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Role of the Metal–Metal Bond in Transition-Metal Clusters. Phosphido-Bridged Diiron Carbonyl Complexes[1]

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The synthesis, characterization, and ligand substitution reactions of $Fe_2(PPh_2)_2(CO)_6$ (**1**) and $Na_2Fe_2(PPh_2)_2(CO)_6 \cdot 5THF$ (**4**) are presented. Reaction of **4** with alkylating agents affords *directly* the acyl complexes $NaFe_2(PPh_2)_2(CO)_5[C(O)R] \cdot 2THF$, (**6**). A mechanism involving intramolecular, metal-promoted alkyl migration is proposed. Reaction of **1** with lithium reagents affords $LiFe_2(PPh_2)_2(CO)_5[C(O)R] \cdot 3THF$.

The presence of adjacent metal sites in polynuclear complexes makes available situations which cannot be duplicated at a single metal site.[2] Noteworthy examples include (i) the binding of a single substrate to two or more metal atoms, (ii) the attachment of substrate fragments to adjacent metal atoms, (iii) the migration of ligands from one metal atom to another, (iv) reactions of metal-metal bonds, and (v) the simultaneous electron transfer from two or more metal atoms to a single substrate.

Several reactions commonly promoted by heterogeneous catalysts are rarely observed in the presence of mononuclear homogeneous catalysts. It is conceivable that those heterogeneously catalyzed reactions might be facilitated by adjacent metal centers in a multinuclear cluster. Important examples are steps found in hydrogenolysis, in re-forming and Fischer–Tropsch processes, and in reductions of nitriles, arenes, dinitrogen, and carbon monoxide.

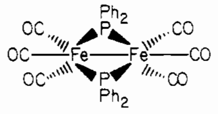
It is currently thought that in selected cases transition-metal cluster complexes may function as soluble analogues of heterogeneous catalysts.[3] It is hoped that the cluster catalyst will mimic the range of activity and reactions of heterogeneous catalysts yet retain the selectivity and efficiency of homogeneous catalysts. Further interest in transition-metal cluster chemistry stems from the suggestion that instructive analogies may be drawn between ligation in organo cluster complexes and chemisorption on metal surfaces.[3b]

The study of cluster complexes is complicated by various reactions which result in fragmentation of the metal framework.[2,4] The stabilities of clusters are generally limited to a narrow range of temperatures and pressures. In metal cluster complexes, the highest occupied molecular orbital (HOMO) is usually a σ-bonding MO of metal–metal bond character, and the lowest unoccupied molecular orbital (LUMO), a corresponding antibonding MO of metal–metal bond character.[5-7] Consequently, metal–metal bonds are easily broken by oxidation, reduction, or the addition of a donor ligand.

Inasmuch as clusters are subject to fragmentation, we have employed binculear complexes containing additional bridging ligands. Herein we describe the synthesis, characterization, and reactions of several phosphido-bridged diiron carbonyl clusters. Of particular interest is a novel metal-promoted alkyl migration, which is promoted by the formation of a metal–metal bond. A summary of recent synthetic, structural, theoretical, and reactivity studies of phosphido-bridged bimetallics is summarized in ref 8.

Results and Discussion

Synthesis and Characterization of $Fe_2(PPh_2)_2(CO)_6$. Bis[μ-(diphenylphosphido)]-bis[tricarbonyliron(I)], $Fe_2(PPh_2)_2(CO)_6$ (**1**), is comprised of two equivalent iron atoms, each bound to three terminal carbonyls and two bridging diphenylphosphido ligands. The complex formally contains an iron–iron single bond. Each of the iron atoms in the parent complex **1** is a coordinatively saturated, 18-electron center. Note that in cluster complexes a single electron is assigned to each metal atom for each metal–metal bond present.



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$Fe_2(PPh_2)_2(CO)_6$ (**1**) was first prepared by Thompson by reaction of iron pentacarbonyl and tetraphenyldiphosphine at 220 °C, a reaction which cannot conveniently be performed on a large scale.[9]

We have developed the alternative synthesis which is outlined in eq 1–3. The reduction of iron pentacarbonyl with

$$2Na + Fe(CO)_5 \xrightarrow[C_4H_8O_2 \atop 100\%]{\Delta} Na_2Fe(CO)_4 \cdot 1.5C_4H_8O_2 + CO \tag{1}$$

$$Na_2Fe(CO)_4 + Fe(CO)_5 \xrightarrow[THF \atop 100\%]{20\ ^\circ C} Na_2Fe_2(CO)_8 + CO \tag{2}$$

$$Na_2Fe_2(CO)_8 + 2Ph_2PCl \xrightarrow[THF \atop 60\%]{20\ ^\circ C} \underset{\mathbf{1}}{Fe_2(PPh_2)_2(CO)_6} \tag{3}$$

