previously observed that the replacement of a tungsten CO group in the bridging carbene complex $(CO)_5W[\mu\text{-}C(OMe)(aryl)]Pt(PMe_3)_2$ with a $PMe_3$ ligand shortens the W–C(carbene) bond from 2.48 (1) to 2.37 (1) Å. This shortening may be understood in terms of increased $\pi$ bonding from the W to the carbene carbon, which stabilizes the compound. Such a $\pi$ bonding must also be responsible in part for the stability of I.

One other interesting aspect of the molecular orbital calculations on this compound is the extensive interaction of both iron and cobalt d functions in a single molecular orbital. This admixture is apparent in levels 38 and 44 and can be traced to the near degeneracy of cobalt and iron d functions. Since sizable percentages of iron and cobalt character are found together, we predict that experimental measurements such as photoelectron spectroscopy would reflect this admixture.

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**Registry No.** I, 83043-22-5; $Na[Co(CO)_4]$, 14878-28-5; $\{Cp(CO)(MeCN)Fe[C(SMe)_2]\}PF_6$, 77781-29-4; Co, 7440-48-4; Fe, 7439-89-6.

**Supplementary Material Available:** Tables of anisotropic thermal parameters for non-hydrogen atoms and calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

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# Reactivity of Diphosphenes, Phospharsenes, and Diarsenes toward Transition-Metal Carbonyls

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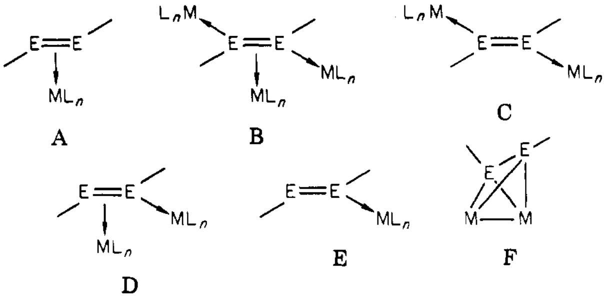
The reactivity of stable diphosphenes, phospharsenes, and diarsenes toward transition-metal carbonyls has been explored. The diphosphene $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2P_2$, **2**, forms adducts with one $Fe(CO)_4$ and one $Ni(CO)_3$ group from reactions with $Fe_2(CO)_9$ and $Ni(CO)_4$, respectively. The iron complex $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2P_2Fe(CO)_4$, **3**, has been structurally characterized by X-ray diffraction. Compound **3** crystallizes in the monoclinic space group $P2_1/c$, with $a = 21.251$ (6) Å, $b = 9.793$ (2) Å, $c = 20.99$ (2) Å, and $\beta = 108.73$ (6)°. The structure reveals that the diphosphene **2** is $\eta^1$ bonded to the $Fe(CO)_4$ group through a phosphorus lone pair. The phospharsene $2,4,6\text{-}t\text{-}Bu_3C_6H_2As{=}PCH(SiMe_3)_2$, **8**, reacts with $Fe_2(CO)_9$ to give complexes with an $Fe(CO)_4$ group attached to As, **9**, or P, **10**. Treatment of the diarsene $2,4,6\text{-}t\text{-}Bu_3C_6H_2As{=}AsCH(SiMe_3)_2$, **11**, with $Cr(CO)_5(THF)$ affords the complex $2,4,6\text{-}t\text{-}Bu_3C_6H_2As{=}AsCH(SiMe_3)_2Cr(CO)_5$, **12**, with the $Cr(CO)_5$ unit $\eta^1$ bonded to the $(Me_3Si)_2CH$-substituted arsenic. This was determined by an X-ray diffraction study. Compound **12** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.710$ (3) Å, $b = 29.770$ (3) Å, $c = 11.984$ (1) Å, and $\beta = 98.02$ (1)°. The structures of and bonding in these complexes are discussed.

## Introduction

The coordination chemistry of compounds featuring double bonds between the heavier group 5A elements existed prior to the isolation of stable uncomplexed systems. Examples of diphosphene complexes include $[(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}P_2H_2)]$,[1] $[Pd(\eta^2\text{-}Ph_2P_2)(Ph_2PCH_2PPh_2)]$,[2] $[Ni(\eta^2\text{-}(Me_3Si)_2P_2)(Et_3P)_2]$,[3] and $[Pt(\eta^2\text{-}(C_6F_5)_2P_2)(Ph_3P)_2]$.[4] In all these complexes and the arsenic analogues $[Fe(\eta^2\text{-}(C_6F_5)_2As_2)(CO)_4]$[5] and $[Pt(\eta^2\text{-}(C_6F_5)_2As_2)(Ph_3P)_2]$,[5] the ligands adopt a trans conformation and the $\eta^2$-bonding mode A. Another bonding mode, B, has been observed in complexes of composition $(PhE{=}EPh)(M(CO)_5)_3$ (E = As,[6] Sb;[7], M = Cr,[6] W[7]). Six-electron donation on the part of the diarsene or distibene ligand is achieved by $\eta^2$ bonding to one $M(CO)_5$ moiety and $\eta^1$ bonding to the other two. The phenyl groups are trans in both cases.



Recent work by Power et al. has resulted in two new modes of ligation, C and D. Thus, treatment of $(Me_3Si)_2CHPCl_2$ with $[Fe(CO)_4]^{2-}$ afforded $[trans\text{-}\{[Fe(CO)_4]_2[PCH(SiMe_3)_2]_2\}]$,[8] an example of a type C complex in which each phosphorus lone pair bonds to an $Fe(CO)_4$ group in an $\eta^1$ fashion. This is the first example of a diphosphene complex containing an unsupported P=P double bond. A similar complex of the isoelectronic ligand $(Me_3Si)_2NP{=}PN(SiMe_3)_2$ has also been described.[9] On the other hand, the reaction of $(2,4,6\text{-}t\text{-}Bu_3C_6H_2O)PCl_2$ with $[Fe(CO)_4]^{2-}$ resulted in a type D complex featuring one $\eta^1$- and one $\eta^2$-bonded $Fe(CO)_4$ group.[10]

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Having ligands with preformed double bonds at our disposal,[11] we realized that new modes of coordination might become possible. In fact, the diphosphene (2,4,6-$t$-$Bu_3C_6H_2)_2P_2$ reacts readily with $Fe_2(CO)_9$ to afford the first example of a type E complex.[12] Virtually simultaneously, Power et al.[10] reported the synthesis of $(Me_3Si)_2CH$- or $(Me_3Si)_2N$-substituted $Cr(CO)_5$ complexes of type E via the reaction of the appropriate phosphorus dichlorides with $[Cr(CO)_5]^{2-}$.

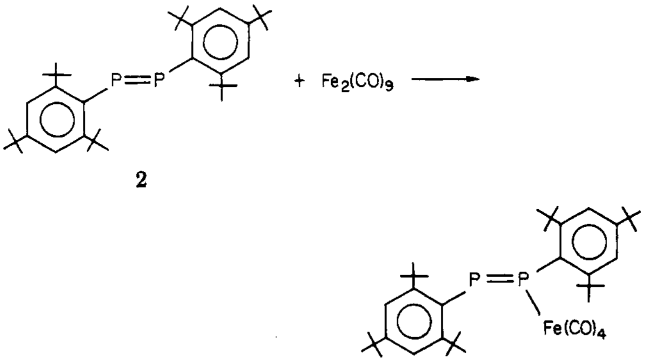
The group 5A double-bonded compounds can also function as ligands in metal clusters. One type of ligation, F, has been recognized so far. The diiron complex [Fe($\mu$-$\eta^2$-($t$-$Bu_2P_2$))$(CO)_6$] features a transverse $\mu$-$\eta^2$ diphosphene geometry and a cis disposition of the $t$-Bu groups.[13]

In this paper we report full details of our synthetic approach to the coordination chemistry of diphosphenes and diarsenes using preformed double bonds. We also report the first coordinated phospharsene.

