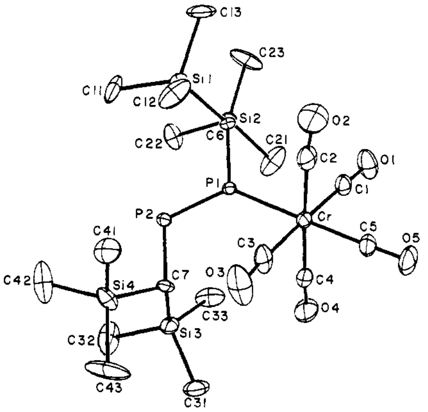

Figure 1. Computer-generated representative diagram for $[Cr(CO)_5[PCH(SiMe_3)_2]_2]$, **2**. Important bond distances (Å) and angles (deg): Cr(1)–P(1) 2.360 (2), P(1)–P(2) 2.027 (3), P(1)–C(6) 1.824 (6), P(2)–C(7) 1.836 (6), Cr(1)P(1)C(6) 120.7 (2), P(2)P(1)C(6) 105.6 (2), P(1)P(2)C(7) 105.9, Cr(1)P(1)P(2) 134.2 (1).

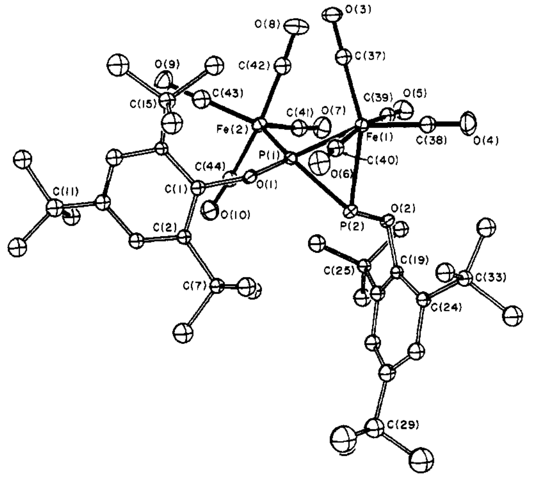

Figure 2. Computer-generated representative diagram for $[Fe(CO)_4[\mu\text{-}Fe(CO)_4][P(2,4,6\text{-}t\text{-}Bu_3C_6H_2O)]_2]$, **3**. Important bond distances (Å) and angles (deg): Fe(1)–P(2) 2.362 (2), Fe(1)–P(1) 2.347 (2), Fe(2)–P(1) 2.226 (2), P(1)–P(2) 2.184 (2), P(2)–O(2) 1.677 (6), P(1)–O(1) 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 found[2] 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 $[Fe(CO)_4[\mu\text{-}Fe(CO)_4][P(2,4,6\text{-}t\text{-}Bu_3C_6H_2O)]_2]$ (**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 diphosphene complexes[1] 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 elsewhere[1] 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: $^{31}P\{^1H\}$ 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 ($SiMe_3$, 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}.

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Registry No. 2, 87841-54-1; **3**, 87830-08-8; $PCl_2[CH(SiMe_3)_2]$, 76505-20-9; $PCl_2(2,4,6\text{-}t\text{-}Bu_3C_6H_2O)$, 796-62-3; $Cr(CO)_5^{2-}$, 71518-79-1; $Fe(CO)_4^{2-}$, 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.

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(6) ^{31}P and ^1H NMR data were obtained in $CDCl_3$ solution. The chemical shifts (ppm) are relative to external 85% H_3PO_4 and Me_4Si, respectively.

Reactivity of Diphosphenes and Phosphaarsenes toward Metal Carbonyls

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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]

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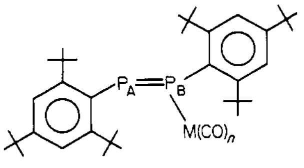
and diarsenes (RAs=AsR)[4] have been isolated, four of which have now been structurally characterized.[2a,m,3,4b] We now report (i) the first indication that compounds with P=P and P=As bonds will react with organometallic reagents, (ii) a new mode of coordination for a diphosphene, and (iii) the first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

