No. 64) and the noncentrosymmetric space group *C2cb* (standard setting *Aba*2, C_{2v}^{17}, No. 41). With $Z = 8$ (Table I) the space group *Cmca* demands that the formula unit possesses a mirror plane and that the Ru, O, C(1), C(4), C(5), C(6) atoms lie at $x = 0$ and $^1/_2$. In *C2cb* no symmetry demands are placed on the formula unit. *Cmca* was initially assumed, and this space group was subsequently verified by the unambiguous, refined structure. Interpretation of the three-dimensional Patterson function gave the Ru coordinates. The carbon and oxygen atoms were found from a Fourier synthesis phased on Ru. Following several cycles of anisotropic least-squares refinement, the thermal ellipsoid of the cyclopentadienyl carbon lying on the mirror plane, C(6), was found to be abnormally extended in the direction perpendicular to the mirror plane. This was taken to indicate some disorder in the cyclopentadienyl ring, with a fraction of the cyclopentadienyls occupying a position rotated by 180° about the ring axis. By trial, the occupany of this rotated position was found to be 0.3. Refinement of the major component, with occupany 0.7, gave well-behaved thermal ellipsoids and improved bond distances. The hydrogen atoms of the Cp and 2-methylallyl ligands were then placed at calculated positions [C–H = 0.95 Å, $B(\mathrm{H}) = B(\mathrm{C}) + 1.0$] during refinement, with the positional and thermal parameters fixed. Full-matrix refinement with weights $w = [\sigma^2(I) + (kF_o^2)^2]^{1/2}$ and $k = 0.08$ gave a final R value of 0.041, $R_w = 0.055$, for 1013 observed reflections. An extinction correction was included in the structure factor calculation and was refined during final least-squares refinement, giving $g = 4.87 \times 10^{-6}$.

Both structure factor calculations used atomic scattering factors for C, O, and Ru, with anomalous dispersion from Cromer and Liberman,[13] and for bonded H from Stewart, Davidson and Simpson.[14]

Registry No. 1, 78037-33-9; 2, 77933-78-9.

Supplementary Material Available: Listings of anisotropic temperature factors, calculated hydrogen atom parameters, and data on least-squares planes (3 pages); listings of observed and calculated structure factor amplitudes (19 pages). Order information is given on any current masthead page.

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(13) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(14) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Versatile Behavior of Hydrido Monometallic or Heterobimetallic Carbonyl Anions toward Dichlorophosphines and 1,1-Dichlorodiphosphines

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The reactivity of 1,1-dichlorodiphosphine (i-Pr$_2$N)$_2$P–PCl$_2$ (**5**) toward [NEt$_4$][HW(CO)$_5$] (**2**) and [NEt$_4$][HFe(CO)$_4$] (**1b**) has been investigated. The first reaction leads to the neutral difunctionalized diphosphine complex (i-Pr$_2$N)P(Cl)–P(H)(N-i-Pr$_2$)W(CO)$_5$ (**9**), implying diisopropylamino group migration, while the second reaction affords [NEt$_4$][(i-Pr$_2$N)P(H)[Fe(CO)$_4$]–P(H)[Fe(CO)$_4$]$_2$] (**10**) in which a phosphorus–nitrogen bond has been cleaved. The structures of **9** and **10** have been determined by X-ray diffraction. **9** is triclinic, space group $P1$, with $a = 9.887$ (4) Å, $b = 10.349$ (4) Å, $c = 14.309$ (4) Å, $\alpha = 75.92$ (3)°, $\beta = 75.50$ (3)°, $\gamma = 64.72$°, and $Z = 2$. The structure has been solved and refined to R and R_w values of 0.028 and 0.027, respectively, by using 3898 reflections. **10** is monoclinic, space group $P2_1/n$, with $a = 10.018$ (5) Å, $b = 29.892$ (13) Å, $c = 12.337$ (5) Å, $\beta = 100.66$ (4)°, and $Z = 4$. The structure has been refined to R and R_w values of 0.086 and 0.081, respectively, by using 2644 reflections. The reaction of dichlorophosphines RPCl$_2$ with [PPh$_4$][HFeW(CO)$_9$] (**3**) has also been examined: the [PPh$_4$][(μ-RP-(Cl)[Fe(CO)$_4$][W(CO)$_5$]] complexes have been obtained (R = Ph, **14a**; R = Me, **14b**; R = 2,5-dimethyl-1,2,3-σ^2-diazaphosphole, **14c**). The formation of [PPh$_4$][PhP(H)[Fe(CO)$_4$][W(CO)$_5$]] (**15a**) from PhPCl$_2$W(CO)$_5$ and [PPh$_4$][HFe(CO)$_4$] (**1a**), which requires 2 equiv of the iron anion, points out the specificity of the reaction of **3**.

Introduction

Over the last 5 years, a significant volume of research has been devoted to the study of the reactivity of Na$_2$Fe(CO)$_4$ or Na$_2$M$_2$(CO)$_{10}$ dianions (M = Cr, Mo, or W) toward dichlorophosphines, RPCl$_2$. Depending on the nature of the organometallic fragments, various compounds of the type [(CO)$_n$M]$_2$PR, [((CO)$_n$M)$_2$(PR)$_2$M(CO)$_n$], and related species have been prepared.[1] In contrast, very few

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investigations of the reactions of hydrido monometallic or heterobimetallic carbonyl anions, $HM(CO)_n^-$ or $HMM'(CO)_n^-$, with chlorinated phosphorus species have appeared. In prior publications, we have demonstrated the synthetic utility of the hydrido carbonyl iron complex $[Ph_4P][HFe(CO)_4]$ (**1a**) which allows either the stabilization by complexation of short-lived phosphorus derivatives such as phosphinidenes, RP, diphosphenes, RP=PR, phosphacumulenes, RP=C=C<, phosphides, R_2P^-, or the preparation of new phosphorus heterocycles difficult to obtain by conventional ways.[2]

Preliminary results have shown that the anionic tungsten hydrido carbonyl metalate $[NEt_4][HW(CO)_5]$ (**2**) reacts similarly to **1a** with phenyldichlorophosphine, $PhPCl_2$, giving rise to the halogenophosphine complex $PhP(H)(Cl)W(CO)_5$ (**4b**).[2a] To our knowledge, similar work has been not undertaken with the anionic heterobinuclear complex $[PPh_4][HFeW(CO)_9]$ (**3**).[3]

The focus of the present work is to provide information concerning the reactions of **2** and **3** with dichlorophosphines or 1,1-dichlorodiphosphines and to compare their behavior with that of **1a**. We report (i) the surprising difference of reactivity of **2** and $[NEt_4][HFe(CO)_4]$ (**1b**) toward the diphosphine $(i\text{-}Pr_2N)_2P\text{-}PCl_2$ (**5**), (ii) the X-ray diffraction studies of the new neutral or anionic functionalized diphosphine complexes, **9** or **10**, and (iii) the versatile behavior of $[Ph_4P][HFeW(CO)_9]$ (**3**) which allows the synthesis of the anionic heterobimetallic phosphido complexes **14a–c**, and **15a**.

