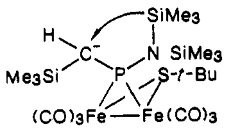
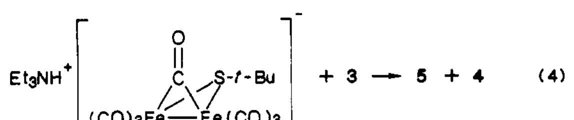


formation of an intermediate anion followed by a 1,3-silyl migration from nitrogen to carbon. Similar silyl shifts are well-known in related Si–N–P–C systems.[18] Quenching of the rearranged anion by a proton either from the solvent (THF) or from moisture encountered during workup (e.g., silicic acid columns or handling in air) would account for the formation of 4. In fact, the ^{31}P NMR spectra of the reaction mixture indicated the presence of both the final isolated product 4 (δ 195) and very weak signals for 5 (δ 188 and 176) as well as a second species (δ 150) which is probably the ionic intermediate. The quantity of this latter species varied when the reaction was repeated, and its disappearance was always facilitated by the addition of methanol and was accompanied by a corresponding increase in the δ 195 resonance. The identity of complex 4 was verified by the ^{13}C and ^{1}H NMR spectra as well as by elemental analysis and IR and mass spectroscopy. The mass spectrum contained peaks for the parent ion at m/z 647 and peaks for the successive elimination of six carbonyl groups. The IR spectrum clearly showed a strong absorption for an N–H stretching vibration at 3350 cm^{-1}. Further evidence for 4 is provided by the ^{1}H NMR which showed two signals (δ 1.0 and 1.3) corresponding to one proton on nitrogen and one on carbon with expected couplings to phosphorus (J_{PCH} = 9 Hz and J_{PNH} = 1.6 Hz) as well as signals for the $(Me_3Si)_2C$, Me_3SiN, and t-Bu groups in an 18:9:9 ratio. The ^{13}C NMR spectrum was, however, particularly diagnostic, since the signal for the $(Me_3Si)_2CH$ carbon was a doublet (δ 28.3) in the off-resonance-decoupled experiment, confirming that only one proton was attached to this carbon.

Since the presumed anionic intermediate is quenched by a proton, we decided to investigate the reaction of 3 with the related complex $Et_3NH[(\mu\text{-}t\text{-BuS})(\mu\text{-CO})Fe_2(CO)_6]$ in which the Et_3NH^+ counterion is known to act as an internal proton source.[19] Not surprisingly, the reaction gave different results (eq 4) with 5 being the major product and 4 present in only small amounts. After purification by column chromatography, the resulting red oil was identified by NMR spectroscopic analysis as isomers of 5 (^{31}P δ 188 and 176 and corresponding double sets of signals in the ^{1}H and ^{13}C spectra). As in the case of 4, the off-resonance-decoupled ^{13}C NMR spectrum was particularly definitive since it contained two triplets (δ 22.6 and 36.0) for the CH_2SiMe_3 carbons. Further evidence for structure 5 was the lack of an N–H stretching vibration in the IR spectrum. The elemental analysis of 5 established the composition of the isomers, as did an independent synthesis by treatment of $Li[(\mu\text{-}t\text{-BuS})(\mu\text{-CO})Fe_2(CO)_6]$ (1) with $(Me_3Si)_2NP(Cl)CH_2SiMe_3$.



Interestingly, 5 converted to 4 on storage for several months, upon refluxing in benzene for several days, or on stirring in THF/H_2O for more than a week. These conditions are presumably favorable for rearrangement of the substituents at the nitrogen and carbon.

The reactions of the $(\mu\text{-}t\text{-BuS})(\mu\text{-CO})Fe_2(CO)_6^-$ ion with low-coordinate phosphorus compounds are clearly dependent on the nature of the substituents at phosphorus and on the counterion (i.e., Li^+ vs Et_3NH^+). Further studies of other factors influencing such reactions and the potential synthetic value of these systems are in progress.