## Results and Discussion

Initial attempts to use diphosphenes as ligands focussed on the reaction of $(Me_3Si)_3CP{=}PC(SiMe_3)_3$,[14] 1, with $Fe_2(CO)_9$ and $Ni(CO)_4$. However, in neither case was any reaction observed even, in the case of $Fe_2(CO)_9$, under forcing conditions (THF reflux overnight). It is presumed that this is due to the large steric bulk of the $(Me_3Si)_3C$ groups which prevents access to the phosphorus lone pairs. This lack of reactivity associated with 1 is not peculiar to metal carbonyl systems, it being by far the least reactive of all diphosphenes studied.[11] The aryl-substituted diphosphene (2,4,6-$t$-$Bu_3C_6H_2)_2P_2$,[15] 2, is much more reactive. Examination of models of 1 and 2 indicates that, while the ortho $t$-Bu groups of 2 provide adequate bulk to stabilize the complex, access to the phosphorus atoms is possible between these groups over the $C_6$ ring. The conical symmetry of the $(Me_3Si)_3C$ group precludes such an approach.

Treatment of 2 in hexane at 0 °C with $Fe_2(CO)_9$ for 2 h led to a color change from orange to dark red. Purification and subsequent recrystallization afforded dark red crystals of (2,4,6-$t$-$Bu_3C_6H_2)_2P_2Fe(CO)_4$, 3, which were characterized initially by $^{31}P$ NMR and IR spectroscopy.



2

3

The $^{31}P\{^1H\}$ NMR spectrum of 3 comprised an AB system,

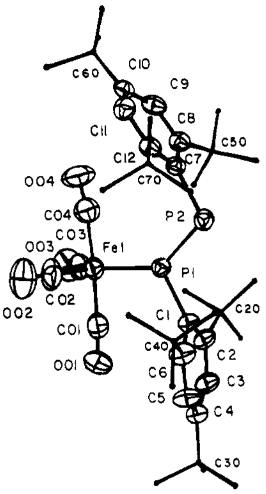


**Figure 1.** ORTEP view of (2,4,6-$t$-$Bu_3C_6H_2)_2P_2Fe(CO)_4$, 3, showing the atom numbering scheme.

Table I. Crystal and Intensity Collection Data for 3 and 13

| | 3 | 13 |
|---|---|---|
| formula | $C_{40}FeH_{58}O_4P_2$ | $C_{30}H_{48}As_2CrO_5Si_2$ |
| fw | 720.70 | 746.70 |
| cryst system | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/n$ |
| $a$/Å | 21.251 (6) | 10.710 (3) |
| $b$/Å | 9.793 (2) | 29.770 (3) |
| $c$/Å | 20.99 (2) | 11.985 (1) |
| $\beta$/deg | 108.73 (6) | 98.02 (1) |
| $U$/Å$^3$ | 4136 (5) | 3784 (1) |
| $Z$ | 4 | 4 |
| $\rho$(calcd)/g cm$^{-3}$ | 1.157 | 1.311 |
| $\mu$(Mo K$\alpha$)/cm$^{-1}$ | 4.7 | 31.6 |
| $\lambda$(Mo K$\alpha$)/Å | 0.710 69 | 0.710 69 |
| cryst size/mm | 0.4 × 0.4 × 0.6 | 0.5 × 0.5 × 0.7 |
| $\omega$ scan angle/deg | $0.8 + 0.35 \tan\theta$ | $0.8 + 0.35 \tan\theta$ |
| $2\theta$ limits/deg | $2.0° \leqslant 2\theta \leqslant 50.0°$ | $2.0° \leqslant 2\theta \leqslant 50.0°$ |
| total unique measd data | 7504 | 6428 |
| no. of data obsd | 4204 | 3891 |
| data omission | $I \geqslant 2.5\sigma(I)$ | $I \geqslant 2.5\sigma(I)$ |
| no. of variables | 465 | 361 |
| $R$[25] | 0.0578 | 0.0459 |
| $R_W$ | 0.0824 | 0.0721 |
| GOF | 1.634 | 1.821 |

$\delta_{P_A}$ +423.6, $\delta_{P_B}$ +396.4, and $^1J_{PP}$ = 578.0 Hz. The low-field chemical shifts and large coupling constant are consistent with the retention of a P=P double bond and chemically inequivalent phosphorus atoms. The IR spectrum showed three terminal CO absorptions at 2046, 1981, and 1965 cm$^{-1}$ indicative of one $Fe(CO)_4$ group. From this information the structure drawn for 3 was postulated and this was confirmed by an X-ray crystallographic study.

The structural study revealed the compound 3 as shown in Figure 1. Tables of atomic positional parameters, bond lengths, and bond angles are given in Tables II–IV, respectively, while pertinent crystallographic data are collected in Table I.

The P–P bond length of 2.050 (1) Å is consistent with a double bond and compares with that in the uncoordinated system of 2.034 (2) Å,[15] i.e., 0.016 Å longer. The phosphorus atom P(1) bonds to the iron (Fe(1)–P(1) = 2.215 (1) Å) and forms one of the equatorial ligands in the trigonal-bipyramidal geometry about the iron, the remaining four ligands being carbonyls. Equatorial coordination of the large diphosphene ligand is expected on steric arguments alone since only two and not three 90° angles occur between ligands. In a related complex,

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**Table II. Atomic Coordinates for $(2,4,6\text{-}t\text{-Bu}_3C_6H_2)_2P_2Fe(CO)_4$, 3**