Results and Discussion

Our previous investigations of the reactivity of the hydrido complex **1a** with dichlorophosphines have clearly shown that the size of the substituent on phosphorus plays a major role in determining the type of product obtained. With the aim of evaluating the role of the hydrido complex and the variation in hydride character of the hydrogen ligand, we have now extended our work to a comparative study of the behavior of complexes **1**, **2**, and **3**.

Although no marked effect of the organometallic fragment was observed when phenyldichlorophosphine was allowed to react with **1a** or **2**,[2a] the same is not true for the reaction of **1b** and **2** with a more bulky dichlorophosphine, i.e. 1,1-dichloro-2,2-bis(diisopropylamino)diphosphine (**5**).[4]

Reaction of $[NEt_4][HW(CO)_5]$ (2) with $(i\text{-}Pr_2N)_2P\text{-}PCl_2$ (5). Addition of **2** in THF to a solution of the diphosphine **5** in the same solvent, at room temperature, yields the new functionalized diphosphine complex **9**. The bis(diisopropylamino)chlorophosphine arising from the partial decomposition of the starting diphosphine **5** is obtained as a byproduct. Two isomers, **9a** and **9b**, in a 1:1 ratio, have been characterized in solution by ^{31}P NMR [**9a**: $\delta(P_1)$ +123.4 (dd), $\delta(P_2)$ −2.9 (dd); $^1J_{P_1P_2}$ = 244.0, $^2J_{P_1H}$ = 46.0, $^1J_{P_2H}$ = 338.1, $^1J_{P_2W}$ = 240.5 Hz. **9b**: $\delta(P_1)$ +148.8 (dd), $\delta(P_2)$ 27.1 (dd); $^1J_{P_1P_2}$ = 298.3, $^2J_{P_1H}$ = 15.0, $^1J_{P_2H}$ = 325.6 Hz]. **9a** was isolated from the resulting mixture by fractional crystallization in 0.7% yield. Examination of the solution ^{31}P NMR spectrum—when addition of **2** to **5** was performed at −65 °C followed by stirring at −40 °C for 4 h—revealed the presence of two doublets [$\delta(P_1)$ +89.6, $\delta(P_2)$ +37.6; $^1J_{P_1P_2}$ = 295.5, $^1J_{P_2H}$ = 330.8, $^2J_{P_1H}$ = 24.0, $^2J_{P_2W}$ = 204 Hz] due to the transient generation of the diphosphine complex **6**. A multistep mechanism can be postulated to explain the formation of **9a,b**.

The first step could afford **6** via the release of tetraethylammonium chloride and the 1,1 addition of $[HW(CO)_5]^-$ to the chlorinated phosphorus atom. Intramolecular elimination of hydrogen chloride might give rise to the transient phosphorus–phosphinidene complex, **7** which rearranges into the η^1-diphosphene complex **8** via an un-

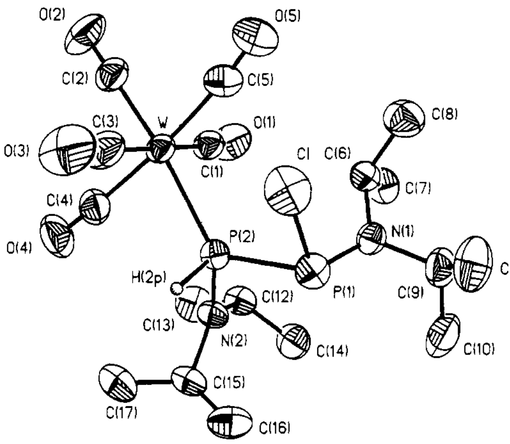

Figure 1. Structure of complex **9a** showing the atomic numbering scheme with the ellipsoids at the 40% probability level.

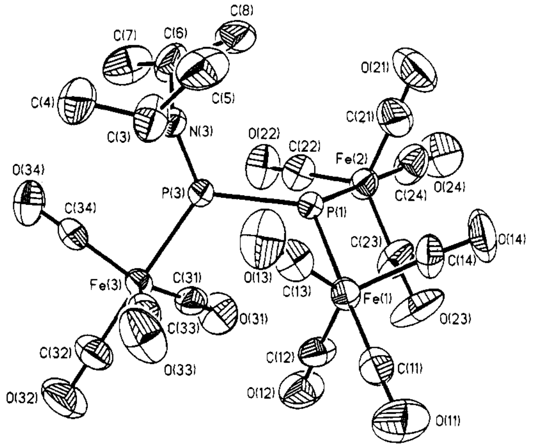

Figure 2. Structure of complex **10** showing the atomic numbering scheme with the ellipsoids at the 30% probability level.