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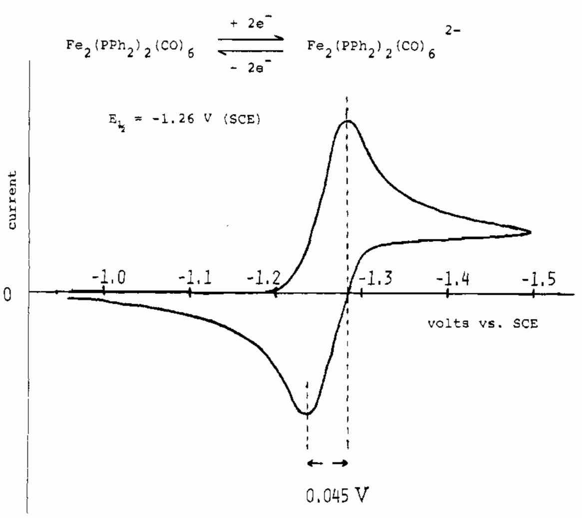


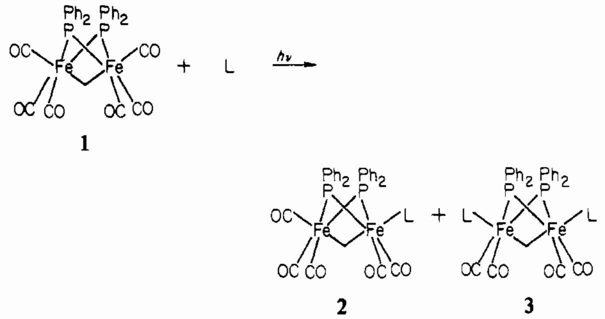
Figure 1. Cyclic voltammogram of $Fe_2(PPh_2)_2(CO)_6$ in acetonitrile containing 0.2 M $N(CH_2CH_3)_4ClO_4$ at a hanging-mercury-drop electrode. The peak-to-peak separation was essentially independent of scan speed in the range of 20–100 mV/s.

sodium in refluxing dioxane affords disodium tetracarbonylferrate(−II), $Na_2Fe(CO)_4{\cdot}1.5C_4H_8O_2$, in quantitative yield (eq 1).[10] The tetracarbonylferrate complex reacts with a second equivalent of $Fe(CO)_5$ to give disodium octacarbonyldiferrate(−I),[11] $Na_2Fe_2(CO)_8$, which upon treatment with 2 equiv of diphenylchlorophosphine affords the parent complex **1** as orange crystals in 60% yield overall (eq 2, 3). It is noteworthy that the entire reaction sequence may be carried out on a scale of tens of grams.

The infrared spectrum of $Fe_2(PPh_2)_2(CO)_6$ in the region of carbonyl stretching vibrations is similar to those of related $Fe_2(X)_2(CO)_6$ (X = PR_2, AsR_2, SR) complexes.[12,13]

An X-ray diffraction study of the parent complex **1** revealed a crystal structure consisting of discrete $Fe_2(PPh_2)_2(CO)_6$ molecules. The presence of an iron–iron bond is reflected in the Fe–Fe separation: 2.623 (2) Å. For structurally related dimers, a "bent" metal–metal bond has been proposed[14] which is conceptually viewed as completing the approximately octahedral coordination about each atom. The $Fe_2(PPh_2)_2$ core is symmetrical and nonplanar with sharply acute Fe–P–Fe bond angles and has idealized C_{2v} geometry. The X-ray data further show that there are two types of carbonyl in complex **1**. Four of the carbonyls are positioned trans to a phosphido ligand, while the remaining two carbonyls are positioned trans to the metal–metal bond.

Ligand Substitution Reactions of $Fe_2(PPh_2)_2(CO)_6$. Prior to our work, a few organosulfur- and organonitrogen-bridged $Fe_2(X)_2(CO)_6$ complexes had been observed to undergo thermally and photochemically initiated carbonyl substitution reactions.[15-17] A single report[18] described the formation of phosphine derivatives of bis[μ-(dimethylphosphido)]-bis[tricarbonyliron(I)], $Fe_2[P(CH_3)_2]_2(CO)_6$, in poor to modest yields upon irradiation of the hexacarbonyl complex in the presence of $P(C_6H_5)_3$ or $P(CH_2CH_3)_3$ with visible light. We found that complex $Fe_2(PPh_2)_2(CO)_6$ (**1**) undergoes thermally initiated carbonyl substitution reactions far less readily than do corresponding organosulfur- and organonitrogen-bridged compounds. Whereas the latter complexes undergo substitution at appreciable rates below 70 °C, the parent complex **1** fails to react with triethyl phosphite in refluxing benzene after 24 h. However, substitution is smoothly effected at room temperature within a day by irradiation with ultraviolet light. Only mono- and disubstituted derivatives result, even in those cases in which large excesses of phosphine or phosphite are employed (eq 4).