| atom | *x* | *y* | *z* | *B*,[a] Å$^2$ |
|---|---|---|---|---|
| Fe(1) | 0.81810 (4) | 0.23615 (8) | 0.53005 (4) | 3.52 (2) |
| P(1) | 0.73845 (6) | 0.3646 (1) | 0.46282 (6) | 2.67 (3) |
| P(2) | 0.72215 (7) | 0.5702 (1) | 0.44754 (7) | 3.05 (3) |
| O(01) | 0.7500 (3) | −0.0088 (4) | 0.4602 (3) | 7.2 (2) |
| O(02) | 0.9316 (2) | 0.1703 (7) | 0.4849 (3) | 9.1 (2) |
| O(03) | 0.8206 (3) | 0.1143 (6) | 0.6589 (2) | 7.3 (1) |
| O(04) | 0.8962 (3) | 0.4509 (5) | 0.6149 (3) | 11.2 (2) |
| C(01) | 0.7752 (3) | 0.0871 (6) | 0.4866 (3) | 4.6 (2) |
| C(02) | 0.8871 (3) | 0.1966 (8) | 0.5024 (4) | 5.6 (2) |
| C(03) | 0.8177 (3) | 0.1622 (6) | 0.6086 (3) | 4.8 (2) |
| C(04) | 0.8635 (4) | 0.3743 (7) | 0.5796 (4) | 6.5 (2) |
| C(1) | 0.6685 (2) | 0.2673 (5) | 0.4004 (2) | 3.0 (1) |
| C(2) | 0.6161 (2) | 0.2123 (5) | 0.4212 (3) | 3.2 (1) |
| C(3) | 0.5826 (3) | 0.0991 (6) | 0.3868 (3) | 3.9 (1) |
| C(4) | 0.5949 (3) | 0.0369 (5) | 0.3330 (3) | 3.5 (1) |
| C(5) | 0.6401 (3) | 0.1035 (6) | 0.3096 (3) | 4.0 (1) |
| C(6) | 0.6765 (3) | 0.2168 (6) | 0.3386 (3) | 3.6 (1) |
| C(7) | 0.7915 (2) | 0.6632 (5) | 0.5094 (2) | 2.7 (1) |
| C(8) | 0.7849 (3) | 0.7096 (5) | 0.5722 (3) | 3.2 (1) |
| C(9) | 0.8415 (3) | 0.7595 (5) | 0.6211 (3) | 3.4 (1) |
| C(10) | 0.9029 (3) | 0.7728 (5) | 0.6121 (3) | 3.1 (1) |
| C(11) | 0.9043 (2) | 0.7488 (5) | 0.5474 (3) | 3.3 (1) |
| C(12) | 0.8509 (3) | 0.6979 (5) | 0.4948 (2) | 3.1 (1) |
| C(20) | 0.5903 (3) | 0.2708 (6) | 0.4780 (3) | 4.0 (1) |
| C(21) | 0.5720 (3) | 0.4204 (7) | 0.4642 (3) | 5.5 (2) |
| C(22) | 0.6393 (3) | 0.2470 (7) | 0.5477 (3) | 5.2 (2) |
| C(23) | 0.5255 (3) | 0.2035 (8) | 0.4790 (4) | 7.0 (2) |
| C(30) | 0.5598 (3) | −0.0923 (6) | 0.2998 (3) | 3.9 (1) |
| C(31) | 0.5140 (6) | −0.0635 (9) | 0.2327 (5) | 10.4 (3) |
| C(32) | 0.6095 (6) | −0.1927 (9) | 0.2945 (6) | 9.0 (3) |
| C(33) | 0.5208 (5) | −0.162 (1) | 0.3402 (5) | 6.2 (3) |
| C(40) | 0.7191 (3) | 0.2810 (7) | 0.2992 (3) | 5.2 (1) |
| C(41) | 0.7105 (5) | 0.2114 (9) | 0.2324 (4) | 11.6 (2) |
| C(42) | 0.7926 (4) | 0.283 (1) | 0.3378 (4) | 7.5 (2) |
| C(43) | 0.6948 (4) | 0.4246 (8) | 0.2794 (3) | 7.5 (2) |
| C(50) | 0.7199 (3) | 0.7114 (6) | 0.5903 (3) | 4.3 (1) |
| C(51) | 0.6620 (3) | 0.7624 (8) | 0.5325 (4) | 6.8 (2) |
| C(52) | 0.7237 (3) | 0.8065 (9) | 0.6496 (4) | 8.0 (2) |
| C(53) | 0.7048 (4) | 0.5712 (8) | 0.6108 (4) | 7.1 (2) |
| C(60) | 0.9651 (3) | 0.8168 (6) | 0.6688 (3) | 3.9 (1) |
| C(61) | 0.9536 (4) | 0.8289 (8) | 0.7368 (3) | 6.4 (2) |
| C(62) | 0.9888 (3) | 0.9551 (7) | 0.6515 (4) | 5.9 (2) |
| C(63) | 1.0189 (4) | 0.7096 (8) | 0.6754 (4) | 6.5 (2) |
| C(70) | 0.8630 (3) | 0.6898 (6) | 0.4255 (3) | 3.8 (1) |
| C(71) | 0.8984 (4) | 0.820 (1) | 0.4147 (4) | 5.5 (2) |
| C(72) | 0.8022 (4) | 0.694 (1) | 0.3653 (3) | 7.8 (2) |
| C(73) | 0.9081 (5) | 0.565 (1) | 0.4270 (4) | 8.3 (3) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) = c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

[*trans*-{[Fe(CO)$_4$]$_2$[PCH(SiMe$_3$)$_2$]$_2$}], 4,[8] a similar equatorial coordination geometry about each iron is observed. However, in this complex the Fe$_2$P$_2$ plane extends to include each of the two sets of equatorial CO ligands. In 3 the reverse is true with the equatorial carbonyls lying perpendicular to the FeP$_2$ plane. This difference appears to result from the different steric requirements of the (Me$_3$Si)$_2$CH and 2,4,6-*t*-Bu$_3$C$_6$H$_2$ groups. One remaining point of interest from comparing the structures of 2 and 3 concerns the P–P–C angles. In diphosphene 2 this angle is 102.8 (1)°.[15] The corresponding angles in 3 P(2)–P(1)–C(1) = 109.3 (1)° and P(1)–P(2)–C(7) = 108.4 (1)° are larger by about 6° in each case. This trend may result from rehybridization at each phosphorus atom. In an uncomplexed diphosphene, R$_2$P$_2$, with idealized P–P–C bond angles of 90°, the π(P–P) and σ(P–R) bonds are formed by overlaps using pure P(3p) AO's. In this model the σ(P–P) bond can be formed via pure P(3p) overlap or by use of sp hybrid orbitals. In either case, the phosphorus lone pairs, sp or s, are not well oriented to interact with an Fe(CO)$_4$ moiety. On the other hand, changing the phosphorus hybridization to sp$^2$ leads to a more favorable P–P–Fe bond angle (120°). The predicted increase in the P–P–C angle upon coordination (ideally 90–120°) is in the opposite direction to that anticipated on steric grounds.

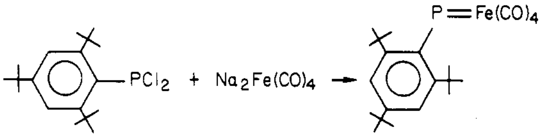
**Table III. Bond Lengths (Å) for $(2,4,6\text{-}t\text{-Bu}_3C_6H_2)_2P_2Fe(CO)_4$, 3[a]**

| | | | |
|---|---|---|---|
| Fe(1)–P(1) | 2.215 (1) | C(9)–H(9) | 0.81 (4) |
| Fe(1)–C(01) | 1.805 (6) | C(10)–C(11) | 1.389 (6) |
| Fe(1)–C(02) | 1.785 (6) | C(10)–C(60) | 1.529 (6) |
| Fe(1)–C(03) | 1.803 (6) | C(11)–C(12) | 1.396 (6) |
| Fe(1)–C(04) | 1.788 (6) | C(11)–H(11) | 0.87 (5) |
| P(1)–P(2) | 2.050 (1) | C(12)–C(70) | 1.556 (6) |
| P(1)–C(1) | 1.893 (4) | C(20)–C(21) | 1.520 (7) |
| P(2)–C(7) | 1.859 (4) | C(20)–C(22) | 1.516 (7) |
| O(01)–C(01) | 1.133 (6) | C(20)–C(23) | 1.533 (6) |
| O(02)–C(02) | 1.147 (6) | C(30)–C(31) | 1.460 (8) |
| O(03)–C(03) | 1.138 (6) | C(30)–C(32) | 1.473 (9) |
| O(04)–C(04) | 1.124 (6) | C(30)–C(33) | 1.525 (9) |
| C(1)–C(2) | 1.426 (5) | C(30)–C(31A) | 1.62 (3) |
| C(1)–C(6) | 1.448 (6) | C(30)–C(32A) | 1.60 (2) |
| C(2)–C(3) | 1.388 (6) | C(30)–C(33A) | 1.53 (2) |
| C(2)–C(20) | 1.571 (6) | C(40)–C(41) | 1.516 (7) |
| C(3)–C(4) | 1.380 (6) | C(40)–C(42) | 1.512 (8) |
| C(3)–H(3) | 0.71 (4) | C(40)–C(43) | 1.509 (8) |
| C(4)–C(5) | 1.375 (6) | C(50)–C(51) | 1.509 (8) |
| C(4)–C(30) | 1.520 (6) | C(50)–C(52) | 1.535 (7) |
| C(5)–C(6) | 1.377 (6) | C(50)–C(53) | 1.504 (7) |
| C(5)–H(5) | 0.80 (4) | C(60)–C(61) | 1.528 (7) |
| C(6)–C(40) | 1.543 (6) | C(60)–C(62) | 1.530 (7) |
| C(7)–C(8) | 1.444 (6) | C(60)–C(63) | 1.526 (7) |
| C(7)–C(12) | 1.433 (5) | C(70)–C(71) | 1.537 (8) |
| C(8)–C(9) | 1.394 (6) | C(70)–C(72) | 1.489 (7) |
| C(8)–C(50) | 1.546 (6) | C(70)–C(73) | 1.546 (10) |
| C(9)–C(10) | 1.384 (6) | | |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The geometries of the 2,4,6-*t*-Bu$_3$C$_6$H$_2$ and CO ligands are normal and deserve no special comment.