Table I. Selected Bond Lengths (Å) and Angles (deg) for 9a

P(1)-P(2)	2.255 (2)	N(1)-P(1)-Cl	106.7 (1)
P(1)-Cl	2.148 (2)	N(1)-P(1)-P(2)	107.7 (1)
P(1)-N(1)	1.651 (4)	Cl-P(1)-P(2)	91.7 (1)
P(2)-N(2)	1.671 (3)	P(1)-P(2)-W	129.1 (1)
P(2)-W	2.549 (1)	P(1)-P(2)-N(2)	105.3 (1)
		W-P(2)-N(2)	117.2 (1)

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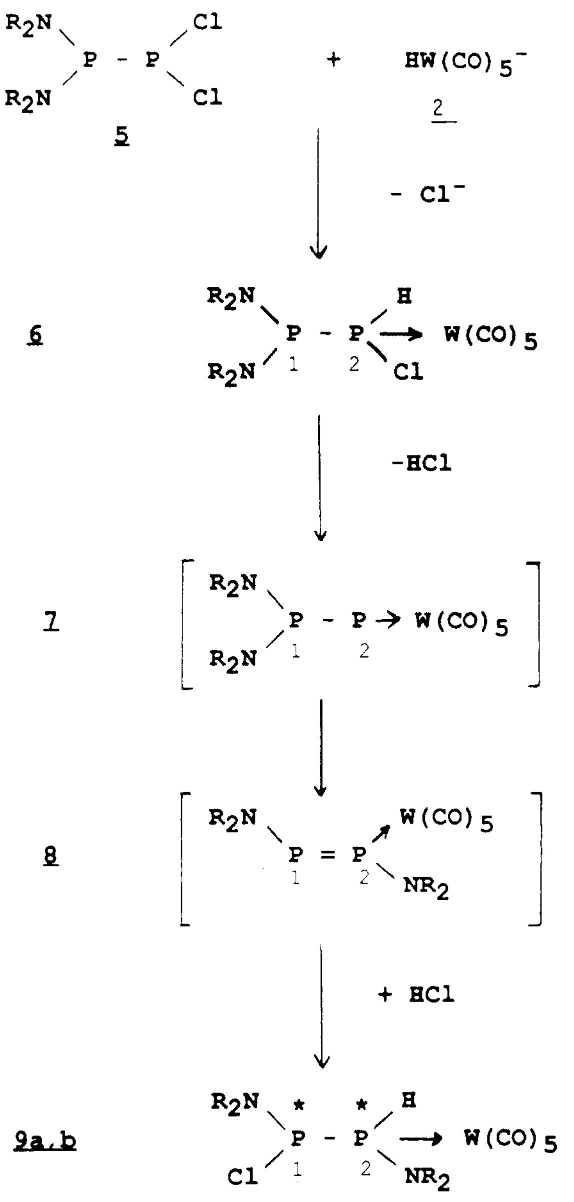
(1) (a) Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085. (b) Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7750. (c) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 7751. (d) Borm, J.; Zsolnai, L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 977. (e) Flynn, K. M.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Organometallics* **1986**, *5*, 813. (f) Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7460. (g) Lang, H.; Orama, O.; Huttner, G. *J. Organomet. Chem.* **1985**, *291*, 293. (h) Bartlett, R. A.; Rasika Dias, H. V.; Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *109*, 5693. (i) Bartlett, R. A.; Rasika Dias, H. V.; Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *109*, 5699.

(2) (a) Mathieu, R.; Caminade, A.-M.; Majoral, J.-P.; Attali, S.; sanchez, M. *Organometallics* **1986**, *5*, 1914. (b) Mathieu, R.; Caminade, A.-M.; Majoral, J.-P.; Daran, J.-C. *J. Am. Chem. Soc.* **1986**, *108*, 8007. (c) Caminade, A.-M.; Majoral, J.-P.; Sanchez, M.; Mathieu, R.; Attali, S.; Grand, A. *Organometallics* **1987**, *6*, 1459. (d) Caminade, A.-M.; Majoral, J.-P.; Mathieu, R.; Yeung Lam Ko, Y. Y. C. *J. Chem. Soc., Chem. Commun.* **1987**, *639*. (e) Caminade, A.-M.; Majoral, J.-P.; Igau, A.; Mathieu, R. *New J. Chem.* **1987**, *6*, 457.

(3) Arndt, L. W.; Darensbourg, M. Y.; Delord, T.; Bancroft, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 2617.

(4) Niecke, E.; Westermann, H.; Nieger, M., in preparation.

Scheme I



usual diisopropylamino group migration from the free to the complexed phosphorus atom. Such an amino group migration may be related to recently reported rearrangments.[5] Lastly, addition of hydrogen chloride to the phosphorus–phosphorus double bond of 8 would produce **9a,b**.

Scheme II

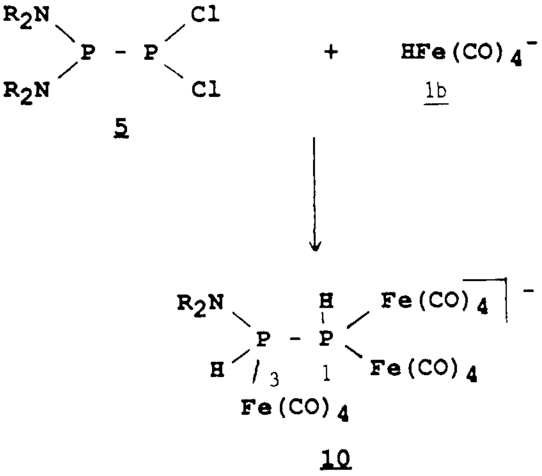


Table II. Selected Bond Lengths (Å) and Angles (deg) for 10

P(1)-P(3)	2.283 (5)	Fe(1-)P(1)-Fe(2)	120.9 (2)
P(1)-Fe(1)	2.315 (4)	Fe(1-)P(1)-P(3)	115.9 (2)
P(1)-Fe(2)	2.328 (4)	Fe(2)-P(1)-P(3)	112.5 (2)
P(3)-Fe(3)	2.250 (4)	P(1)-P(3)-Fe(3)	118.8 (2)
P(3)-N(3)	1.640 (10)	P(1)-P(3)-N(3)	111.2 (4)
		Fe(3)-P(3)-N(3)	121.6 (4)
Fe(1)-C(eq)[a]	1.79 (2)	Fe(2)-C(24)	1.79 (2)
Fe(1)-C(11)	1.69 (2)	Fe(3)-C(eq)[a]	1.76 (2)
Fe(2)-C(eq)[a]	1.76 (2)	Fe(3)-C(32)	1.75 (2)

[a] Average.

