

Figure 1. Computer-generated representative diagram for $[\text{Cr}(\text{CO})_5\text{-}[\text{PCH}(\text{SiMe}_3)_2]_2]$, **2**. Important bond distances (Å) and angles (deg): Cr(1)–P(1) 2.360 (2), P(1)–P(2) 2.027 (3), P(1)–C(6) 1.824 (6), P(2)–C(7) 1.836 (6), Cr(1)P(1)C(6) 120.7 (2), P(2)P(1)C(6) 105.6 (2), P(1)P(2)C(7) 105.9, Cr(1)P(1)P(2) 134.2 (1).

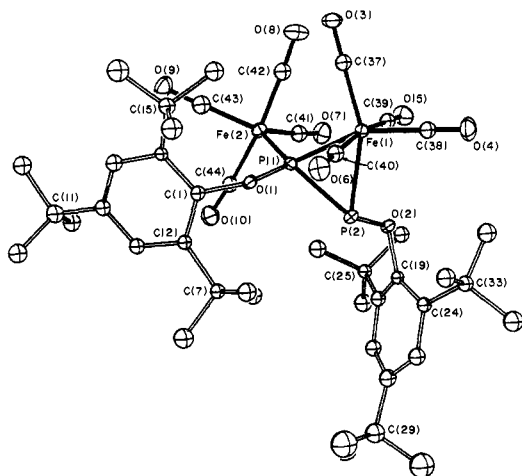


Figure 2. Computer-generated representative diagram for $[\text{Fe}(\text{CO})_4][\mu\text{-Fe}(\text{CO})_4][\text{P}(2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2\text{O})]_2$, **3**. Important bond distances (Å) and angles (deg): Fe(1)–P(2) 2.362 (2), Fe(1)–P(1) 2.347 (2), Fe(2)–P(1) 2.226 (2), P(1)–P(2) 2.184 (2), P(2)–O(2) 1.677 (6), P(1)–O(1) 1.681 (6), P(1)Fe(1)P(2) 55.3 (1), Fe(1)P(2)P(1) 62.0 (1), Fe(1)P(1)P(2) 62.7 (1), Fe(1)P(1)Fe(2) 124.9 (1), Fe(2)P(1)O(1) 118.7 (2), P(1)P(2)O(2) 112.7 (2), Fe(1)P(2)O(2) 108.0 (2), P(2)P(1)O(1) 95.1 (2), Fe(1)P(1)O(1) 102.7 (1).

(3) Å, is close to those found² in **1** (2.039 (1) Å) and in uncoordinated diphosphenes.⁵ The angles C(7)P(2)P(1), 105.9 (2)°, and C(6)P(1)P(2), 105.6(2)°, are similar to the corresponding angles in **1**. The Cr(1)–P(1) distance of 2.360 (2) Å is normal for a trialkyl phosphine Cr(CO)₅ complex.

Figure 2 illustrates the structure of $[\text{Fe}(\text{CO})_4][\mu\text{-Fe}(\text{CO})_4][\text{P}(2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2\text{O})]_2$ (**3**). The unique feature of this molecule is the behavior of the diphosphene ligand as both a side-on (to Fe(1)) and end-on (to Fe(2)) bonding ligand. The effects of this novel binding scheme are (i), due to side-on bonding of the diphosphene to Fe(1), the P(1)–P(2) distance, 2.184 (2) Å, is considerably longer than the usual P–P double bond,^{1,2,5} (ii) the diphosphene ligand remains in a trans configuration, (iii) the O(1)P(1)P(2)O(2) array is at an angle of ca. 94.0° to the Fe(1)P(1)P(2) plane; this allows each P atom to behave as a potential two-electron donor to Fe(2) while π -bonding to Fe(1). In the case of **3**, only one iron is end-on bound due to crowding by the bulky phosphorus substituents (this suggests that less crowded di-