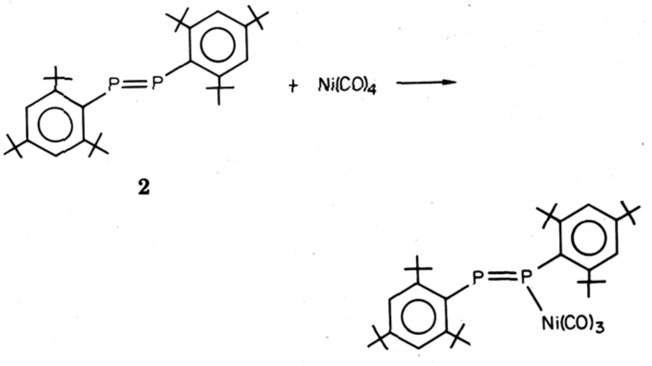
Complex 3 is also formed, along with free 2, in the reaction between Na$_2$Fe(CO)$_4$ and (2,4,6-*t*-Bu$_3$C$_6$H$_2$)PCl$_2$ in THF solution. The formation of 3 by this route is analogous to the formation of 4 described by Power[8] from Na$_2$Fe(CO)$_4$ and (Me$_3$Si)$_2$CHPCl$_2$. The exact course of this reaction is unclear, but an attractive intermediate is the terminal phosphinidene complex A. Loss of Fe(CO)$_4$ from



A

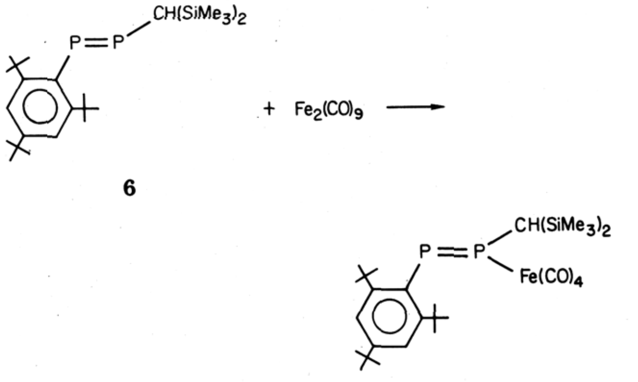
A would generate a free phosphinidene group (RP) which could yield diphosphene 2 by dimerization. In turn, 2 would react with Fe$_2$(CO)$_9$ to afford 3. Alternatively, 3 could result from the reaction of A with an RP moiety. The formation of a complex containing two Fe(CO)$_4$ groups appears to be ruled out by the use of models which shows that for 3 insufficient space remains for another Fe(CO)$_4$ group.

To further extend this chemistry, diphosphene 2 was treated with excess Ni(CO)$_4$ in Et$_2$O at 25 °C. The $^{31}$P{$^1$H} NMR data ($\delta_{P_A}$ +449.0, $\delta_{P_B}$ +442.0, and $^1J_{PP}$ = 540.3 Hz) and IR data ($\nu_{CO}$ = 1800, 1860, and 1955 cm$^{-1}$) indicate the formation of a mono Ni(CO)$_3$ adduct, 5. No reaction between 2 and Cr(CO)$_5$(THF) was observed. Having examined the reactions of 2 with simple carbonyl species, the corresponding chemistry of the unsymmetrical diphosphene 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$P=PCH(SiMe$_3$)$_2$, 6, was investigated. Treatment with Fe$_2$(CO)$_9$ led to a color change



2

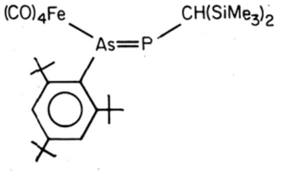
5



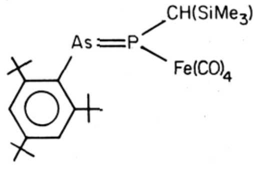
6

7

from yellow to dark red. The $^{31}P\{^1H\}$ NMR spectrum for the new complex 7 comprised an AB system with $\delta_{P_A}$ +424.0, $\delta_{P_B}$ +416.0, and $^1J_{PP}$ = 519.0 Hz. Additional coupling to the $CH(SiMe_3)_2$ proton in the $^1H$-coupled $^{31}P$ spectrum showed $^2J_{PH}$ = 30.0 Hz and $^3J_{PH}$ = −3.2 Hz. The IR spectrum, $\nu_{CO}$ = 1970 (br) and 2060 $cm^{-1}$, was indicative of a single $Fe(CO)_4$ group. These data indicate a similar structure to that of 3 but do not allow an unambiguous decision as to which phosphorus is attached to the $Fe(CO)_4$ group. However, the two phosphorus ligands 2,4,6-*t*-$Bu_3C_6H_2$ and $(Me_3Si)_2CH$ differ markedly in size, the latter being smaller. On this basis it is assumed that the $Fe(CO)_4$ group bonds to the phosphorus linked to the $(Me_3Si)_2$ CH group. This structure is corroborated by results from the diarsene chemistry (see later).



9



10

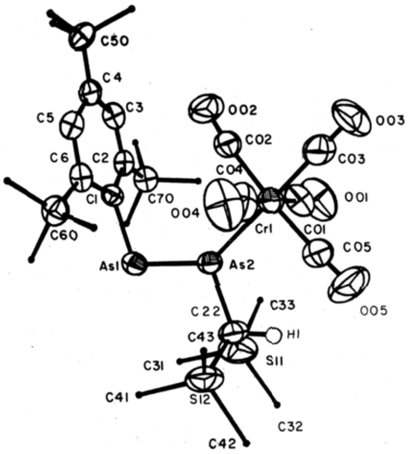
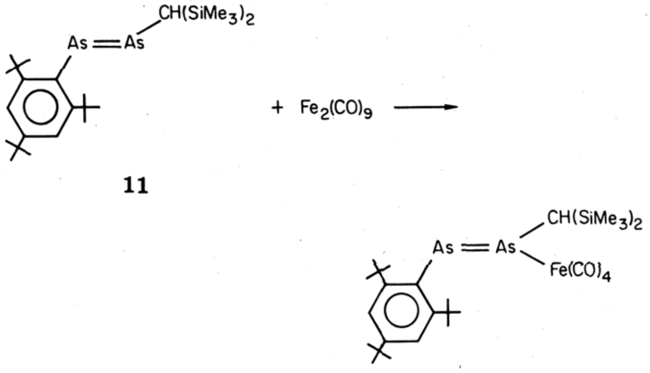


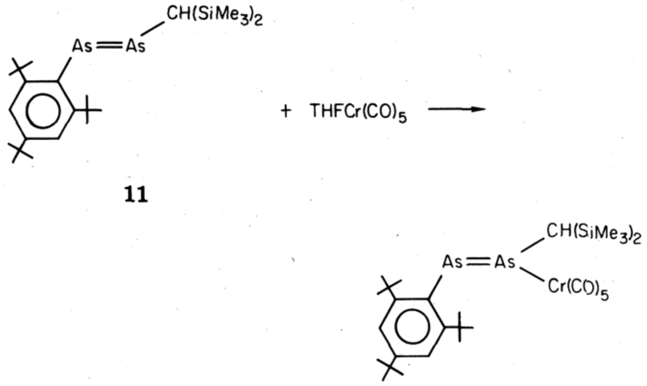
**Figure 2.** ORTEP view of 2,4,6-*t*-$Bu_3C_6H_2As{=}AsCH(SiMe_3)_2Cr(CO)_5$, 13, showing the atom numbering scheme.