Reaction of [NEt$_4$][HFe(CO)$_4$] (1b) with (i-Pr$_2$N)$_2$P–PCl$_2$ (5). Entirely different results were obtained when the reaction was carried out with **1b** instead of **2**. In this case, the trimetallic anionic diphosphine species **10** was formed in 19% yield. The ^{31}P NMR spectra of **10** consist of two doublets of doublets for each phosphorus with expected large $^1J_{P-P}$ and $^1J_{PH}$ values [$\delta(P_1)$ 77.8, $\delta(P_2)$ 1.91; $^1J_{PP} = 249.8$, $^1J_{P_1H} = 369.7$, $^1J_{P_2H} = 259.0$ Hz]. Such a different behavior may be the consequence of the reduced steric requirements of [HFe(CO)$_4$]$^-$ in comparison to [HW(CO)$_5$]$^-$ or at least alternatively more likely a result of the very different acidities of the metal hydrides and electronic properties of the metal fragments.

X-ray Structural Analysis of 9a and 10. Views of complexes **9a** and **10** are shown in Figures 1 and 2. Selected bond lengths and angles are summarized in Tables I and II. The structure found for **9a** is in perfect agreement with our formulation and confirms the migration of a diisopropylamino group from a phosphorus atom to another one. Moreover only one phosphorus atom is coordinated to the W(CO)$_5$ fragment. The P–N, P–P, and P–W distances are within the normal range for such bonds: 1.651 and 1.671 Å[6] for the P–N, 2.180 and 2.2670 Å[7] for the P–P, and 2.549 Å[8] for the P–W bond length.

The X-ray structure of **10** shows that the two Fe(CO)$_4$ groups are bridged by a [R$_2$N–P(H)–(Fe(CO)$_4$)]PH unit. The P–P bond length (2.283 Å) is fully consistent with a P–P single bond and is actually very close to the values observed in neutral diphosphine complexes (Cr(CO)$_5$)$_2$P$_2$Ph$_2$Cl$_2$, namely, 2.29 and 2.327 Å.[9] The salient feature of the structure is the difference between the P(1)–Fe(1) and P(1)–Fe(2) bond distances, 2.315 and 2.328 Å, respectively, which are essentially identical, and the P(3)–Fe(3) bond length, 2.250 Å. These data, in marked contrast with the value observed for the two P–Fe bonds

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(5) (a) King, R. B.; Sundaram, P. M. *J. Organomet. Chem.* **1984**, *49*, 1784. (b) King, R. B.; Sadanani, N. D. *J. Org. Chem.* **1984**, *50*, 1719. (c) Schäefer, H. G.; Schoeller, W. W.; Niemann, J.; Hang, W.; Dabisch, T.; Niecke, E. *J. Am. Chem. Soc.* **1986**, *108*, 7481. (d) King, R. B.; Wu, F. J.; Holt, E. M. *J. Am. Chem. Soc.* **1987**, *109*, 7764.

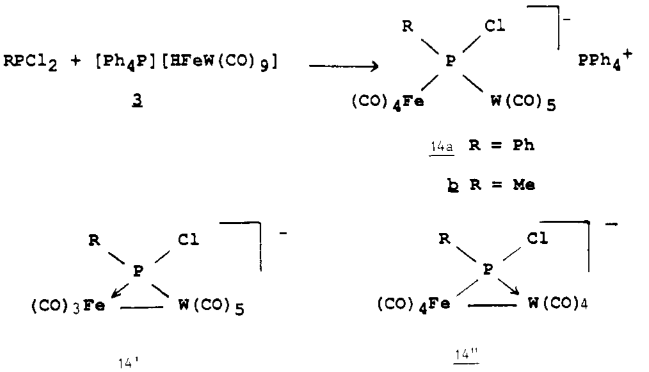
(6) See for example: Jaud, J.; Benhamou, M.; Majoral, J.-P.; Navech, J. *Z. Kristallogr.* **1982**, *60*, 69.

(7) See for example: (a) Appel, R.; Casser, R.; Knock, F. *J. Organomet. Chem.* **1985**, *297*, 21. (b) Elmes, P. S.; Gatehouse, B. M.; West, B. O. *J. Organomet. Chem.* **1974**, *82*, 235. (c) Gilje, J. W.; Sheldrick, W. S.; Weferling, N.; Schmutzler, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 379. (d) Crumbliss, A. L.; Topping, R. J.; Szewczyk, J.; McPhail, A. T.; Quin, L. D. *J. Chem. Soc., Dalton Trans.* **1986**, 1895.

(8) See for example: (a) Mercier, F.; Fischer, J.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 357. (b) Borm, J.; Huttner, G.; Zsolnai, L.; Evertz, K.; Berke, H. *J. Organomet. Chem.* **1987**, *327*, 223.

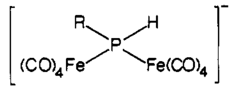
(9) See for example: Huttner, G.; Friedrich, P.; Wellenberg, H.; Muller, H. D. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 260 and references therein.

Scheme III



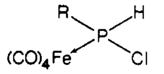
in the anionic bimetallic phosphido complex $[PPh_4][((CO)_4Fe)_2PHOMe]$, i.e. 2.26 Å,[2c] suggest that the negative charge is much more delocalized in the Fe(1)–P(1)–Fe(2) fragment of $[((CO)_4Fe)_2PHOMe]^-$ than in the Fe–P–Fe moieties of **10** and reflect the steric hindrance at the diphosphine moiety of **10**.

Reaction of $[PPh_4][HFeW(CO)_9]$ (3) with Dichlorophosphines. It has been shown that the reactions of dichlorophosphines $RPCl_2$ (R = Me, *t*-Bu, *i*-Pr_2 N) with 2 equiv of **1a** produce anionic phosphido complexes **11**.[2c]

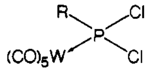


11

We thought that with use of an anionic heterobinuclear complex such as **3** instead of **1a**, a synthesis of heterobimetallic complexes of functionalized phosphides might be accessed. Darensbourg et al.[3] have demonstrated that the hydride in **3** is attached to the more electronegative metal Fe and that there is no evidence of it every being transferred to the $W(CO)_5$ unit. Indeed, all chemical reactions disruptive of **3** produce $[HFe(CO)_4]^-$ and $W(CO)_5$ fragments. For example, addition of triphenylphosphine to **3** afforded $[HFe(CO)_4]^-$ and $Ph_3PW(CO)_5$. Therefore, the reactions of **3** and phenyl- or methyldichlorophosphine should lead to secondary halophosphine complexes **12** and dichlorophosphine complexes **13**.