Experimental Section

General Comments. All reactions were carried our under an atmosphere of prepurified tank nitrogen. The following reagents were prepared by published procedures: $Fe_3(CO)_{12}$,[20] $(Me_3Si)_2C{=}PCl$,[9] $(Me_3Si)_2NP{=}C(SiMe_3)H$,[15] and $(Me_3Si)_2NP(Cl)CH_2SiMe_3$.[15] Tetrahydrofuran was distilled from sodium/benzophenone prior to use. Pentane, t-BuSH, and MeOH were used as obtained from commercial sources.

Filtration chromatography involved dissolution of the reaction products in pentane and pouring this solution onto the top of a bed of silicic acid in a 250-mL fritted glass filter. Elution by pentane was acelerated by suction filtration. Column chromatography was performed on 25 × 250 mm columns of silicic acid with elution by pentane. All chromatography was carried out without exclusion of moisture.

Most ^{1}H and all ^{31}P NMR spectra were recorded on a JEOL FX-90Q or IBM WP-200SY FT NMR spectrometer. All ^{13}C and selected ^{1}H NMR spectra were recorded on a Bruker 250 or 270 NMR spectrometer. Off-resonance-decoupled ^{13}C NMR spectra were also recorded and were used to assign the ^{13}C resonances. Positive ^{1}H and ^{13}C NMR shifts are downfield from external Me_4Si while positive ^{31}P NMR shifts are downfield from external H_3PO_4. All NMR spectra were recorded as $CDCl_3$ solutions unless noted otherwise. Mass spectra were obtained with a Varian MAT-44 instrument operating at 70 eV. IR spectra were recorded by using a Perkin-Elmer 457A grating infrared spectrophotometer. Melting points were determined on analytically pure samples by using a Büchi capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, or by Galbraith Laboratories, Inc., Knoxville, TN.

Crystal data: $C_{17}H_{27}Fe_2O_6PSSi_2$; M_r 558.3; monoclinic; a = 11.002 (2) Å, b = 15.621 (3) Å, c = 15.772 (2) Å; β = 99.13 (1)°; U = 2676.6 (7) Å^3, Z = 4, D_{calcd} 1.386 g cm^{-3}; Cu Kα radiation (λ = 1.54 18 Å); space group $P2_1/n$.

Collection and Reduction of X-ray Data. A crystal of dimensions 0.05 × 0.10 × 0.60 mm was cleaved from a larger, platelike crystal, mounted on a glass fiber, and attached to an automated Syntex $P2_1$ diffractometer. Cell constants were obtained, at room temperature, from a least-squares fit of setting angles for 15 reflections. A quadrant of data ($\pm h,k,l$; 4.0° $\le 2\theta \le$ 130°) was measured. Of the 4466 independent reflections, 2586 were regarded as observed ($I \ge 2\sigma(I)$). Empirical absorption corrections were made to the data via a Ψ scan using the 040 reflection whose I/I(max) ranged from 0.56 to 1.0.

Structure Solution and Refinement. The structure was solved by direct methods,[21] and successive F_0 maps revealed the positions of the rest of the non-hydrogen atoms. Hydrogen atoms were calculated to be 1.04 Å from their bonded atoms. Full-matrix least-squares iterations on positional parameters and anisotropic thermal parameters for non-hydrogen atoms brought refinement to convergence at $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.072 and $R_w = [\sum w||F_o| - |F_c||^2/\sum|F_o|^2]^{1/2}$ = 0.077. The least-squares weighting that was used was $w^{1/2} = 1$ for $|F_o| \le 31.0$ and $w^{1/2} = 31.0/|F_o|$ for $|F_o| \ge 31.0$. The atomic scattering factors for the non-hydrogen atoms were those from Cromer and Waber[22] and those for hydrogen atoms were from Stewart.[23] Anomalous dispersion factors for the Fe, S, P, and Si atoms were from ref 24. All calculations