phosphene complexes¹ should also coordinate additional metals). The P(1)–Fe(1) and P(2)–Fe(1) distances, 2.347 (2) and 2.362 (2) Å, are significantly longer than the P(1)–Fe(2) distance of 2.226 (2) Å. Such differences have been noted elsewhere¹ but are more evident here, perhaps because the aryloxy substituents make the P–P bond a poor side-on π -donor but enhance its π -acceptor properties when behaving as an end-on ligand. For the carbonyls bound to Fe(1), all the CO distances (mean 1.128 (6) Å) are consistently shorter than the CO distances at Fe(2) (mean 1.150 (6) Å) and vice versa for the Fe–C distances, Fe(1)–C(mean) = 1.827 (13) and Fe(2)–C(mean) = 1.787 (16) Å. This suggests that back donation from Fe(2) into CO is greater than for Fe(1) into CO or, in other words, that the side-on diphosphene is a better π -acceptor than the end on.

NMR data are as follows: ³¹P {¹H} NMR:⁶ **2**, d of d, 480.4, 474.1, 449.4, 443.0 ppm, ¹J_{PP} = 510 Hz; **3**, d of d, 237.1, 230.4, 196.8, 190.0 ppm, ¹J_{PP} = 532 Hz. ¹H NMR: **2**, 0.269, 0.30 (SiMe₃, d), 0.85 (CH, m) ppm; **3** 1.46, 1.65, 1.80 (*t*-Bu, m, m, s), 7.45 (aromatic CH, br s) ppm. IR ν_{CO} (Nujol): **2**, 2060 (sh, m), 1955 (sh, br), 1934 (sh, m) cm⁻¹; **3**, 2095, 2055, 2040, 2030, 2018, 1988, 1972, 1960 cm⁻¹.

Acknowledgment. We are grateful to the NSF (CHE-8116355) for generous financial support and to Professor Alan Cowley for discussions of his results prior to publication.

Registry No. **2**, 87841-54-1; **3**, 87830-08-8; PCl₂[CH(SiMe₃)₂], 76505-20-9; PCl₂(2,4,6-*t*-Bu₃C₆H₂O), 796-62-3; Cr(CO)₅²⁻, 71518-79-1; Fe(CO)₄²⁻, 22321-35-3.

Supplementary Material Available: Listing of atom coordinates, thermal parameters, bond distances and angles (5 pages). Ordering information is given on any current masthead page.

(6) ³¹P and ¹H NMR data were obtained in CDCl₃ solution. The chemical shifts (ppm) are relative to external 85% H₃PO₄ and Me₄Si, respectively.

Reactivity of Diphosphenes and Phosphaarsenes toward Metal Carbonyls

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Received July 20, 1983

Recent months have witnessed a flurry of activity in the chemistry of kinetically stabilized compounds featuring double bonds between group 4A and group 5A elements.¹ In group 5A, several diphosphenes (RP=PR),² phosphaarsenes (RP=AsR),³

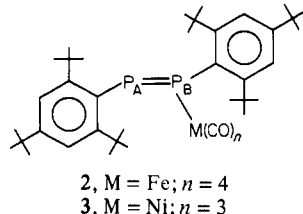
(1) Cowley, A. H. *Polyhedron*, in press.

(2) (a) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587. (b) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. *Ibid.* **1982**, *104*, 5820. (c) Bertrand, G.; Couret, C.; Escudie, J.; Majid, S.; Majoral, J.-P. *Tetrahedron Lett.* **1982**, *23*, 3567. (d) Cetinkaya, B.; Hudson, A.; Lappert, M. F.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1982**, 609. (e) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J.; Goldwhite, H. *Ibid.* **1982**, 691. (f) Couret, C.; Escudie, J.; Satge, J. *Tetrahedron Lett.* **1982**, *23*, 4941. (g) Cowley, A. H.; Kilduff, J. E.; Pakulski, M.; Stewart, C. A. *J. Am. Chem. Soc.* **1983**, *105*, 1655. (h) Niecke, E.; Rüger, R. *Angew. Chem.* **1983**, *95*, 154; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 155. (i) Yoshifuji, M.; Shibayama, K.; Inamoto, N. *J. Am. Chem. Soc.* **1983**, *105*, 2495. (j) Yoshifuji, M.; Ando, K.; Toyota, K.; Shima, I.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1983**, 419. (k) Cowley, A. H.; Kilduff, J. E.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1983**, 528. (l) Lee, J.-G.; Cowley, A. H.; Boggs, J. E. *Inorg. Chim. Acta* **1983**, *77*, L61. (m) Cowley, A. H.; Kilduff, J. E.; Norman, N. C.; Atwood, J. L.; Pakulski, M.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 4845.