12a: R = Ph
b: R = Me

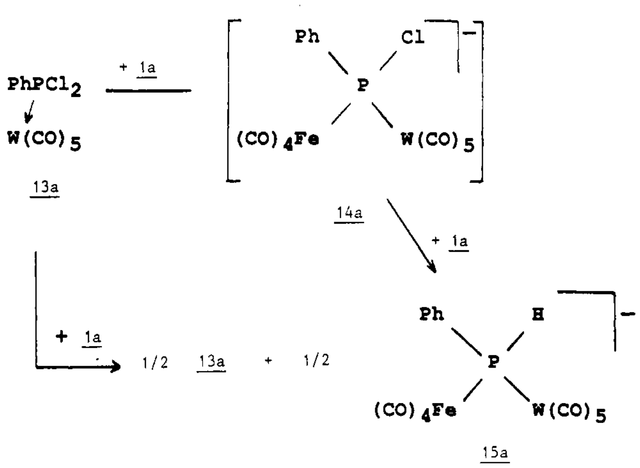


13a: R = Ph
b: R = Me

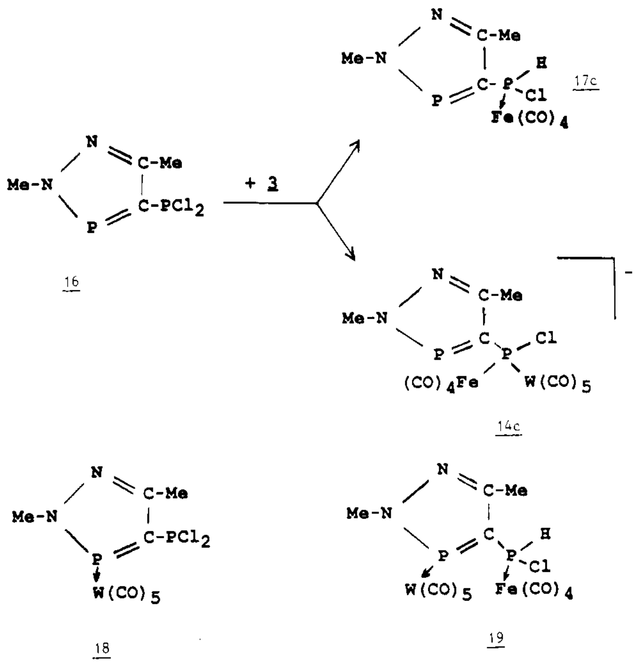
Actually, relatively stable anionic bimetallic phosphides **14a,b**, are formed as unique products. Spectroscopic data and chemical analysis do not allow for an unambiguous structure assignment for **14a,b**, the acyclic complex **14**, or the two cyclic complexes **14′** and **14″** although the ^{31}P chemical shift values argue for the acyclic form [δ 182 (R = Ph), 178.6 (R = Me) ppm]. We have been unable to obtain crystals for an X-ray analysis. Nevertheless, further reactions suggest assignment of an open structure, **14**.

Thus, stoichiometric addition of the hydride **1a** to phenyldichlorophosphine complexed by a $W(CO)_5$ fragment **13a** leads to a new heterobimetallic anionic phosphido complex, **15a**, half of the unreacted complex **13a** being recovered. Further addition of a second equivalent of **1a** to the resulting mixture only afforded **15a** and $Fe_3(CO)_{12}$. These results suggest that the first step of the reaction is the generation of the anionic species **14a** which reacts with a second equivalent of iron hydride **1a** to give **15a**. Indeed, the same result is observed when compound **14a**, isolated from the reaction of **3** with phenyldichlorophosphine, is directly added to $[HFe(CO)_4]^-$: the derivative **15a** is obtained as the unique phosphorus-containing complex.

Scheme IV



Scheme V



All these experiments seem to indicate that **14a** is better described as the open form of **14** rather than the cyclic ones **14′** or **14″** and demonstrate that the anion **1a** is far more reactive than **3**.

The derivatives **14a,b** are the first heterobimetallic complexes of functionalized phosphides.

A similar heterocyclic Fe–W bond cleavage was noted when 4-(dichlorophosphino)-2,5-dimethyl-1,2,3-σ^2-diazaphosphole (**16**)[10] was allowed to react with **3**. In this case, we were able to isolate not only the stable anionic complex **14c** as the major product but also the halophosphine complex **17c**.[11] Obviously, **17c** comes from the direct reaction of **16** with $[HFe(CO)_4]^-$ which arises from the disruption of **3** into $[HFe(CO)_4]^-$ and $W(CO)_5$. No com-

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(10) (a) Luber, J.; Schmidpeter, A. *J. Chem. Soc., Chem. Commun.* **1976**, 887. (b) Neumaier, J. H.; Brunnhuber, G.; Schmidpeter, A. *Chem. Ber.* **1980**, *113*, 2278.

(11) Galindo del Pozo, A.; Caminade, A.-M.; Dahan, F.; Majoral, J.-P.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1988**, 574.

pound resulting from the complexation of the low-coordinated phosphorus atom of the diazaphosphole unit, i.e. **18** or **19**, was detected.

These reactions illustrate the versatile behavior of $[HFeW(CO)_9]^-$ (**3**), reacting as either a monometallic or a heterobimetallic carbonyl anion. It is noteworthy that no hydride transfer from the metal to the phosphorus atom was observed here, while this transfer is the main reaction with **1a**,**b** or **2**.