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Table I. Fractional Atomic Coordinates ($\times 10^4$) for the Non-Hydrogen Atoms, with Estimated Standard Deviations in Parentheses

atom	*x*/*a*	*y*/*b*	*z*/*c*
Fe(1)	976 (1)	782 (1)	3479 (1)
Fe(2)	384 (1)	525 (1)	1846 (1)
S	–520 (2)	1504 (2)	2619 (1)
P	2119 (2)	1049 (2)	2520 (1)
Si(1)	4816 (2)	1420 (2)	3317 (2)
Si(2)	3954 (3)	1288 (3)	1263 (2)
C(1)	3535 (8)	1208 (6)	2393 (6)
C(2)	–333 (8)	2672 (6)	2407 (6)
C(3)	–1361 (10)	2859 (7)	1667 (7)
C(4)	–580 (12)	3132 (8)	3211 (8)
C(5)	910 (10)	2912 (7)	2181 (9)
C(6)	4291 (10)	1633 (9)	4365 (8)
C(7)	5689 (14)	2391 (10)	3099 (11)
C(8)	5807 (12)	473 (10)	3480 (11)
C(9)	5583 (12)	1057 (10)	1244 (8)
C(10)	3150 (15)	486 (19)	510 (9)
C(11)	3483 (17)	2278 (14)	809 (11)
C(12)	1279 (9)	1553 (7)	4357 (6)
O(12)	1462 (8)	2021 (6)	4898 (5)
C(13)	2068 (9)	–15 (7)	3904 (6)
O(13)	2774 (8)	–515 (5)	4177 (5)
C(14)	–273 (9)	169 (8)	3834 (7)
O(14)	–1037 (7)	–227 (6)	4030 (6)
C(15)	172 (9)	904 (7)	843 (6)
O(15)	–13 (10)	1211 (6)	145 (5)
C(16)	1220 (10)	–418 (8)	1699 (7)
O(16)	1764 (9)	–1023 (6)	1607 (7)
C(17)	–1018 (10)	–87 (7)	1845 (7)
O(17)	–1894 (7)	–486 (6)	1832 (7)

Table II. Interatomic Distances (Å) and Angles (deg), with Estimated Standard Deviations in Parentheses