(4)

2a, 3a: L = $P(OCH_2CH_3)_3$
2b, 3b: L = $P(CH_3)_2Ph$
3c: L = $P(CH_3)Ph_2$

The infrared spectra of complexes **2** and **3a–c** are similar to those reported previously for derivatives of related dimers $Fe_2(X)_2(CO)_6$ [X = SR, NR_2, $P(CH_3)_2$]. Infrared,[16a,17] ^{13}C NMR,[15c,16a] Mössbauer,[17a] and mass[16a] spectra suggest that the ligand(s) L is positioned trans to the metal–metal bond in all such derivatives. This assignment has been established in two X-ray crystal structures.[16b,19]

Shortly following our discovery of photochemically induced displacement of carbon monoxide from $Fe_2(PPh_2)_2(CO)_6$ (**1**) by phosphines and phosphites, Ellgen and co-workers reported related thermal substitutions in complex **1** above 140 °C.[20]

Synthesis and Characterization of $Fe_2(PPh_2)_2(CO)_6^{2-}$. The cyclic voltammogram of $Fe_2(PPh_2)_2(CO)_6$ (**1**) exhibits a single, two-electron, reversible reduction wave at −1.26 V vs. the standard calomel electrode (Figure 1). The peak-to-peak separation (45 mV) of less than 59 mV indicates, *in the absence of complicating factors such as adsorption*, that more than one electron is involved. The chemical reversibility of the process is evidenced by the equivalent heights of the anodic and cathodic waves. Although reversible at a hanging-mercury-drop electrode, the reduction is totally irreversible at a platinum electrode. Chemiadsorption to the platinum surface may account for the different behavior.

A single, two-electron reduction requires that the reduction potential for the introduction of the second electron fall more anodic than that for the first; the second reduction must be thermodynamically more favorable than the first. In the case of cluster complex **1**, we speculate that this phenomenon results from entrance of the first electron into a σ-antibonding mo-

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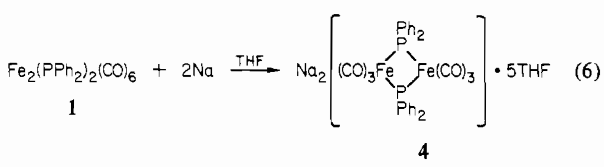
lecular orbital of metal–metal bond character, which causes a reduction of the metal–metal bond order to $^1/_2$. Bond breaking could then lead to a different geometry and a different ligand field in which the energy of the LUMO is lowered and, hence, "trigger" the introduction of the second electron.

A complementary explanation is found in a consideration of the magnitude of the equilibrium constant K_D for the disproportionation of the hypothetical $Fe_2(PPh_2)_2(CO)_6^-$ into the parent $Fe_2(PPh_2)_2(CO)_6$ and the fully reduced $Fe_2(PPh_2)_2(CO)_6^{2-}$ (eq 5). A single, two-electron reduction of $Fe_2(PPh_2)_2(CO)_6$ (**1**) requires that the disproportionation constant K_D be large. Attempts were made to detect the hypothetical $Fe_2(PPh_2)_2(CO)_6^-$. Infrared and visible spectra of the solution resulting from a mixture of equal volumes of 10^{-1} M solutions of $Fe_2(PPh_2)_2(CO)_6$ (**1**) and $Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF$ (**4**) (vide infra) in tetrahydrofuran exhibit no perceptible absorptions other than those attributable to individual complexes **1** and **4**. Furthermore, the ESR spectrum of the solution resulting from a mixture of equal volumes of 10^{-3} M solutions of complexes **1** and **4**, both of which are diamagnetic, in 2-methyltetrahydrofuran shows no signals above noise at 77 K in the region of 1000–5000 G at 9.15 GHz. By ESR spectroscopy, paramagnetic species are detectable in concentrations as low as 10^{-11} M. Hence, we calculate that the disproportionation constant K_D of eq 5 could be as large as $(10^{-3})^2/(10^{-11})^2 = 10^{16}$!

$$2Fe_2(PPh_2)_2(CO)_6^- \overset{K_D}{\rightleftharpoons} Fe_2(PPh_2)_2(CO)_6 + Fe_2(PPh_2)_2(CO)_6^{2-} \quad (5)$$

$Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF$ (**4**) is isolated as red-orange crystals (>90%) following reduction of the parent complex **1** with sodium dispersion in tetrahydrofuran (eq 6). The presence of the five tetrahydrofuran molecules as solvate was quantitatively determined by GLC analysis and ^1H NMR employing conventional internal standard methods. As expected, the carbonyl vibrations in $Fe_2(PPh_2)_2(CO)_6^{2-}$ appear at lower frequencies than those in $Fe_2(PPh_2)_2(CO)_6$. Note that the dianion **4** formally contains no metal–metal bond and consists of two five-coordinate iron(0) centers.