Experimental Section

All experiments were performed in an atmosphere of dry argon. Dry and oxygen-free solvents were used at all times. Melting points are uncorrected. ^1H NMR spectra were recorded on a Bruker WM250 or a Bruker AC80 spectrometer. ^1H chemical shifts are reported in parts per million relative to Me_4Si as internal reference. ^{31}P NMR spectra were obtained on a Bruker WM250 or a Bruker AC80. Downfield shifts are expressed with a positive sign, in parts per million relative to external 85% H_3PO_4. Infrared spectra were recorded on a Beckman IR 10 or Perkin-Elmer 225 spectrometer, using polystyrene for calibration. Mass spectra were obtained on a Varian MAT 311A. $[Et_4N]$- or $[PPh_4][HFe(CO)_4]$, $[Et_4N][HW(CO)_5]$, and $[PPh_4][HFeW(CO)_9]$ were synthetized by published procedures.[3,11,12]

Synthesis of (i-Pr$_2$N)-P(Cl)-P(H)(N-i-Pr$_2$)W(CO)$_5$ (9). In a typical reaction, $[Et_4N]^+[HW(CO)_5]^-$ (4.4 mmol) was added to a solution of the diphosphine **5** (4.4 mmol) in 5 mL of THF at −65 °C. The mixture immediately turned dark yellow and, after the mixture was stirred for 4 h at −40 °C, the ^{31}P NMR spectrum revealed an AB pattern of **6** (80%) besides the signals of the starting diphosphine and its decomposition product, $(i\text{-}Pr_2N)_2PCl$. When the reaction mixture was warmed to 25 °C, the ^{31}P NMR signals of **6** disappeared in favor of the formation of **9a**,**b** (**9a**/**9b** = 1:1). After removal of the volatiles, the residue was extracted with 20 mL of pentane and filtered. Evaporation of the solvent left 0.38 g (14%) of crude **9a**,**b**. The residue was taken up in a small amount of THF/Et_2O and crystallized at −30 °C. This gave 0.02 g (0.7%) of **9a**, mp 123–127 °C dec. Anal. Calcd for. $C_{17}H_{29}ClN_2O_5P_2W$: C, 32.79; H, 4.69; N, 4.50. found: C, 33.08; H, 4.74; N, 4.58.

Synthesis of [Et$_4$N$^+$][i-Pr$_2$N-P(H){Fe(CO)$_4$}-P(H)[Fe(CO)$_4$]$_2$$^-$] (10). In a typical reaction, $[Et_4N]^+[HFe(CO)_4]^-$ (5 mmol), dissolved in 20 mL of THF, was added to a solution of diphosphine **5** (5 mmol) in 5 mL of THF at −65 °C. The mixture readily turned red-brown. After being stirred for 1 h at −40 °C and warmed to 25 °C, the reaction mixture was filtered and evaporated. This left crude **10** (0.78 g, 19% yield) as an oily residue. Dissolving the remaining **10** in a small amount of THF/Et_2O and cooling to −30 °C afforded suitable crystals for X-ray analysis; mp 116–117 °C dec. Anal. Calcd for $C_{26}H_{36}N_2Fe_3O_{12}P_2$: C, 39.14; H, 4.51; N, 3.51. Found: C, 39.78; H, 4.85; N, 3.60.

Synthesis of [PPh$_4$][{μ-PhP(Cl)}Fe(CO)$_4$W(CO)$_5$] (14a). To 0.215 g (1.2 mmol) of phenyldichlorophosphine in 5 mL of CH_2Cl_2 was added quickly 1 g (1.2 mmol) of $[Ph_4P][HFeW(CO)_9]$ in 15 mL of CH_2Cl_2 at room temperature. The solution was evaporated to dryness and the residue extracted with 2 × 15 mL of diethyl ether. Evaporation of diethyl ether gave **14a** as a red oil (90% yield): ^{31}P NMR (CH_2Cl_2) δ 182 ($^1J_{PW}$ = 214.7 Hz), 22.6 (PPh_4); ^1H NMR ($CDCl_3$) δ 7.4 (m, Ph); IR (CH_2Cl_2) 2060, 2022, 1970, 1930 (ν (C=O)) cm^{-1}. Anal. Calcd for $C_{39}H_{25}FeWP_2ClO_9$: C, 48.07; H, 2.57; Cl, 3.64. Found: C, 47.97; H, 2.30; Cl, 3.19.

Synthesis of [PPh$_4$][{μ-MeP(Cl)}Fe(CO)$_4$W(CO)$_5$] (14b). To methyldichlorophosphine (0.070 g, 0.6 mmol) dissolved in 5 mL of CH_2Cl_2 was added quickly $[Ph_4P][HFeWCO)_9]$ (0.500 g, 0.6 mmol) in 10 mL of CH_2Cl_2. After evaporation of the solvent, the residue was extracted with 15 mL of diethyl ether. Evaporation of diethyl ether gave **14b** as an orange oil (85% yield): ^{31}P NMR (CH_2Cl_2) δ 178.6 ($^1J_{PW}$ = 212.1 Hz), 22.5 (PPh_4); ^1H NMR ($CDCl_3$) δ 2.56 (d, $^2J_{HP}$ = 2.3 Hz, 3 H, Me), 7.46 (m, 20 H, Ph); IR (CH_2Cl_2) 2055, 2018, 1970, 1930 (ν(C=O)) cm^{-1}. Anal. Calcd

Table III. Summary of Crystal Data, Intensity Collection, and Structure Solution and Refinement for 9a

formula	$C_{17}H_{29}ClN_2O_5P_2W$
space group	P1
M_r	622.68
cryst system	triclinic
a (Å)	9.887 (4)
b (Å)	10.349 (4)
c (Å)	14.309 (4)
α (deg)	75.92 (3)
β (deg)	75.50 (3)
γ (deg)	64.72 (3)
Z	2
$\bar{V}$ (Å^3)	1266
d_{calcd} (g/cm^3)	1.633
cryst dimens (mm^3)	0.4 × 0.4 × 0.4
radiatn	Mo Kα
μ (cm-1)	48.96
unique data	4443
data used in refinement	3898, $\lvert F\rvert > 4\sigma(F)$