(a) Bond Lengths			
Fe(1)–Fe(2)	2.586 (2)	Si(1)–C(7)	1.857 (16)
Fe(1)–S	2.260 (3)	Si(1)–C(8)	1.831 (15)
Fe(1)–P	2.156 (3)	Si(2)–C(1)	1.904 (11)
Fe(1)–C(12)	1.826 (10)	Si(2)–C(9)	1.832 (14)
Fe(1)–C(13)	1.785 (11)	Si(2)–C(10)	1.851 (24)
Fe(1)–C(14)	1.833 (11)	Si(2)–C(11)	1.748 (21)
Fe(2)–S	2.280 (3)	C(2)–C(3)	1.519 (15)
Fe(2)–P	2.190 (3)	C(2)–C(4)	1.518 (15)
Fe(2)–C(15)	1.672 (10)	C(2)–C(5)	1.515 (14)
Fe(2)–C(16)	1.770 (12)	C(12)–O(12)	1.117 (13)
Fe(2)–C(17)	1.813 (11)	C(13)–O(13)	1.137 (13)
S–C(2)	1.873 (10)	C(14)–O(14)	1.126 (14)
P–C(1)	1.621 (9)	C(15)–O(15)	1.189 (13)
Si(1)–C(1)	1.890 (10)	C(16)–O(16)	1.141 (15)
Si(1)–C(6)	1.866 (13)	C(17)–O(17)	1.146 (13)
(b) Bond Angles			
Fe(2)–Fe(1)–S	55.67 (7)	Fe(2)–S–C(2)	119.3 (3)
Fe(2)–Fe(1)–P	54.11 (7)	Fe(1)–P–Fe(2)	73.0 (1)
Fe(2)–Fe(1)–C(12)	147.7 (3)	Fe(1)–9–C(1)	142.7 (4)
Fe(2)–Fe(1)–C(13)	108.3 (3)	Fe(2)–P–C(1)	141.4 (4)
Fe(2)–Fe(1)–C(14)	98.1 (3)	C(1)–Si(1)–C(6)	114.6 (5)
S–Fe(1)–P	86.1 (1)	C(1)–Si(1)–C(7)	110.1 (6)
S–Fe(1)–C(12)	98.9 (3)	C(1)–Si(1)–C(8)	108.7 (6)
S–Fe(1)–C(13)	162.9 (3)	C(6)–Si(1)–C(7)	105.1 (7)
S–Fe(1)–C(14)	86.2 (4)	C(6)–Si(1)–C(8)	106.3 (6)
P–Fe(1)–C(12)	110.4 (4)	C(7)–Si(1)–C(8)	111.9 (7)
P–Fe(1)–C(13)	88.0 (3)	C(1)–Si(2)–C(9)	112.5 (5)
P–Fe(1)–C(14)	149.8 (4)	C(1)–Si(2)–C(10)	113.0 (6)
C(12)–Fe(1)–C(13)	98.2 (5)	C(1)–Si(2)–C(11)	109.8 (7)
C(12)–Fe(1)–C(14)	99.7 (5)	C(9)–Si(2)–C(10)	103.0 (8)
C(13)–Fe(1)–C(14)	90.8 (5)	C(9)–Si(2)–C(11)	113.3 (8)
Fe(1)–Fe(2)–S	54.93 (7)	C(10)–Si(2)–C(11)	104.8 (10)
Fe(1)–Fe(2)–P	52.90 (7)	P–C(1)–Si(1)	123.1 (5)
Fe(1)–Fe(2)–C(15)	149.7 (4)	P–C(1)–Si(2)	120.2 (5)
Fe(1)–Fe(2)–C(16)	101.9 (3)	Si(1)–C(1)–Si(2)	116.5 (5)
Fe(1)–Fe(2)–C(17)	99.4 (4)	S–C(2)–C(3)	103.6 (7)
S–Fe(2)–P	84.9 (1)	S–C(2)–C(4)	105.8 (7)
S–Fe(2)–C(15)	105.2 (4)	S–C(2)–C(5)	114.3 (7)
S–Fe(2)–C(16)	155.1 (4)	C(3)–C(2)–C(4)	109.9 (8)
S–Fe(2)–C(17)	84.9 (3)	C(3)–C(2)–C(5)	111.2 (9)
P–Fe(2)–C(15)	107.8 (4)	C(4)–C(2)–C(5)	111.6 (9)
P–Fe(2)–C(16)	86.7 (4)	Fe(1)–C(12)–O(12)	179.5 (9)
P–Fe(2)–C(17)	150.8 (4)	Fe(1)–C(13)–O(13)	179.2 (10)
C(15)–Fe(2)–C(16)	99.7 (5)	Fe(1)–C(14)–O(14)	177.6 (11)
C(15)–Fe(2)–C(17)	101.2 (5)	Fe(2)–C(15)–O(15)	176.3 (10)
C(16)–Fe(2)–C(17)	91.2 (5)	Fe(2)–C(16)–O(16)	179.7 (10)
Fe(1)–S–Fe(2)	69.42 (8)	Fe(2)–C(17)–O(17)	178.5 (10)
Fe(1)–S–C(2)	120.2 (3)		

were performed on a VAX 11/780 computer. There is some disorder observed in the trimethylsilyl groups with one group showing quite exaggerated carbon manifolds. The atomic coordinates are shown in Table I, and bond lengths and angles are shown in Table II.