$$Fe_2(PPh_2)_2(CO)_6 + 2Na \xrightarrow{THF} Na_2[(CO)_3Fe(PPh_2)_2Fe(CO)_3]{\cdot}5THF \quad (6)$$

1 4

$(NaCRYPT)_2Fe_2(PPh_2)_2(CO)_6$ (**5**) was crystallized by vapor diffusion of hexane into a 1-methyl-2-pyrrolidinone solution of complex **4** and 2,2,2-cryptand in 1:2 molar ratio (CRYPT = 2,2,2-cryptand = $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$). An X-ray diffraction study of complex **5** revealed a crystal structure consisting of discrete $NaCRYPT^+$ and $Fe_2(PPh_2)_2(CO)_6^{2-}$ ions.[1b] The dianion displays trigonal-bipyramidal geometry about each iron atom. The junction of the two trigonal bipyramids is along a common axial–equatorial edge. In sharp contrast to the neutral parent complex **1**, the Fe_2P_2 core of the dianion is planar. The absence of an iron–iron bond in **5** is reflected in the large Fe–Fe separation of 3.630 (3) Å. The nonbonding Fe–Fe distance in the dianion **5** is 1.01 Å greater than the bonding Fe–Fe distance in the parent complex **1**.

Dessy et al. have reported that the related complex $Fe_2[P(CH)_3)_2]_2(CO)_6$ exhibits one two-electron, polarographic reduction wave which is unsplit on investigation by cyclic voltammetry.[21] The reported $E_{1/2}$ value of −2.1 V (vs. the $AgClO_4/Ag$ electrode with 0.1 M Bu_4NClO_4 as supporting electrolyte), which, on the basis of an estimated potential difference of ca. +0.7 V between the $AgClO_4/Ag$ and SCE reference electrodes,[22] corresponds to −1.4 V (vs. SCE). This value is comparable to −1.26 V (vs. SCE), the $E_{1/2}$ reported herein for the reduction of the diphenylphosphido-bridged dimer. Infrared data characteristic of $Fe_2[P(CH_3)_2]_2(CO)_6^{2-}$, which was generated in solution by exhaustive controlled-potential electrolysis, reported by Dessy and Wieczovek,[22] are similar to those characteristic of $Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF$ (**4**). A comparison between the dimethylphosphido- and diphenylphosphido-bridged compounds of the corresponding carbonyl stretching frequencies (viz., 1909 (w) vs. 1930 (m), 1879 (vs) vs. 1905 (vs), 1810 (vs) vs. 1845 (vs), and 1800 (vs) vs. 1825 (s) and 1800 (vs) cm^{-1}) reflects the expected carbonyl shift associated with the greater inductive effect of the alkyl substituents.

Dessy et al. later published a detailed ^1H NMR, ESR, and Mössbauer study of $Fe_2[P(CH_3)_2]_2(CO)_6$ and its corresponding dianion.[23a] They concluded from their spectroscopic solution measurements (which revealed that the exo and endo methyl hydrogens are not equivalent in both the parent and dianion complexes) that the dimethylphosphido-bridged dimer maintains its nonplanarity in the dianion. The determined[1b] planarity of the Fe_2P_2 core in $Fe_2(PPh_2)_2(CO)_6^{2-}$ suggests that the Fe_2P_2 core in the dimethylphosphido-bridged dimer is likewise planar and not bent as proposed by Dessy and coworkers. Their spectroscopic observation of two different methyl groups (which become magnetically equivalent at sufficiently high temperature) may instead reflect their unsymmetrical disposition relative to the Fe_2P_2 plane, as was found[1b] for the phenyl groups in the $Fe_2(PPh_2)_2(CO)_6^{2-}$ dianion.

In contrast to our observations of the diphenylphosphido-bridged dimers, Dessy et al. report that admixture of the dimethylphosphido-bridged dianion with the neutral parent complex (neither of which exhibit ESR signals) affords a solution of radical anion, displaying an ESR signal 7.5 G wide, centered at $g = 1.999$, with some unresolved hyperfine structure. The existence of the proposed $Fe_2[P(CH_3)_2]_2(CO)_6^-$ monoanion indicates that, unlike the related diphenylphosphido-bridged dimer reported herein, $Fe_2[P(CH_3)_2]_2(CO)_6$ reduces in two one-electron steps, and the reduction potential for the introduction of the second electron is equal to or falls more cathodic than that of the first electron. This may reflect differences in the two K_D values (cf. eq 5).