11

12

Analogous chemistry with the phospharsene 2,4,6-*t*-$Bu_3C_6H_2As{=}PCH(SiMe_3)_2$,[17,18] 8, and $Fe_2(CO)_9$ affords two products. While it did not prove possible to separate these, the reaction was clean as followed by $^{31}P\{^1H\}$ NMR spectroscopy which showed two resonances at δ +429 and +390. It is proposed that these correspond to $Fe(CO)_4$ complexes where the iron atom bonds to either As (compound 9, $^{31}P$ δ +429) or P (compound 10, $^{31}P$ δ +390). Reactions with the diarsene 2,4,6-*t*-$Bu_3C_6H_2As{=}AsCH(SiMe_3)_2$,[17,18] 11, were next investigated. Treatment of 11 with $Fe_2(CO)_9$ gave a red complex characterized as the $Fe(CO)_4$ adduct 12 by mass spectrometry. It is assumed on steric grounds that the $Fe(CO)_4$ group bonds to the $(Me_3Si)_2CH$-substituted As atom. However, this complex appears unstable in solution which precluded further attempts at characterization.



11

13

The reaction of 11 with $Cr(CO)_5(THF)$ proved more successful and afforded a red complex, 13. IR and mass spectral data indicated the attachment of one $Cr(CO)_5$ unit, and this was confirmed by an X-ray structural study.[19] The structure of 13 is shown in Figure 2, and Tables of bond lengths, bond angles, and atomic positional parameters appear in Tables V–VII. The chromium atom is octahedrally coordinated to five carbonyl ligands and As(2) (Cr(1)–As(2) = 2.454 (1) Å). The As–As bond length of

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(16) Cowley, A. H.; Kilduff, J. E.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1983**, 528.

(17) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R.; Atwood, J. L.; Hunter, W. E. *Inorg. Chem.*, in press.

(18) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M. *J. Am. Chem. Soc.* **1983**, *105*, 5506.

(19) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 978.

Table IV. Bond Angles (deg) for $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2P_2Fe(CO)_4$, 3[a]

| | | | | | |
|---|---|---|---|---|---|
| P(1)-Fe(1)-C(01) | 88.8 (2) | C(2)-C(1)-C(6) | 118.2 (3) | C(7)-C(8)-C(50) | 125.7 (4) |
| P(1)-Fe(1)-C(02) | 117.1 (2) | C(1)-C(2)-C(3) | 117.6 (4) | C(9)-C(8)-C(50) | 116.3 (4) |
| P(1)-Fe(1)-C(03) | 125.7 (2) | C(1)-C(2)-C(20) | 126.2 (3) | C(8)-C(9)-C(10) | 124.0 (4) |
| P(1)-Fe(1)-C(04) | 95.7 (2) | C(3)-C(2)-C(20) | 116.2 (4) | C(8)-C(9)-H(9) | 120 (3) |
| C(01)-Fe(1)-C(02) | 89.7 (3) | C(2)-C(3)-C(4) | 125.3 (4) | C(10)-C(9)-H(9) | 116 (3) |
| C(01)-Fe(1)-C(03) | 89.3 (2) | C(2)-C(3)-H(3) | 118 (4) | C(9)-C(10)-C(11) | 115.9 (4) |
| C(01)-Fe(1)-C(04) | 174.9 (2) | C(4)-C(3)-H(3) | 116 (4) | C(9)-C(10)-C(60) | 122.5 (4) |
| C(02)-Fe(1)-C(03) | 117.1 (2) | C(3)-C(4)-C(5) | 114.9 (4) | C(11)-C(10)-C(60) | 121.6 (4) |
| C(02)-Fe(1)-C(04) | 90.4 (3) | C(3)-C(4)-C(30) | 123.2 (4) | C(10)-C(11)-C(12) | 124.5 (4) |
| C(03)-Fe(1)-C(04) | 86.1 (3) | C(5)-C(4)-C(30) | 121.9 (4) | C(10)-C(11)-H(11) | 124 (3) |
| Fe(1)-P(1)-P(2) | 135.52 (6) | C(4)-C(5)-C(6) | 125.5 (4) | C(12)-C(11)-H(11) | 111 (3) |
| Fe(1)-P(1)-C(1) | 115.1 (1) | C(4)-C(5)-H(5) | 115 (3) | C(7)-C(12)-C(11) | 117.6 (4) |
| P(2)-P(1)-C(1) | 109.3 (1) | C(6)-C(5)-H(5) | 119 (3) | C(7)-C(12)-C(70) | 127.5 (4) |
| P(1)-P(2)-C(7) | 108.4 (1) | C(1)-C(6)-C(5) | 117.4 (4) | C(11)-C(12)-C(70) | 114.9 (4) |
| Fe(1)-C(01)-O(01) | 177.8 (4) | C(1)-C(6)-C(40) | 126.8 (4) | C(2)-C(20)-C(21) | 109.7 (4) |
| Fe(1)-C(02)-O(02) | 179.5 (5) | C(5)-C(6)-C(40) | 115.7 (4) | C(2)-C(20)-C(22) | 112.2 (4) |
| Fe(1)-C(03)-O(03) | 176.7 (5) | P(2)-C(7)-C(8) | 120.3 (3) | C(2)-C(20)-C(23) | 112.7 (4) |
| Fe(1)-C(04)-O(04) | 172.7 (5) | P(2)-C(7)-C(12) | 121.5 (3) | C(21)-C(20)-C(22) | 112.8 (4) |
| P(1)-C(1)-C(2) | 119.7 (3) | C(8)-C(7)-C(12) | 118.1 (3) | C(21)-C(20)-C(23) | 103.9 (4) |
| P(1)-C(1)-C(6) | 120.0 (3) | C(7)-C(8)-C(9) | 118.0 (4) | C(22)-C(20)-C(23) | 105.2 (4) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Positional Parameters and Their Estimated Standard Deviations for $2,4,6\text{-}t\text{-}Bu_3C_6H_2As{=}AsCH(SiMe_3)_2Cr(CO)_5$, 13

| atom | $x$ | $y$ | $z$ | $B$,[a] Å$^2$ |
|---|---|---|---|---|
| As(1) | 0.83678 (7) | 0.14644 (2) | 0.22774 (6) | 3.67 (2) |
| As(2) | 0.72228 (7) | 0.14205 (2) | 0.05624 (6) | 3.19 (1) |
| Cr(1) | 0.6202 (1) | 0.08422 (4) | −0.07106 (9) | 3.50 (2) |
| Si(1) | 0.8689 (3) | 0.22919 (9) | −0.0242 (3) | 7.43 (7) |
| Si(2) | 0.6002 (3) | 0.23992 (8) | 0.0690 (2) | 6.69 (7) |
| O(01) | 0.8368 (6) | 0.0864 (2) | −0.2038 (5) | 8.3 (2) |
| O(02) | 0.7274 (6) | 0.0049 (2) | 0.0698 (5) | 7.7 (2) |
| O(03) | 0.5135 (6) | 0.0122 (2) | −0.2306 (5) | 7.4 (2) |
| O(04) | 0.3879 (5) | 0.0842 (3) | 0.0471 (5) | 8.2 (2) |
| O(05) | 0.4939 (8) | 0.1526 (2) | −0.2331 (6) | 9.6 (2) |
| C(01) | 0.7584 (8) | 0.0857 (3) | −0.1506 (6) | 5.1 (2) |
| C(02) | 0.6931 (7) | 0.0364 (2) | 0.0225 (6) | 4.9 (2) |
| C(03) | 0.5513 (7) | 0.0401 (3) | −0.1705 (6) | 4.8 (2) |
| C(04) | 0.4755 (8) | 0.0840 (3) | 0.0049 (7) | 5.5 (2) |
| C(05) | 0.5408 (8) | 0.1274 (3) | −0.1695 (7) | 5.3 (2) |
| C(1) | 0.8478 (5) | 0.0835 (2) | 0.2813 (5) | 2.7 (1) |
| C(2) | 0.9469 (6) | 0.0546 (2) | 0.2550 (5) | 3.0 (1) |
| C(3) | 0.9397 (6) | 0.0105 (2) | 0.2813 (5) | 3.2 (1) |
| C(4) | 0.8434 (6) | −0.0082 (2) | 0.3337 (5) | 2.9 (1) |
| C(5) | 0.7596 (6) | 0.0210 (2) | 0.3688 (5) | 3.4 (1) |
| C(6) | 0.7586 (6) | 0.0668 (2) | 0.3475 (5) | 3.0 (1) |
| C(22) | 0.7135 (7) | 0.2050 (2) | 0.0021 (6) | 4.4 (2) |
| C(31) | 0.972 (1) | 0.2479 (5) | 0.104 (1) | 14.9 (5) |
| C(32) | 0.845 (1) | 0.2787 (5) | −0.108 (1) | 15.2 (5) |
| C(33) | 0.966 (1) | 0.1892 (4) | −0.085 (1) | 17.5 (4) |
| C(41) | 1.167 (1) | 0.2428 (5) | −0.282 (1) | 15.0 (4) |
| C(42) | 0.556 (1) | 0.2902 (4) | −0.015 (1) | 11.7 (4) |
| C(43) | 0.456 (1) | 0.2081 (4) | 0.082 (1) | 12.1 (4) |
| C(50) | 0.8411 (6) | −0.0590 (2) | 0.3546 (5) | 3.5 (1) |
| C(51) | 0.8255 (8) | −0.0838 (3) | 0.2416 (7) | 5.5 (2) |
| C(52) | 0.9640 (8) | −0.0734 (3) | 0.4253 (6) | 4.8 (2) |
| C(53) | 0.7305 (7) | −0.0732 (3) | 0.4168 (7) | 5.3 (2) |
| C(60) | 0.6591 (6) | 0.0956 (3) | 0.4025 (6) | 4.0 (2) |
| C(61) | 0.7184 (8) | 0.1384 (3) | 0.4553 (7) | 6.0 (2) |
| C(62) | 0.5461 (7) | 0.1066 (3) | 0.3147 (7) | 5.4 (2) |
| C(63) | 0.6106 (8) | 0.0702 (3) | 0.4972 (7) | 6.1 (2) |
| C(70) | 1.0637 (6) | 0.0705 (2) | 0.2011 (6) | 3.6 (2) |
| C(71) | 1.1189 (7) | 0.1150 (3) | 0.2488 (7) | 5.3 (2) |
| C(72) | 1.0329 (8) | 0.0719 (3) | 0.0747 (6) | 5.6 (2) |
| C(73) | 1.1726 (7) | 0.0357 (3) | 0.2271 (7) | 5.3 (2) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table VI. Bond Lengths (Å) for $2,4,6\text{-}t\text{-}Bu_3C_6H_2As{=}AsCH(SiMe_3)_2Cr(CO)_5$, 13[a]