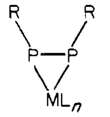
In a typical reaction, 0.563 g (1.02 mmol) of (2,4,6-*t*-$Bu_3C_6H_2)_2P_2$ (**1**)[2a] was treated with 0.51 g (1.40 mmol) of $Fe_2(CO)_9$ in 45 mL of *n*-hexane at 0 °C. The dark-red reaction mixture was allowed to warm to ambient temperature, and stirring was continued for 6 h. After filtration, the 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*-$Bu_3C_6H_2)_2P_2Fe(CO)_4$ (**2**) (mp 168–170 °C dec) formed from *n*-hexane solutions held at −20 °C (yield 65%). **2**: $^{31}P\{^1H\}$ 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 (CH_2Cl_2) λ_{max} 486 (ϵ = 5200), 288 (ϵ = 18 700), 244 nm (ϵ = 26 000).



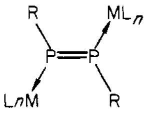
2, M = Fe; *n* = 4
3, M = Ni; *n* = 3

The X-ray structure of **2**[5] (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 C_2P_2Fe 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 I[9] or II.[8]



I



II

Compound **2** is also formed (along with **1**) when (2,4,6-*t*-$Bu_3C_6H_2)PCl_2$ is treated with $Na_2Fe(CO)_4$ in THF solution. The 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 Et_2O). [2,4,6-*t*-$Bu_3C_6H_2]_2P_2Ni(CO)_3$ (**3**): $^{31}P\ \{^1H\}$ 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 $(Me_3Si)_3CP=PC(SiMe_3)_3$[2b,f,m] does not react with $Ni(CO)_4$ at 25 °C.

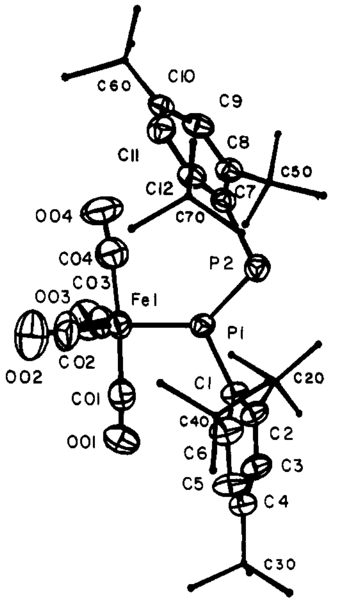


Figure 1. View of the (2,4,6-*t*-$Bu_3C_6H_2)_2P_2Fe(CO)_4$ (**2**) molecule showing the atom numbering scheme. Important parameters: P(1)–P(2) 2.050 (1), P(1)–Fe(1) 2.215 (1), P(1)–C(1) 1.893 (4), P(2)–C(7) 1.859 (4) Å; P(1)–P(2)–C(7) 108.4 (1)°, P(2)–P(1)–Fe(1) 135.52 (6)°, P(2)–P(1)–C(1) 109.3 (1)°, C(1)–P(1)–Fe(1) 115.1 (1)°.

The unsymmetrical diphosphene, (2,4,6-*t*-$Bu_3C_6H_2)P=PCH(SiMe_3)_2$ also reacts with $Fe_2(CO)_9$ to afford the corresponding $(Me_3Si)_2CHP$-bound $Fe(CO)_4$ complex **4** in 63% yield. **4**: ^{31}P 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 phosphaarsene (2,4,6-*t*-$Bu_3C_6H_2)As=PCH(SiMe_3)_2$[3] indicate the formation of two products, **5a** and **5b**, in which the $Fe(CO)_4$ moiety is attached to phosphorus and arsenic atoms, respectively. ^{31}P NMR: **5a**, s +390; **5b**, s +429 ppm.

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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.

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(5) Crystal data for (**2**): $C_{40}FeH_{58}O_4P_2$, M = 720.7, monoclinic, space group $P2_1/c$ (No. 14), a = 21.251 (6) Å, b = 9.793 (2) Å, c = 20.99 (2) Å, β = 108.73 (6)°, U = 4136 (5) Å,^{3} 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 ($I > 2.5\sigma(I)$) were used to solve (MULTAN[6] and difference Fourier) and refine (full matrix, least squares) the structure of **2**. All nonhydrogen 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 scheme[7] 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 $w = (4F^2/\sigma^2(F^2) + P^2F^4)$ with P = 0.08.

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

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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

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