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and diarsenes (RAs=AsR)⁴ have been isolated, four of which have now been structurally characterized.^{2a,m,3,4b} We now report (i) the first indication that compounds with P=P and P=As bonds will react with organometallic reagents, (ii) a new mode of coordination for a diphosphene, and (iii) the first phospharsene complexes.

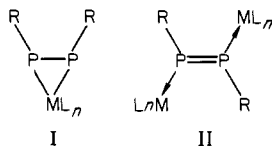
In a typical reaction, 0.563 g (1.02 mmol) of (2,4,6-*t*-Bu₃C₆H₂)₂P₂ (1)^{2a} was treated with 0.51 g (1.40 mmol) of Fe₂(CO)₉ in 45 mL of *n*-hexane at 0 °C. The dark-red reaction mixture was allowed to warm to ambient temperature, and stirring was continued for 6 h. After filtration, the solvent and volatiles were removed by pumping in vacuo. Purification was effected by chromatography at -78 °C (*n*-hexane/Florisil). Red-brown crystals of (2,4,6-*t*-Bu₃C₆H₂)₂P₂Fe(CO)₄ (2) (mp 168-170 °C



dec) formed from *n*-hexane solutions held at -20 °C (yield 65%). 2: ³¹P{¹H} NMR (AB pattern) δ_A +423.6, δ_B +396.4, ¹J_{PP} = 578.0 Hz; IR (*n*-hexane) ν_{CO} 1940, 1915, 1895, 1880 cm⁻¹; UV-vis (CH₂Cl₂) λ_{max} 486 (ε = 5200), 288 (ε = 18 700), 244 nm (ε = 26 000).

The X-ray structure of 2⁵ (Figure 1) reveals a P(1)-P(2) bond length of 2.050 (1) Å, which is comparable to those reported for other compounds with P=P bonds.^{2a,m,8} Furthermore, within experimental error the C₂P₂Fe framework is planar. The P-P-C bond angles in 2 are 6° larger than those in the free ligand, 1.^{2a} Steric crowding is also evidenced by the fact that the P(1)-C(1) bond is 0.03 Å longer than the P(2)-C(7) bond.

Compound 2 represents a new mode of coordination for a diphosphene. Previously reported complexes were of type I⁹ or II.⁸



Compound 2 is also formed (along with 1) when (2,4,6-*t*-Bu₃C₆H₂)PCL₂ is treated with Na₂Fe(CO)₄ in THF solution. The

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(5) Crystal data for (2): C₄₀FeH₅₈O₄P₂, M = 720.7, monoclinic, space group P2₁/c (No. 14), a = 21.251 (6) Å, b = 9.793 (2) Å, c = 20.99 (2) Å, β = 108.73 (6)°, U = 4136 (5) Å³, D_c = 1.157 g cm⁻³, Z = 4, λ(Mo Kα) = 0.71069 Å (graphite monochromator), μ(Mo Kα) = 4.7 cm⁻¹. From a total of 7504 unique reflections, measured on an Enraf-Nonius CAD-4F diffractometer, 4204 (I > 2.5σ(I)) were used to solve (MULTAN⁶ and difference Fourier) and refine (full matrix, least squares) the structure of 2. All non-hydrogen atoms were refined with anisotropic thermal parameters. However, under these conditions, the methyl carbon C(41) did not refine well and in the final cycle was given an isotropic temperature factor. All hydrogen atoms were fixed in idealized geometries 0.95 Å from their respective carbon atom. These were included in the structure factor calculation but not refined due to insufficient data. Refinement with a weighting scheme⁷ converged smoothly to give final residuals R = 0.0578, R_w = 0.0824, GOF = 1.634.