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 9a

	x	y	z	U(eq)[a]
W	1512 (1)	4430 (1)	1737 (1)	50 (1)
Cl	−1715 (2)	6163 (2)	4134 (1)	87 (1)
P(1)	−544 (1)	7604 (1)	3711 (1)	56 (1)
P(2)	1466 (1)	5993 (1)	2884 (1)	45 (1)
N(1)	−1442 (4)	8937 (4)	2901 (2)	50 (2)
N(2)	2812 (4)	6661 (4)	2593 (2)	49 (2)
O(1)	1595 (6)	6689 (5)	−192 (3)	94 (3)
O(2)	1990 (6)	2371 (5)	−303 (3)	106 (3)
O(3)	1524 (7)	2001 (6)	3583 (3)	130 (4)
O(4)	5084 (5)	3099 (5)	1565 (3)	103 (2)
O(5)	−2016 (5)	5299 (6)	1903 (4)	110 (3)
C(1)	−1545 (6)	5915 (5)	514 (4)	61 (2)
C(2)	1796 (7)	3099 (6)	848 (4)	71 (3)
C(3)	1499 (7)	2894 (6)	2935 (4)	80 (3)
C(4)	3809 (7)	3615 (6)	1625 (4)	72 (3)
C(5)	−773 (7)	5055 (6)	1863 (4)	75 (3)
C(6)	−1735 (5)	8749 (5)	1987 (3)	54 (2)
C(7)	−1335 (6)	9771 (6)	1113 (3)	68 (2)
C(8)	−3361 (6)	8890 (7)	2080 (5)	85 (3)
C(9)	−2373 (6)	10373 (6)	3242 (4)	70 (3)
C(10)	−1408 (8)	11071 (8)	3364 (6)	109 (4)
C(11)	−3525 (8)	10292 (8)	4135 (5)	107 (4)
C(12)	2908 (5)	7613 (5)	1641 (3)	54 (2)
C(13)	4416 (6)	6972 (7)	986 (4)	81 (3)
C(14)	2594 (7)	9126 (6)	1766 (4)	78 (3)
C(15)	3836 (6)	6463 (6)	3260 (3)	64 (2)
C(16)	3014 (8)	7179 (7)	4156 (4)	92 (4)
C(17)	4829 (6)	4894 (7)	3533 (4)	82 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Summary of Crystal Data, Intensity Collection, and Structure Solution and Refinement for 10

formula	$C_{26}H_{36}N_2O_{12}P_2Fe_3$
space group	$P2_1/n$
M_r	798.1
cryst system	monoclinic
a (Å)	10.018 (5)
b (Å)	29,892 (13)
c (Å)	12.337 (5)
β (deg)	100.66 (4)
Z	4
V (Å^3)	3630
d_{calcd} (g/cm^3)	1.46
cryst dimens (mm^3)	0.4 × 0.2 × 0.6
radiatn	Mo $K\alpha$
μ (cm^{-1})	13.2
unique data	4756
data used in refinement	2644, $\lvert F\times > 4\sigma(F)$

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(12) Mitsudo, T.; Watanabe, Y.; Nakanishi, H.; Morishima, I.; Inubushi, T.; Takegami, Y. *J. Chem. Soc., Dalton Trans.* **1978**, 1298.

(13) Gibson, D. H.; Ahmed, F. U.; Phillips, K. R. *Organometallics* **1982**, *5*, 679.

Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 10

	x	y	z	$U(\mathrm{eq})$[a]
Fe(1)	13003 (2)	1281 (1)	6996 (2)	65 (1)
C(11)	14503 (19)	1026 (6)	6967 (15)	98 (8)
O(11)	15558 (13)	845 (5)	6919 (12)	145 (7)
C(12)	12206 (16)	806 (6)	6311 (14)	83 (7)
O(12)	11740 (13)	490 (5)	5846 (11)	127 (7)
C(13)	13404 (15)	1359 (5)	8477 (15)	85 (7)
O(13)	13731 (13)	1414 (5)	9386 (10)	131 (7)
C(14)	13440 (15)	1755 (6)	6226 (14)	90 (8)
O(14)	13756 (13)	2035 (5)	5771 (12)	139 (7)
P(1)	10924 (4)	1630 (1)	6917 (3)	56 (1)
Fe(2)	9708 (2)	1901 (1)	5255 (2)	75 (1)
C(21)	10304 (21)	2423 (7)	5807 (16)	110 (10)
O(21)	10660 (19)	2770 (5)	6178 (4)	158 (9)
C(22)	8080 (18)	1718 (6)	5454 (13)	87 (8)
O(22)	7008 (13)	1608 (5)	5477 (10)	120 (6)
C(23)	10615 (18)	1541 (7)	4532 (13)	105 (9)
O(23)	11136 (16)	1311 (6)	3989 (11)	168 (8)
C(24)	8989 (20)	2174 (7)	3988 (16)	120 (10)
O(24)	8558 (18)	2338 (6)	3173 (12)	176 (9)
Fe(3)	9506 (2)	584 (1)	8221 (2)	61 (1)
P(3)	9548 (5)	1332 (1)	8013 (3)	78 (2)
N(3)	9388 (11)	1673 (3)	9022 (8)	56 (4)
C(3)	10443 (18)	1665 (7)	10033 (14)	109 (9)
C(4)	9966 (20)	1541 (7)	11033 (12)	124 (10)
C(5)	11293 (18)	2106 (6)	10145 (15)	129 (10)
C(6)	8290 (19)	2003 (7)	8939 (15)	108 (9)
C(7)	6940 (18)	1825 (7)	8886 (17)	136 (11)
C(8)	8392 (22)	2367 (6)	8137 (16)	147 (12)
C(31)	8959 (17)	570 (5)	6764 (16)	86 (8)
O(31)	8527 (13)	529 (5)	5835 (10)	125 (6)
C(32)	9344 (20)	1 (6)	8261 (15)	107 (9)
O(32)	9245 (17)	−388 (5)	8286 (13)	159 (8)
C(33)	11192 (19)	541 (5)	8936 (15)	91 (8)
O(33)	12259 (13)	478 (5)	9449 (12)	142 (7)
C(34)	8285 (18)	638 (5)	9052 (14)	87 (8)
O(34)	7451 (14)	667 (5)	9593 (11)	135 (7)
N(1)	5373 (17)	769 (6)	2684 (11)	117 (7)
C(1A)	5170 (31)	551 (11)	1563 (20)	217 (13)
C(2A)	5607 (62)	70 (14)	1929 (56)	228 (27)[b]
C(2A′)	5305 (86)	80 (16)	1084 (72)	256 (40)[c]
C(1B)	6735 (26)	654 (12)	3327 (28)	255 (15)
C(2B)	8041 (38)	693 (14)	2877 (30)	289 (17)
C(1C)	4295 (75)	434 (25)	2814 (47)	343 (49)[d]
C(1C′)	5146 (62)	714 (23)	3834 (26)	266 (32)[d]
C(2C)	3938 (41)	429 (14)	3975 (34)	298 (19)
C(1D)	5529 (95)	1260 (10)	2537 (108)	414 (77)[c]
C(2D)	6888 (64)	1231 (20)	2122 (50)	183 (22)[c]
C(1D′)	4201 (47)	1090 (17)	2335 (48)	241 (26)[b]
C(2D′)	4210 (56)	1509 (19)	3022 (44)	229 (24)[b]

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] sof = 0:56. [c] sof = 0.44. [d] sof = 0.50.

for $C_{34}H_{23}FeWClO_9P_2$: C, 44.76; H, 2.52; Cl, 3.89. Found: C, 45.11; H, 2.21; Cl, 3.40.