Synthesis of $\{[\mu\text{-}(Me_3Si)_2C{=}P)][\mu\text{-}t\text{-}BuS]\}Fe_2(CO)_6$ (2). The complex $Li[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ (1) was prepared in situ[8] by treatment of $Fe_3(CO)_{12}$ (1.5 g, 3.0 mmol) in THF (ca. 20 mL) with *n*-BuLi (1.2 mL, 3.0 M in hexane) and *t*-BuSH (0.34 mL, 3.0 mmol) at –78 °C. After being stirred for 30 min at –78 °C, the solution was warmed to room temperature and stirred for 1 h. The resulting red solution was cooled to 0 °C, and $(Me_3Si)_2C{=}PCl$ (0.67 g, 3.0 mmol) was added via syringe. Stirring at 0 °C for 10 min and then at room temperature for 1 h resulted in a brown-red solution. Removal of THF in vacuo and frit chromatography yielded orange solid **2**, which was further purified by recrystallization from pentane; yield 1.3 g (77%); mp 125–126 °C; ^{31}P NMR (C_6D_6) δ 489.9, 475.3; ^1H NMR (C_6D_6) (major isomer) δ 0.43 (s, 18 H, Me_3Si), 1.09 (s, 9 H, CMe_3); $^{13}C[^1H]$ NMR (C_6D_6) δ 1.77 (d, J_{PCSiC} = 5.2 Hz, Me_3Si), 32.3 (s, CMe_3), 48.9 (S, CMe_3), 171.5 (d, J_{PC} = 42.4 Hz, C=P), 207.4, 210.1 (br s, CO); mass spectrum, *m*/*z* (relative intensity) 558 (M^+, 7), 530 (M^+ – CO, 7), 474 (M^+ – 2 CO, 23), 446 (M^+ – 4 CO, 14), 418 (M^+ – 5 CO, 30), 390 (M^+ – 6 CO, 51), 333 ($Fe_2SPC(SiMe_3)_2^+$, 20), 260 ($Fe_2SPCSiMe_3^+$, 8), 245 ($Fe_2SPCSiMe_2^+$, 17), 163 ($FeS(t\text{-}Bu)P^+$, 28), 155 (Fe_2PC^+, 8), 73 (Me_3Si^+, 100), 57 ($t\text{-}Bu^+$, 34). Anal. Calcd for $C_{17}H_{27}Fe_2O_6PSSi_2$: C, 36.57; H, 4.87. Found: C, 36.85; H, 4.97.

Reaction of 2 with MeOH. A sample of **2** (0.48 g, 0.86 mmol) was dissolved in THF (ca. 5 mL) or CH_2Cl_2 (5 mL), and an excess of methanol (0.1 mL) was added. After the mixture was stirred at room temperature for 4 h, the reaction was incomplete as determined by the ^{31}P NMR spectrum of the mixture which showed a large signal at δ 489 and very small resonances at δ 298 and 285. After 2 days the signal for **2** was gone, so the volatile components of the reaction mixture were removed and the residue was purified by frit chromatography: yield 0.30 g (59%); ^{31}P NMR; δ 298.5, 284.9; ^1H NMR δ 0.26, 0.23 (s, Me_3Si), 1.47, 1.40 (s, *t*-Bu), 3.62, 3.43 (d, J_{POCH} = 12.31, 9.96 Hz, OMe). Anal. Calcd for $C_{18}H_{31}Fe_2O_7PSSi_2$: C, 36.62; H, 5.29. Found: C, 37.25; H, 5.55.