| | | | |
|---|---|---|---|
| As(1)-As(2) | 2.246 (1) | O(04)-C(04) | 1.126 (7) |
| As(1)-C(1) | 1.978 (5) | O(05)-C(05) | 1.136 (7) |
| As(2)-Cr(1) | 2.454 (1) | C(1)-C(2) | 1.435 (6) |
| As(2)-C(22) | 1.981 (5) | C(1)-C(6) | 1.414 (7) |
| Cr(1)-C(01) | 1.869 (7) | C(2)-C(3) | 1.355 (7) |
| Cr(1)-C(02) | 1.911 (6) | C(2)-C(70) | 1.559 (6) |
| Cr(1)-C(03) | 1.856 (7) | C(3)-C(4) | 1.396 (6) |
| Cr(1)-C(04) | 1.904 (7) | C(4)-C(5) | 1.358 (7) |
| Cr(1)-C(05) | 1.868 (7) | C(4)-C(50) | 1.534 (7) |
| Si(1)-C(22) | 1.880 (6) | C(5)-C(6) | 1.389 (7) |
| Si(1)-C(31) | 1.848 (12) | C(6)-C(60) | 1.582 (7) |
| Si(1)-C(32) | 1.785 (10) | C(50)-C(51) | 1.531 (8) |
| Si(1)-C(33) | 1.797 (10) | C(50)-C(52) | 1.523 (7) |
| Si(2)-C(22) | 1.862 (6) | C(50)-C(53) | 1.545 (7) |
| Si(2)-C(41) | 1.847 (9) | C(60)-C(61) | 1.521 (8) |
| Si(2)-C(42) | 1.827 (9) | C(60)-C(62) | 1.524 (8) |
| Si(2)-C(43) | 1.835 (11) | C(60)-C(63) | 1.516 (8) |
| O(01)-C(01) | 1.124 (7) | C(70)-C(71) | 1.529 (8) |
| O(02)-C(02) | 1.130 (7) | C(70)-C(72) | 1.505 (8) |
| O(03)-C(03) | 1.137 (7) | C(70)-C(73) | 1.558 (8) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

2.246 (1) Å is consistent with retention of the double bond albeit slightly longer than that in the uncomplexed diarsene 11 with As(1)–As(2) = 2.224 (2) Å.[17,18] The arsenic atom As(2) bonds to the $(Me_3Si)_2CH$ group with As(2)–C(22) = 1.989 (5) Å, while As(1) is attached to the 2,4,6-$t$-$Bu_3C_6H_2$ ligand with As(1)–C(1) = 1.964 (5) Å. The bond angles at arsenic (As(1)–As(2)–C(22) = 103.9 (2)° and A(2)–As(1)–C(1) = 104.0 (1)°) are both significantly larger than the corresponding angles in the uncomplexed diarsene (99.9 (3)° and 93.6 (3)°).[17,18] This follows the same trend as that observed in the structure of 3, presumably for similar reasons to those described earlier.

The atoms C(1), As(1), As(2), C(22), and Cr(1) are all coplanar, mean deviation 0.04 Å, an observation also consistent with an As=As double bond. Finally, the ligands are disposed so as to minimize steric strain. Thus carbonyl C(05)–O(05) is placed to bisect the Si(1)–C(22)–Si(2) angle on the same side as the proton H(1). The 2,4,6-$t$-$Bu_3C_6H_2$ group is arranged such that C(02)–O(02) falls between the ortho $t$-Bu groups.

In addition, the structural determination confirms the attachment of the metal carbonyl fragment to the $(Me_3Si)_2CH$-substituted As atom, i.e., the least sterically hindered site. This provides support for the structures of 7 and 12 as indicated above.

## Conclusions

The spectroscopic studies indicate and the structural studies confirm that for the diphosphenes, phospharsenes,

Table VII. Bond Angles (deg) for 2,4,6-$t$-$Bu_3C_6H_2As{=}AsCH(SiMe_3)_2Cr(CO)_5$, 13[a]