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(7) The weighting scheme used was of the form w = (4F²/σ²(F²) + P²F⁴) with P = 0.08.

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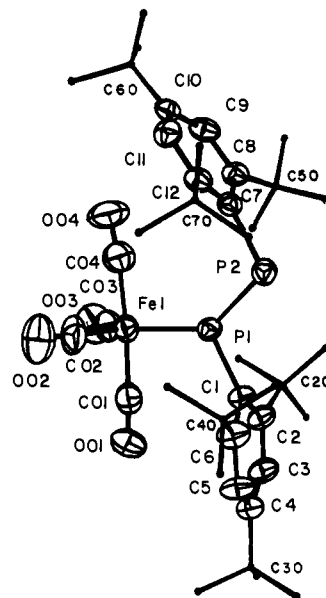


Figure 1. View of the (2,4,6-*t*-Bu₃C₆H₂)₂P₂Fe(CO)₄ (2) molecule showing the atom numbering scheme. Important parameters: P(1)-P(2) 2.050 (1), P(1)-Fe(1) 2.215 (1), P(1)-C(1) 1.893 (4), P(2)-C(7) 1.859 (4) Å; P(1)-P(2)-C(7) 108.4 (1)°, P(2)-P(1)-Fe(1) 135.52 (6)°, P(2)-P(1)-C(1) 109.3 (1)°, C(1)-P(1)-Fe(1) 115.1 (1)°.

fact that only one Fe(CO)₄ attaches is a consequence of steric effects. Likewise, only one Ni(CO)₃ group attaches even when 1 is treated with excess Ni(CO)₄ (in Et₂O). [2,4,6-*t*-Bu₃C₆H₂]₂P₂Ni(CO)₃ (3): ³¹P{¹H} NMR (AB pattern) δ_A +449.0, δ_B +422.0, ¹J_{PP} = 540.3 Hz; IR (*n*-hexane) ν_{CO} 1800, 1860, 1955 cm⁻¹. The very bulky diphosphene (Me₃Si)₃CP=PC(SiMe₃)₃^{2b,f,m} does not react with Ni(CO)₄ at 25 °C.

The unsymmetrical diphosphene, (2,4,6-*t*-Bu₃C₆H₂)P=PCH-(SiMe₃)₂ also reacts with Fe₂(CO)₉ to afford the corresponding (Me₃Si)₂CHP-bound Fe(CO)₄ complex 4 in 63% yield. 4: ³¹P NMR (ABX system) δ_A +424, δ_B +416, ¹J_{PP} = 519.0, ²J_{PH} = 30.0, ³J_{PH} = -3.2 Hz; IR (*n*-hexane) ν_{CO} = 1970 (br), 2060 cm⁻¹. Preliminary studies of the reaction of the phospharsene (2,4,6-*t*-Bu₃C₆H₂)As=PCH(SiMe₃)₂³ indicate the formation of two products, 5a and 5b, in which the Fe(CO)₄ moiety is attached to phosphorus and arsenic atoms, respectively. ³¹P NMR: 5a, s +390; 5b, s +429 ppm.

Acknowledgment. Generous financial support from the National Science Foundation (Grant CHE-8205871) and the Robert A. Welch Foundation is acknowledged. We are also grateful to Professor Philip P. Power for discussing his work prior to publication.

Registry No. 1, 79073-99-7; 2, 87937-39-1; 3, 87937-40-4; 4, 87937-

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters (8 pages). Ordering information is given on any current masthead page.

Six-Membered Ring Phosphites in Twist Conformations. The Methyl and Phenyl Trans-3',5'-Cyclic Phosphites of Thymidine

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Received July 11, 1983

The replacement of the ring carbons of cyclohexane with heteroatoms containing electron lone pairs may greatly affect the relative free energies of potentially populated conformations as