Synthesis of [PPh$_4$][{μ-PhP(H)}Fe(CO)$_4$WCO)$_5$] (15a). (i) From 14a. To **14a** (1.054 g, 1.08 mmol) in 10 mL of CH_2Cl_2 was added dropwise a solution of [Ph$_4$P][HFe(CO)$_4$] (0.55 g, 1.08 mmol) in 10 mL of CH_2Cl_2. The solution was stirred for 4 h at room temperature and then evaporated to dryness. Extraction of the residue with 2 × 15 mL of diethyl ether and evaporation of ether gave **15a** as a red oil (yield 95%): ^{31}P NMR (CH_2Cl_2) δ −69.5 (d, $^1J_{HP}$ = 291 Hz, $^1J_{PW}$ = 180 Hz), 22.9 (PPh$_4$); ^1H NMR (CDCl$_3$) δ 4.86 (d, $^1J_{HP}$ = 291 Hz, 1 H, PH), 7.41 (m, 25 H, Ph); IR (CH_2Cl_2) 2052, 1998, 1970, 1925 (ν(C=O)) cm^{-1}. Anal. Calcd for $C_{39}H_{26}FeWP_2O_9$: C, 49.84; H, 2.76. Found: C, 49.52; H, 2.32.

(ii) From PhPCl$_2$W(CO)$_5$ (13a). To a solution of **13a** (0.594 g, 1.18 mmol) in 10 mL of CH_2Cl_2 was added dropwise a solution of [PPh$_4$][HFe(CO)$_4$] (0.6 g, 1.18 mmol) in 10 mL of CH_2Cl_2. The solution was stirred for 4 h at room temperature and then evaporated to dryness. Extraction of the residue with 2 × 15 mL of diethyl ether gave **15a**.

Synthesis of 14c. A solution of [PPh$_4$][HFeW(CO)$_9$] (1.4 g, 1.68 mmol) in 10 mL of CH_2Cl_2 was quickly added to a solution of **16** (0.36 g, 1.68 mmol) in 5 mL of CH_2Cl_2. After evaporation of the solvent, the residue was extracted with 4 × 15 mL of diethyl ether. Evaporation of diethyl ether gave an orange oil (80% yield): ^{31}P NMR (CH_2Cl_2) δ 232 (d, $^2J_{PP}$ = 52.5 Hz, P=C), 154.5 (d, $^2J_{PP}$ = 52.5 Hz, $^1J_{PW}$ = 221.2 Hz, PW), 22.8 (s, PPh$_4$); ^1H NMR (CDCl$_3$) δ 2.49 (br s, 3 H, CMe), 3.78 (br s, 3 H, NMe), 7.65 (m, 20 H, Ph); IR (CH_2Cl_2) 2063, 2025, 1970, 1930 cm^{-1}. Anal. Calcd for $C_{37}H_{26}ClN_2FeWP_3O_9$: C, 43.98; H, 2.57; Cl, 3.52. Found: C, 44.12; H, 2.26; Cl, 3.22.

X-ray Studies. Complex **9a** was obtained as white crystals. Cell parameters are recorded with other crystal data in Table III.

The intensities of 4443 reflections ($2\theta_{max}$ = 50°) were collected on an automatic Stoe-Siemens four-circle diffractometer using graphite-monochromatized Mo Kα radiation [3898 with $|F| > 4\sigma(F)$ were treated as observed, with empirical absorption correction (R_{int} = 0.021 for 369 azimuthal scans)]. The structure was solved by Patterson and Fourier methods. All nonhydrogen atoms were refined anisotropically, riding model being employed for H atoms with C–H = 0.96 Å. Hydrogen at P(2) was located in a difference electron map and refined riding on P(2) with P–H = 1.42 Å. Calculations were performed with SHELXS-86 and SHELX-76 (extended version). The final full-matrix least-squares refinement converged to R = 0.028 and R_w = 0.027 ($w^{-1} = \sigma^2(F) + 0.000\,12F^2$). Final atomic parameters and equivalent isotropic displacement parameters are reported in Table IV.

Complex **10** was obtained as red prisms. Cell parameters are recorded with other crystal data in Table V. The intensities of 9269 reflections were measured at room temperature on a Nicolet R3m diffractometer ($2\theta_{max}$ = 45°) (4756 symmetry-independent reflections (R_{merge} = 0.023)). A total of 2644 reflections with $|F| > 4\sigma(F)$ were used for structure solution (Patterson and Fourier techniques) and refinement (385 parameters). Non-hydrogen atoms (except carbon atoms of disordered tetraethylammonium ion) were refined anisotropically and empirical absorption correction applied on the basis of psi-scan measurements. The structure was solved with SHELXS-86 and refined with SHELX-76. The final full-matrix least-squares refinement converged to R = 0.086 and R_w = 0.081 ($w^{-1} = \sigma^2(F) + 0.0012F^2$). Final atomic parameters and equivalent isotropic displacement parameters are reported in Table VI.

Registry No. **3**, 117406-00-5; **5**, 117270-09-4; **6**, 117308-47-1; **9a**, 117308-48-2; **9b**, 117405-99-9; **10**, 117308-50-6; **13a**, 18461-46-6; **14a**, 117339-87-4; **14b**, 117339-89-6; **14c**, 117339-91-0; **15a**, 117308-52-8; **16**, 62241-71-8; [Et$_4$N][HFe(CO)$_4$], 25879-01-0; [PPh$_4$][HFe(CO)$_4$], 103616-27-9; [Et$_4$N][HW(CO)$_5$], 80907-47-7; PhPCl$_2$, 644-97-3; MePCl$_2$, 676-83-5.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for **9** and **10** (8 pages); listings of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.