| | | | | | |
|---|---|---|---|---|---|
| As(2)-As(1)-C(1) | 104.0 (1) | C(04)-Cr(1)-C(05) | 88.6 (3) | As(1)-C(1)-C(2) | 120.6 (4) |
| As(1)-As(2)-Cr(1) | 138.51 (3) | C(22)-Si(1)-C(31) | 114.4 (4) | As(1)-C(1)-C(6) | 120.0 (3) |
| As(1)-As(2)-C(22) | 103.9 (2) | C(22)-Si(1)-C(32) | 110.4 (5) | C(2)-C(1)-C(6) | 119.4 (4) |
| Cr(1)-As(2)-C(22) | 117.6 (2) | C(22)-Si(1)-C(33) | 112.8 (4) | C(1)-C(2)-C(3) | 117.5 (4) |
| As(2)-Cr(1)-C(01) | 89.1 (2) | C(31)-Si(1)-C(32) | 104.1 (6) | C(1)-C(2)-C(70) | 124.8 (5) |
| As(2)-Cr(1)-C(02) | 92.7 (2) | C(31)-Si(1)-C(33) | 103.2 (6) | C(3)-C(2)-C(70) | 117.6 (4) |
| As(2)-Cr(1)-C(03) | 176.8 (2) | C(32)-Si(1)-C(33) | 111.4 (5) | C(2)-C(3)-C(4) | 124.1 (5) |
| As(2)-Cr(1)-C(04) | 91.6 (2) | C(22)-Si(2)-C(41) | 113.0 (4) | C(3)-C(4)-C(5) | 116.5 (5) |
| As(2)-Cr(1)-C(05) | 91.9 (2) | C(22)-Si(2)-C(42) | 110.8 (4) | C(3)-C(4)-C(50) | 119.8 (4) |
| C(01)-Cr(1)-C(02) | 91.7 (3) | C(22)-Si(2)-C(43) | 110.7 (4) | C(5)-C(4)-C(50) | 123.6 (5) |
| C(01)-Cr(1)-C(03) | 87.8 (3) | C(41)-Si(2)-C(42) | 109.5 (3) | C(4)-C(5)-C(6) | 124.1 (5) |
| C(01)-Cr(1)-C(04) | 177.6 (3) | C(41)-Si(2)-C(43) | 108.3 (5) | C(1)-C(6)-C(5) | 117.4 (4) |
| C(01)-Cr(1)-C(05) | 89.1 (3) | C(42)-Si(2)-C(43) | 108.3 (5) | C(1)-C(6)-C(60) | 126.2 (5) |
| C(02)-Cr(1)-C(03) | 86.7 (2) | Cr(1)-C(01)-O(01) | 176.1 (6) | C(5)-C(6)-C(60) | 116.4 (4) |
| C(02)-Cr(1)-C(04) | 90.5 (3) | Cr(1)-C(02)-O(02) | 172.0 (5) | As(2)-C(22)-Si(1) | 114.5 (3) |
| C(02)-Cr(1)-C(05) | 175.3 (3) | Cr(1)-C(03)-O(03) | 177.3 (6) | As(2)-C(22)-Si(2) | 113.0 (3) |
| C(03)-Cr(1)-C(04) | 91.6 (3) | Cr(1)-C(04)-O(04) | 178.1 (6) | Si(1)-C(22)-Si(2) | 120.3 (3) |
| C(03)-Cr(1)-C(05) | 88.7 (3) | Cr(1)-C(05)-O(05) | 177.1 (7) | | |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

and diarsenes studied, attachment of only one $M(CO)_x$ group occurs. Furthermore, in unsymmetrical compounds it bonds at the least sterically hindered phosphorus or arsenic site.[20] Thus in no case is attachment of two $M(CO)_x$ groups observed. $\eta^2$ Coordination of the $M(CO)_x$ group is also not seen although the absence of this type of linkage cannot be solely, if at all, attributed to steric reasons.

The size of the $M(CO)_x$ unit that will complex is critically dependent on the size of the ligands bound to either phosphorus or arsenic. Thus with two $(Me_3Si)_3C$ groups, no complexes are observed. For diphosphenes or phospharsenes containing 2,4,6-$t$-$Bu_3C_6H_2$ or $(Me_3Si)_2CH$ as ligands, complexes with $Fe(CO)_4$ and $Ni(CO)_3$ groups are observed but not with $Cr(CO)_5$. Only the diarsene 11 forms a complex with chromium, presumably as a result of a longer As–As bond coupled with the relatively small $(Me_3Si)_2CH$ group, to which end the $Cr(CO)_5$ unit bonds.

## Experimental Section

**General Data.** All experiments were performed under an atmosphere of dry dinitrogen by using standard Schlenk techniques. All solvents used were freshly distilled over $CaH_2$ or Na/benzophenone prior to use. Microanalytical data were obtained from the Canadian Microanalytical Service Ltd.

**Spectroscopic Measurements.** UV spectra were recorded on a Cary Model 15 spectrophotometer. $^1H$ NMR spectra were recorded on Varian EM390 and Nicolet NT200 instruments operating at 90.0 and 200.0 MHz, respectively. $^{13}C$ spectra were recorded on Varian FT80A and Bruker WH90 instruments operating at 20.0 and 22.615 MHz. $^{31}P$ spectra were recorded on Varian FT80A and Nicolet NT200 instruments operating at 32.384 and 80.988 MHz, respectively. $^1H$ and $^{13}C$ spectra were referenced to internal $Me_4Si$ (0.0 ppm) and $^{31}P$ spectra to external 85% $H_3PO_4$ (0.0 ppm), positive values to high frequency in all cases. Medium- and high-resolution mass spectra were measured on Du Pont Consolidated Model 21-491 and 21-100 instruments, respectively. Perfluorokerosene was used as the calibrant for HRMS. IR spectra were measured on a Perkin-Elmer 1330 spectrophotometer.

The synthesis of the uncomplexed diphosphene, phospharsene, and diarsene are as described in ref 17.

**Preparations. Preparation of (2,4,6-*t*-$Bu_3C_6H_2)_2P_2Fe(CO)_4$, 3.**[12] The diphosphene (2,4,6-$t$-$Bu_3C_6H_2)_2P_2$,[15] 2 (0.562 g, 1.02 mmol), and $Fe_2(CO)_9$ (0.51 g, 1.4 mmol) were dissolved in 50 mL of dry degassed hexane under dry dinitrogen at 0 °C. The solution was stirred for 6 h and allowed to warm to room temperature resulting in a color change from orange to dark red. Concentration, filtration (Celite/$n$-hexane) and column chromatography (silica gel/$n$-hexane/−40 °C) yielded a dark red solution. Removal of most of the solvent and cooling to −20 °C produced dark red crystals of **3** (0.50 g, 70% yield): $^1H$ NMR ($CD_2Cl_2$) $\delta$ 1.30 (m, 18 H, $t$-Bu), 1.55 (s, 18 H, $t$-Bu), 1.65 (s, 18 H, $t$-Bu), 7.50 (m, 4 H, $C_2H_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 30.8 (s, para $C(CH_3)_3$), 33.4 (m, nonequivalent ortho $C(CH_3)_3$), 34.6 (m, nonequivalent ortho $C(CH_3)_3$), 38.8 (s, para $C(CH_3)_3$), 40.0 (s, ortho $C(CH_3)_3$), 123.2 (m, nonequivalent meta $C_6H_2$), 151.0 (s, para $C_6H_2$), 154.9 (m, nonequivalent ortho $C_6H_2$), ipso and carbonyl carbon signals were not observed; $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$) $\delta$ 423.6 (uncoordinated P), 396.4 (coordinated P), AB system, $^1J_{PP} = 578.0$ Hz; mp 168–170 °C dec; IR $\nu_{C{\equiv}O}$ (hexane) 2046, 1981, 1965 cm$^{-1}$; UV–vis ($CH_2Cl_2$) $\lambda_{max}$ 486 ($\epsilon$ 5200), 288 ($\epsilon$ 18 700), 244 nm ($\epsilon$ 26 000); HRMS calcd for $C_{40}FeH_{48}O_4P_2$ 636.331 11, found 636.329 60.

**Preparation of (2,4,6-*t*-$Bu_3C_6H_2)_2P_2Ni(CO)_3$, 5.** A 0.052-g (0.095-mmol) sample of **2** was dissolved in 15 mL of dry $Et_2O$ and the solution cooled to −196 °C. The flask was evacuated, and an excess of $Ni(CO)_4$ (approximately 0.5 mL) was allowed to condense inside. The system was then allowed to warm to room temperature under $N_2$. After the solution was stirred for 2 h, the $Et_2O$ was removed in vacuo and the resulting dark solid redissolved in THF. $^{31}P\{^1H\}$ NMR and IR data are given in the text and are consistent with the structure shown. No other products were detected spectroscopically.