Reaction of $Li[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ (1) with $(Me_3Si)_2NP{=}C(H)SiMe_3$ (3). The complex $Li[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ (1) was prepared as described above and then treated with the (methylene)phosphine **3** (0.83 g, 3.0 mmol) at 0 °C. After the mixture was stirred overnight at room temperature, either the reaction was quenched with MeOH before solvent removal or the solvent was simply removed at reduced pressure. The residue was dissolved in pentane and purified by frit chromatography. The ^{31}P NMR spectrum of the red solid remaining after removal of the pentane had a major signal at δ 195 with very small signals at δ 475, 188, and 176. Recrystallization from pentane facilitated removal of the small impurity signals to yield pure **4**: yield 1.2 g (62%); mp 137–140 °C; ^{31}P NMR δ 195.4; ^1H NMR δ 0.22 (s, 9 H, Me_3SiN), 0.31 [s, 18 H, $(Me_3Si)_2C$], 1.0 (d, J_{PCH} = 9 Hz, 1 H, Si_2CH), 1.26 (d, J_{PNH} = 1.6 Hz, 1 H, NH), 1.48 (s, 9 H, CMe_3); $^{13}C[^1H]$ NMR δ 2.02 (s, Me_3SiN), 2.67 (s, Me_3SiC), 28.26 (s, Me_3SiC), 33.72 (s, CMe_3), 49.92 (d, J_{PFeSC} = 20.87, CMe_3), 213.00 (br s, CO); IR ($CHCl_3$) 3350 (s), 2045 (vs), 1990 (vs, br) cm^{-1}; mass spectrum, *m*/*z* (relative intensity) 647 (M^+, 7), 619 (M^+ – CO, 2), 591 (M^+ – 2 CO, 9), 563 (M^+ – 3 CO, 15), 535 (M^+ – 4 CO, 27), 507 (M^+ – 5 CO, 16), 479 (M^+ – 6 CO, 60), 423 [$Fe_2SPCN(SiMe_3)_3^+$, 48], 333 [$Fe_2SPC(SiMe_3)_2^+$, 10], 262 ($Fe_2SPNSiMe_3^+$, 9), 245 ($Fe_2SPCSiMe_2^+$, 10), 163 ($FeS(t\text{-}Bu)P^+$, 4), 146 ($Fe_2SH_2^+$, 100), 144 (Fe_2S^+, 6), 73 (Me_3Si^+, 96), 57 ($t\text{-}Bu^+$,

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(24) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. III.

34). Anal. Calcd for $C_{20}H_{38}Fe_2NO_6PSSi_3$: C, 37.10; H, 5.92; N, 2.16. Found: C, 36.98; H, 6.11; N, 2.24.

Reaction of $Et_3NH[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ with $(Me_3Si)_2NP{=}C(H)SiMe_3$ (3). A solution of $Et_3NH[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$[19] was prepared by mixing $Fe_3(CO)_{12}$ (1.50 g, 3.0 mmol), t-BuSH (0.34 mL, 3.0 mmol), and Et_3N (0.42 mL, 3.0 mmol) in ca. 20 mL of THF at room temperature. After the mixture was stirred for ca. 2.5 h, the (methylene)phosphine (0.83 g, 3.0 mmol) was added to the red–brown solution of the anion at room temperature. Monitoring by ^{31}P NMR spectroscopy after ca. 15 min indicated that the reaction was still incomplete since a signal at δ 308 for the methylene phosphine was observed along with a very small signal at δ 195 and large signals at δ 176 and 188. The solution was stirred overnight, at which time the signal for the starting material was gone. By frit chromatography two fractions (1.1 g) were isolated with the ^{31}P NMR spectrum of the first showing signals predominantly at δ 176 and 188 with a small resonance at δ 195, while the second band showed only a signal at δ 195. The first band was further purified by column chromatography which yielded an analytically pure sample of isomers of **5**. The red oil resisted attempts at crystallization from a variety of organic solvents: ^{31}P NMR δ 188.1, 176.3; ^1H NMR δ 0.18, 0.23 (s, 9 H, Me_3SiC), 0.41, 0.44 [s, 18 H, $(Me_3Si)_2N$], 1.44, 1.48 (s, 9 H, t-Bu), 1.58, 1.97 (d, J_{PCH} = 12.8, 8.8 Hz, 2 H, $SiCH_2$); $^{13}C[^1H]$ NMR δ 0.4, 0.9 (s, *Me*$_3$SiC), 36.0 (d, J_{PC} = 6.3 Hz, CH_2), 49.34 (d, J_{PC} = 20.2 Hz, CMe_3), 48.8 (s, CMe_3), 212.2, 212.8 (s, CO); IR ($CHCl_3$); 2050 (s), 1980 (vs, br) cm^{-1}. Anal. Calcd for $C_{20}H_{38}Fe_2NO_6PSSi_3$: C, 37.10; H, 5.92; N, 2.16. Found: C, 36.68; H, 6.04; N, 2.06.