Reaction of $Fe_2(PPh_2)_2(CO)_6^{2-}$ with Dioxygen. Exposure of the dianion **4** to dioxygen results in a rapid, quantitative regeneration of the parent complex **1** (eq 7).

$$\underset{\mathbf{4}}{Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF} \xrightarrow[THF]{O_2} \underset{\mathbf{1}}{Fe_2(PPh_2)_2(CO)_6} \quad (7)$$

Because the dianion **4** is a two-electron reductant, a one-electron reduction of dioxygen by **4** demands a stoichiometry of $O_2{:}Fe_2^{2-} = 2.0$. A two-electron reduction of dioxygen demands a stoichiometry of 1.0. A four-electron reduction demands a stoichiometry of 0.5. The uptake of dioxygen by a 1-methyl-2-pyrrolidinone solution of $Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF$ (**4**) was observed in four independent measurements to occur in a ratio of $O_2{:}Fe_2^{2-} = 1.5 \pm 0.2$. Attack of the solvent (which was carefully dried by distillation from calcium hydride prior to use) by the initial product(s) of reduction of O_2 may occur under the aprotic conditions employed. The product(s) of such a reaction may expel or react further with

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Table I. ^{13}C NMR Resonances

complex	M-CO	M-C(O)R	CH_3
$NaFe(CO)_4(CH_3)^{a,b}$	223.0[c]		−16.4
$NaFe(CO)_4(C(O)CH_3)^{a,b}$	220.5	277.2	51.8
$NaFe_2(PPh_2)_2(CO)_5(C(O)CH_3)\cdot 2THF$ (6a)[d]	221.7, 219.3	273.3	50.5

[a] Reference 25. [b] THF solution. [c] In parts per million from external Me_4Si. [d] Dimethyl-d_6 sulfoxide solution.

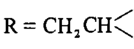
dioxygen and thus complicate the interpretation of the data. Stabilization of the product(s) of reduction of dioxygen by addition of proton sources is not feasible in this and the following experiments because the dianion **4** itself reacts rapidly with acids (vide infra).

When the oxygenation of complex **4** is carried out in tetrahydrofuran, no precipitate is discernible. Attempts to detect sodium peroxide in the reaction mixture qualitatively by three independent methods[24] failed. Authentic samples of Na_2O_2 in the presence of $Fe_2(PPh_2)_2(CO)_6$ (**1**) gave positive tests.

The ESR spectrum of the solution resulting from the addition of dioxygen to complex **4** in 2-methyltetrahydrofuran exhibits no signals above noise at 77 K in the region of 1000–5000 G at 9.15 GHz.

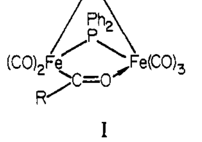
Reaction of $Fe_2(PPh_2)_2(CO)_6{}^{2-}$ with Alkylating Agents. Metal-Promoted Alkyl Migration. Addition of *alkyl* halides and sulfonates to the dianion **4** results in the formation of red, crystalline *acyl* complexes $NaFe_2(PPh_2)_2(CO)_5[C(O)R]\cdot 2THF$ (**6**) (eq 8).

$$\underset{4}{Na_2Fe_2(PPh_2)_2(CO)_6\cdot 5THF} + RX \xrightarrow[-X^-]{THF} NaFe_2(PPh_2)_2(CO)_5[C(O)R]\cdot 2THF \qquad (8)$$

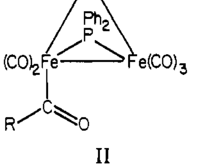
6a, R = CH_3; **6b**, R = CH_2CH_3; **6c**, R = $CH(CH_3)_2$;
6d, R = $CH_2C(CH_3)_3$; **6e**, R = $CH_2C_6H_5$; **6f**, R = $CH_2CH{=}CH_2$;
6g, R = $(CH_2)_4CH{=}CH_2$; **6h**, R =  $CH_2CH{<}\begin{smallmatrix}CH_2\\ |\\ CH_2\end{smallmatrix}$

Complexes **6** exhibit acyl absorption bands at 1545–1590 cm^{-1}, in addition to terminal carbonyl bands at 1885–1995 cm^{-1}. The ^1H NMR spectrum of the acetyl complex (**6a**, R = CH_3), for example, displays the expected singlet at 2.25 ppm. The ^{13}C NMR spectrum of complex **6a** is also consistent with the acyl formulation (Table I). Carbon resonances similar to that of $NaFe(CO)_4[C(O)CH_3]$, a known iron acetyl complex, are observed, while no resonances characteristics of an alkyl complex appear.

The molecular structure of acyl complexes **6** was considered likely to be one of the two hypothetical structures I and II.