**Preparation of {2,4,6-*t*-$Bu_3C_6H_2P{=}PCH(SiMe_3)_2\}Fe(CO)_4$, 7.** The diphosphene 2,4,6-$t$-$Bu_3C_6H_2P{=}PCH(SiMe_3)_2$,[18] **6** (0.47 g, 1.0 mmol), and $Fe_2(CO)_9$ (0.73 g, 2.0 mmol) were dissolved in 100 mL of dry $Et_2O$ and the solution stirred for 3 h, resulting in a color change from orange to dark red. After reduction of the solvent volume in vacuo, the crude product was purified by column chromatography on silica gel in hexane. Recrystallization of the single dark red fraction from pentane at −20 °C afforded red crystals of 7 (0.4 g, 63% yield): $^{31}P$ NMR ($CH_2Cl_2$) $\delta_{P_A}$ 416.0 ($P$-2,4,6-($t$-Bu)$_3C_6H_2$), $\delta_{P_B}$ 424 ($P$-$CH(SiMe_3)_2Fe(CO)_4$, AB part of ABX, $^1J_{PP} = 519$ Hz, $^2J_{PH} = 30$ Hz, $^3J_{PH} = -3.2$ Hz; IR (hexane) $\nu_{C{\equiv}O}$ 1970 (br), 2060 (sh) cm$^{-1}$; HRMS for $C_{29}H_{48}FeO_4P_2Si_2$ calcd 634.191 56, found 634.189 68; UV–vis ($C_6H_{12}$) $\lambda_{max}$ 221 ($\epsilon$ 28 450), 241 ($\epsilon$ 16 800), 286 ($\epsilon$ 9490), 328 ($\epsilon$ 3970), 453 nm ($\epsilon$ 2470).

**Reaction of 2,4,6-(*t*-Bu)$_3C_6H_2As{=}PCH(SiMe_3)_2$, 8, with $Fe_2(CO)_9$.** The phospharsene 8 (0.51 g, 1.0 mmol) and $Fe_2(CO)_9$ (0.73 g, 2.0 mmol) were dissolved in 50 mL of dry hexane and the solution stirred at room temperature. After 3 h a color change to dark red occurred. Purification by column chromatography (silica gel/$n$-hexane) afforded a dark red solution. $^{31}P$ NMR data are given in the text and indicate the presence of two complexes. Separation by either chromatography or crystallization did not prove possible.

**Reaction of 2,4,6-*t*-$Bu_3C_6H_2As{=}AsCH(SiMe_3)_2$, 11, with $Fe_2(CO)_9$.** The diarsene[18] **11** (0.554 g, 1.0 mmol) and $Fe_2(CO)_9$ (0.73 g, 2.0 mmol) were dissolved in $n$-hexane (50 mL). The workup procedure is the same as that given for the phospharsene complexes and produced a dark red solution. Mass spectral data showed M − 3 CO at $m/e$ 638. HRMS for $C_{26}H_{48}As_2OSi_2Fe$ (M − 3 CO): calcd 638.102 71, found 638.103 86. Further characterization proved difficult due to decomposition.

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(20) The reaction of the phospharsene 8 and $Fe_2(CO)_9$ appears to be anomalous in this respect.

**Preparation of {2,4,6-*t*-Bu$_3$C$_6$H$_2$As=AsCH(SiMe$_3$)$_2$}Cr(CO)$_5$, 13.** A solution of Cr(CO)$_5$(THF)[21] in THF (60 mL of 0.033 M solution, 2.0 mmol) was added to a stirred solution of the diarsene 11 (0.554 g, 1.0 mmol) in 50 mL of THF. Stirring of the reaction mixture for an additional 2 h at −25 °C afforded a dark orange solution which was purified by column chromatography (silica gel/*n*-hexane). Crystallization from *n*-pentane at −20 °C afforded orange red crystals of 12 (0.5 g, 67% yield): UV–vis (CH$_2$Cl$_2$) $\lambda_{max}$ 240 ($\epsilon$ 36 700), 293 ($\epsilon$ 16 750), 345 ($\epsilon$ 3800), 470 nm ($e$ 7800); IR (hexane) $\nu_{C\equiv O}$ 1950 (br), 2050 (sh); mp 138–139 °C; $^1$H NMR (CD$_2$Cl$_2$) $\delta$ 0.3 (s, 18 H, SiMe$_3$), 2.8 (s, 1 H, CH), 1.34 (s, 9 H, para *t*-Bu), 1.50 (s, 18 H, ortho *t*-Bu), 7.5 (s, 2 H, C$_6$H$_2$); $^{13}$C{$^1$H} NMR (CDCl$_3$) $\delta$ 0.1 (m, nonequivalent SiMe$_3$), 28.8 (s, CH), 31.3 (s, para C(*C*H$_3$)$_3$), 34.7 (m, nonequivalent ortho C(*C*H$_3$)$_3$), 125.2 (s, meta *C*$_6$H$_2$), 153.2 (s, ortho *C*$_6$H$_2$), 213.7 (s, Cr(*C*O)$_5$), other quaternary carbons not observed; HRMS for C$_{30}$H$_{48}$As$_2$O$_5$Si$_2$Cr calcd 746.087 94, found 746.086 38.

**X-ray Analysis of 3.** A suitable single crystal of 3 was grown from hexane at −20 °C and mounted on a glass fiber for data collection. The unit cell dimensions were determined from a least-squares fit to 25 reflections $10° \le 2\theta \le 20°$ and subsequently refined by using higher angle data. These indicated a monoclinic cell. Data were collected for one independent quadrant on an Enraf-Nonius CAD-4F diffractometer using parameters listed in Table I. The data were reduced in the monoclinic space group $P2_1/c$, deduced from systematic absences, with corrections for Lorentz and polarization effects but not for absorption. The structure was solved by using MULTAN[22] which revealed the positions of the iron and phosphorus atoms. Subsequent refinement using full-matrix least-squares revealed the positions of all non-hydrogen atoms, all of which were refined with anisotropic thermal parameters. The hydrogen atoms H(3), H(5), H(9), and H(11) were located and refined positionally. All others were included in the structure factor calculation in calculated positions 0.95 Å from the respective carbon atom. The final difference map revealed a slight disorder in the methyl carbons C(31)–C(33) and C(71)–C(73). For the former *t*-Bu group an alternate orientation C(31A)–C(33A) was observed, and for both, the site occupancy factors were allowed to refine freely leading to an occupancy ratio of 5:1. The second orientation for the latter group C(71A)–C(73A) refined to a much lower occupancy and was subsequently removed from the refinement. No other chemically significant peaks were present in the final difference map. In the final cycles of refinement a weighting scheme was introduced to downweight intense reflections leading to final residuals shown in Table I. Complex neutral atom scattering factors were used throughout.

**X-ray Analysis of 13.** The experimental method for this structure determination differs in no fundamental manner from that of 3. Pertinent data are presented in Table I. No problems relating to disorder of methyl group positions were encountered in this structure. Details of thermal parameters, calculated hydrogen positions, and tables of observed and calculated structure factors for both structures are available as supplementary material. All calculations were performed on a DEC PDP 11/44 computer using the Enraf-Nonius SDP structure solution programs.[24]

**Registry No.** 2, 83466-54-0; 3, 87937-39-1; 5, 87937-40-4; 6, 89746-77-0; 7, 87937-41-5; 8, 89746-78-1; 9, 87937-43-7; 10, 87937-42-6; 11, 86528-38-3; 12, 89746-76-9; 13, 87922-34-7; Fe$_2$(CO)$_9$, 15321-51-4; Ni(CO)$_4$, 13463-39-3; Cr(CO)$_5$(THF), 15038-41-2; Na$_2$Fe(CO)$_4$, 14878-31-0; (2,4,6-*t*-Bu$_3$C$_6$H$_2$)PCl$_2$, 79074-00-3.

**Supplementary Material Available:** Tables of positional parameters and esd's, thermal parameters, structure factors, hydrogen positions, and selected bond angles for 3 and 13 (94 pages). Ordering information is given on any current masthead page.

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(21) Produced by photolysis of Cr(CO)$_6$ in THF for 2 h.

(22) MULTAN 82. A direct method program for structure determination: Main, P. University of York, York, England, 1982.

(23) Cramer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321. Stewart, R. F.; Davidson, E. F.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(24) Frenz, B. A. B. A. Frenz Associates Ltd., College Station, TX.

(25) $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and GOF $= [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO = number of observations, NV = number of parameters varied, $w = 4F_o^2/\sigma^2(F_o^2)$, and $\sigma^2(F_o^2) = \sigma_o^2(F_o^2) + (pF^2)^2$. $p$ is the factor used to downweight intense reflections and was set to 0.08 for 3 and 0.05 for 12.