A sample of **5** was dissolved in THF, and an excess of H_2O was added to the solution. After 20 h the ^{31}P NMR spectrum of the solution showed a signal at δ 195 as well as several signals clustered between δ 185 and δ 188 and a small signal at δ 176. The signal at δ 195 continued to increase over a 2-week period until all the other signals were gone. Purification of the product by frit chromatography and characterization by ^1H and ^{31}P NMR analysis indicated that the material was **4**.

Reaction of $Li[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ (1) with $(Me_3Si)_2NP(Cl)CH_2SiMe_3$. A THF solution of the anion (3.0 mmol), prepared as described above, was treated with $(Me_3Si)_2NP(Cl)CH_2SiMe_3$ (0.94 g, 3.0 mmol) at 0 °C. After the solution was stirred for 2 days, ^{31}P NMR analysis showed that the predominant species present was **5** (^{31}P NMR δ 188.4, 176.6, 152.6, 75.4, 63.3, 59.8). Solvent removal under vacuum, followed by frit chromatography yielded 1.0 g of a red oil; ^{31}P NMR δ 187.9, 176.0 (ca. equal intensity), 63.8 (ca. 10% of the intensity of the other two signals).

Acknowledgment. The generous financial support of the National Science Foundation Visiting Professorships for Women in Science and Engineering Program is gratefully acknowledged. P.W.-N. also thanks the Department of Chemistry at Massachusetts Institute of Technology for providing the facilities, technical support, and collaborative arrangements which made this work possible while she was a visiting professor in that department.

Registry No. 1, 107099-49-0; 2, 112925-78-7; 3, 76173-65-4; 4, 112925-79-8; 5, 112925-80-1; $[(\mu\text{-}t\text{-}BuS)(\mu\text{-}P(OMe)CH(SiMe_3)_2)Fe_2(CO)_6]$, 112925-81-2; $Et_3NH[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$, 105040-77-5; $(Me_3Si)_2C{=}PCl$, 79454-85-6; $(Me_3Si)_2NP(Cl)CH_2SiMe_3$, 76946-89-9.

Supplementary Material Available: Listings of thermal parameters and idealized of thermal parameters (4 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Coordination Chemistry of the New 2,3,4,5-Tetramethylphospholyl (C_4Me_4P) π-Ligand. Crystal and Molecular Structure of $(\eta^5\text{-}C_4Me_4P)_2ZrCl_2\cdot{}^1/_2C_{10}H_8$

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Received August 26, 1987

The new 1-phenyl-2,3,4,5-tetramethylphosphole (**6c**) has been prepared from 2-butyne, $AlCl_3$, $PhPCl_2$, and $(n\text{-}Bu)_3P$. Reaction of this phosphole with $Mn_2(CO)_{10}$ and $[CpFe(CO)_2]_2$ yields $(\eta^5\text{-}C_4Me_4P)Mn(CO)_3$ and $(\eta^5\text{-}C_4Me_4P)(\eta^5\text{-}C_5H_5)Fe$, respectively. Cleavage of the P–Ph bond of **6c** can be easily achieved with lithium, as with other phospholes. Reaction of the resulting phospholyl anion **14** with iron(II) chloride affords $(\eta^5\text{-}C_4Me_4P)_2Fe$ and with $ZrCl_4$, $(\eta^5\text{-}C_4Me_4P)ZrCl_2$, which is the first heterocyclopentadienylzirconium compound that has been completely characterized. Its X-ray crystal structure shows the normal expected features of a η^5-phospholyl complex and of a $(\eta^5\text{-}L)_2ZrCl_2$ complex.

Phospholyl or phosphacyclopentadienyl ligands **1**[1] have been successfully used as substitutes for the isoelectronic cyclopentadienyl ligand in a number of compounds. Many derivatives of mono-[2] and diphosphaferrocenes[3] (**2** and **3**, respectively) and phosphacymantrenes[2c,4] **4** have thus been prepared. However, the phospholyl ligands have thus far proven much less versatile than the ubiquitous Cp ligand: apart from the iron and manganese families, only four

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[1] For a general review of phospholyl complexes, see: Mathey, F.; Fischer, J.; Nelson, J. H. *Struct. Bonding (Berlin)* **1983**, *55*, 153.

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