I



II

Structure I has a bridging acyl group and no metal–metal bond, while structure II has a single metal–metal bond and no additional coordination of the acyl oxygen to the second iron atom. A few binuclear acyl complexes have been reported by Mills,[26] Fischer,[27] and Kaesz,[28] all of structural type I. A single-crystal X-ray diffraction study of the sodium and bis(triphenylphosphine)iminium (PPN) salts of $Fe_2(PPh_2)_2(CO)_5[C(O)CH_3]^-$ revealed a structure of type II, with an iron–iron single bond and no additional coordination of the acyl oxygen to the second iron atom.[1c]

Table II. Cation Dependence in the Acyl Stretching Frequency in $Fe_2(PPh_2)_2(CO)_5(C(O)CH_3)^-$

cation	acyl freq,[a] cm^{-1}
$(Ph_3P)_2N^+$	1587
$(Na\cdot CRYPT)^{+\,b}$	1588
Na^+	1570
Li^+	1545

[a] Tetrahydrofuran solutions. [b] CRYPT = 2,2,2-cryptand = $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$.

The crystal structure of $PPNFe_2(PPh_2)_2(CO)_5[C(O)CH_3]$ (**7**) consists of discrete PPN^+ and $Fe_2(PPh_2)_2(CO)_5[C(O)CH_3]^-$ ions. The geometry of $Fe_2(PPh_2)_2(CO)_5[C(O)CH_3]^-$ is similar to that of the neutral parent complex (**1**). The $Fe_2(PPh_2)_2$ core is symmetrical and nonplanar with sharply acute Fe–P–Fe bond angles. The presence of an iron–iron bond is reflected in the Fe–Fe separation of 2.718 (5) Å. The lack of coordination of the acyl oxygen to the second iron atom is reflected in the O–Fe separation of 5.11 (3) Å. The acyl ligand is positioned cis to the metal–metal bond.

The crystal structure of $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_3]\cdot 2THF$ (**6a**) is largely comparable to that of the PPN^+ salt **7**, except with regard to coordination of the acyl oxygen. Whereas the $Fe_2(PPh_2)_2(CO)_5[C(O)CH_3]^-$ anion is unperturbed by the PPN^+ cation in **7**, the acyl oxygen is strongly coordinated to the sodium ion in compound **6a**. The sodium ion further coordinates a terminal carbonyl of the $Fe(CO)_3$ fragment, a terminal carbonyl of an adjacent molecule of **6a** in the crystal, and two THF solvate molecules.

The fact that the acyl oxygen is the cation binding site in $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_3]\cdot 2THF$ is consistent with the expectation that an alkoxy carbene resonance structure may significantly contribute to the actual structure of the complex. Alkoxy carbene character is apparent in $M^+Fe_2(PPh_2)_2(CO)_5[C(O)R]^-$ complexes from their solution infrared spectra. The acyl stretching frequency in the acetyl anion decreases with a reduction in the size and polarizability of the cation (Table II). These data also indicate that the structures of acyl complexes $M^+Fe_2(PPh_2)_2(CO)_5[C(O)R]^-$ in solution do not dramatically differ from those in the solid state. That is, both in solution and in the solid state, the site of cation binding is the acyl oxygen.

Mechanism of Metal-Promoted Alkyl Migration. Typically, the alkylation of mononuclear metal carbonyls affords metal *alkyl* and not *acyl* complexes.[29] Rearrangement of alkyls to acyls usually takes place in the presence of an external ligand. The mechanism of such reactions normally involves a rapid prior equilibrium in which migration of alkyl to CO yields an unsaturated acyl complex, followed by capture of the resulting site of unsaturation by the external ligand.[30,31] In this binuclear case, it is likely that the acyl is formed in the absence of an external ligand because the internal capture of the site

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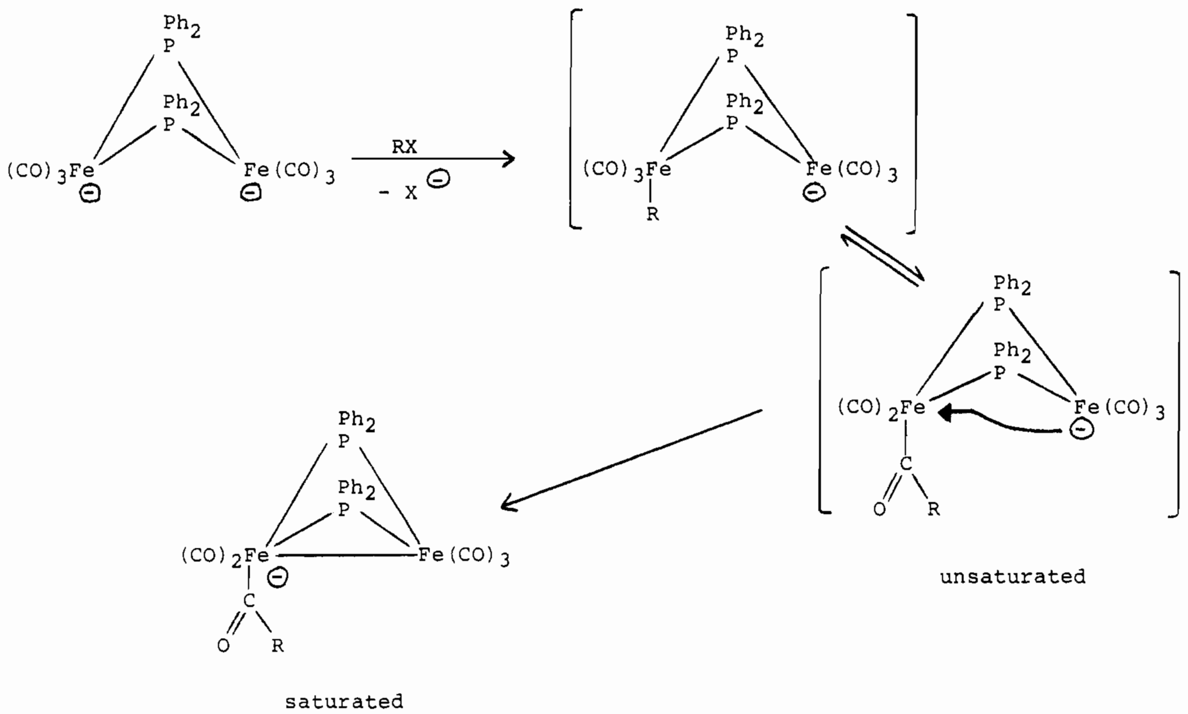

Figure 2. Mechanism of metal-promoted alkyl migration.

of unsaturation occurs via the formation of a metal–metal bond (Figure 2).

Although unknown for mononuclear iron alkyls, there is a report of an *intermolecular* metal-promoted alkyl migration for $CH_3Mn(CO)_5$ by $NaMn(CO)_5$.[32] More commonly, reactions of metal carbonyl anions with alkylmetal carbonyl compounds result in intermolecular alkyl transfer by a type of nucleophilic displacement.[32]

Reaction of $Fe_2(PPh_2)_2(CO)_6$ with Alkyllithium Reagents. The lithium salt of the acetyl complex **6a** results upon treatment of the parent cluster complex **1** with 1 equiv of methyllithium. Similarly, the benzoyl complex **8b**, inaccessible by the migration route (eq 8), results upon treatment of **1** with phenyllithium (eq 9). Related reactions of mononuclear transition-metal carbonyl complexes are well documented.[33]

$$\underset{\mathbf{1}}{Fe_2(PPh_2)_2(CO)_6} + RLi \xrightarrow{THF} \underset{\mathbf{8a},\ R = CH_3;\ \mathbf{8b},\ R = Ph}{LiFe_2(PPh_2)_2(CO)_5(C(O)R)\cdot 3THF} \quad (9)$$

Infrared and ^1H NMR spectra of lithium acyl complexes **8** indicate structures similar to those of acyl complexes **6** generated by alkylation of $Na_2Fe_2(PPh_2)_2(CO)_6\cdot 5THF$ (**4**). Confirmation of the assignment was provided by a single-crystal X-ray diffraction study of the benzoyl complex **8b**.[1c] The crystal structure of $LiFe_2(PPh_2)_2(CO)_5[C(O)Ph]\cdot 3THF$ (**8b**) is largely comparable to that of $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_3]\cdot 2THF$ (**6a**). The presence of an iron–iron single bond is reflected in the Fe–Fe separation of 2.670 (2) Å. The acyl oxygen is strongly coordinated to the lithium ion, which further coordinates the three tetrahydrofuran solvate molecules in a nearly tetrahedral arrangement.

Reaction of $Fe_2(PPh_2)_2(CO)_6^{2-}$ with Proton. In light of our discovery of a new way to facilitate migration reactions, we hoped to promote the migration of a hydride, a group which has not been observed to migrate, although the reverse reaction is well-known.[34]

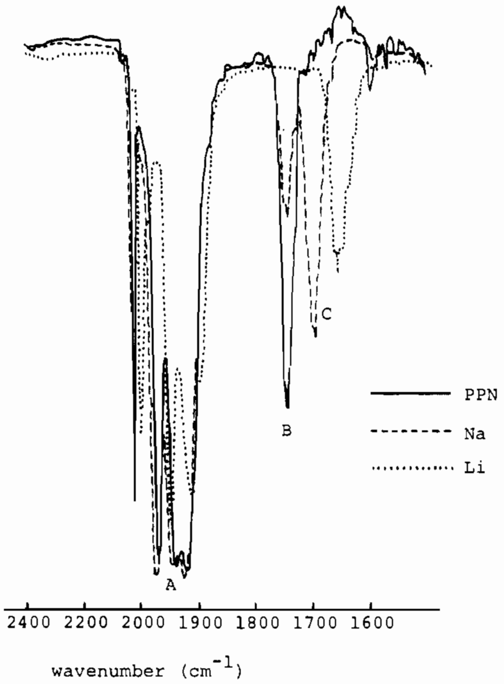

Figure 3. Infrared spectra of $MHFe_2(PPh_2)_2(CO)_6$ complexes (M = Li, Na, PPN) as tetrahydrofuran solutions in the region of 2400–1600 cm^{-1}.

The addition of 1 equiv of a protonic acid to $Na_2Fe_2(PPh_2)_2(CO)_6\cdot 5THF$ (**4**) in tetrahydrofuran affords a hydride complex, formulated as $NaHFe_2(PPh_2)_2(CO)_6\cdot x THF$ (**9**); however, no formyl complex was detected. Compound **9** was converted to the PPN^+ salt by metathesis with bis(triphenylphosphin)iminium chloride (PPN^+Cl^-). The ^1H NMR spectrum of $PPN[HFe_2(PPh_2)_2(CO)_6]$ (**10**) exhibits the ex-

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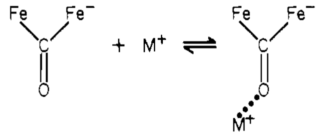
pected triplet, centered at −20.3 ppm (J_{PH} = 42.5 Hz).

The infrared spectra of the lithium, sodium, and PPN salts of $HFe_2(PPh_2)_2(CO)_6^-$ are illustrated in Figure 3. The three complexes exhibit absorption bands of nearly identical position and relative intensity in the region of 2100–1850 cm^{-1}, a region characteristic of terminal metal hydride and terminal metal carbonyl stretching vibrations. In addition, absorptions are observed in the region of 1750–1600 cm^{-1}, a region characteristic of bridging metal carbonyl stretching vibrations.

The positions and relative intensities of absorption bands B and C in the bridging carbonyl region as a function of the cation M^+ are consistent with the proposed equilibrium shown in eq 10.

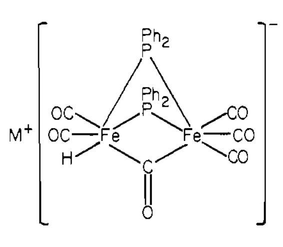


(10)

Absorption band B is assigned to the bridging carbonyl vibration of the unperturbed anion. Absorption band C is assigned to the bridging carbonyl vibration of the anion in which the carbonyl oxygen is ion paired to the cation. The proposal of the bridging carbonyl oxygen as the cation binding site in $HFe_2(PPh_2)_2(CO)_6^-$ is consistent with the fact that bridging carbonyls are better π acids than terminal carbonyls.[35] The assignment of absorption band B to the free anion and band C, which appears at the lower frequency, to the ion pair is consistent with the expectation that ion pairing would result in a reduction of the order of the C–O bond.

As would be anticipated, the position of absorption band B for the free anion is independent of the nature of the cation. As expected for the smaller, less polarizable Li^+, the absorption band C for $LiHFe_2(PPh_2)_2(CO)_6$ (**11**) appears at a lower frequency than that for $NaHFe_2(PPh_2)_2(CO)_6$ (**9**). Furthermore, note the relative intensities of absorption bands B and C as a function of the cation. In the case of the large and highly polarizable PPN^+ cation, ion pairing is expected to be absent, and only a single band in the bridging carbonyl region is seen at 1735 cm^{-1}. In the case of the smallest and least polarizable Li^+ cation, ion pairing is expected to be strongest, and a strong band of type C at 1647 cm^{-1} and no band at 1735 cm^{-1} is seen. An equilibrium mixture of dissociated and ion-paired forms is present in the case of the intermediate Na^+ cation, as evidenced by the two bands at 1735 and 1686 cm^{-1}.

A structure consistent with these data and the 18-electron rule is shown below. The proposed structure is novel in that it contains a bridging carbonyl ligand and no metal–metal bond, a combination which has seldom been established.[36]



Compound **9** behaves chemically as do other metal hydrides.[37] Reactions of **9** with proton, benzoyl chloride, and carbon tetrachloride afford dihydrogen, benzaldehyde, and chloroform, respectively, in good yields. In all three cases, the iron-containing product is the neutral parent complex **1**.

The reaction of the dianion **4** with 2 equiv of CF_3CO_2D (>97 atom % D) in protio tetrahydrofuran affords D_2 in high yield [$D_2/(D_2 + HD + H_2)$ > 88%]. The reaction of the dianion with the first equivalent of CF_3CO_2D gives the iron deuteride, which reacts with the second equivalent to give D_2.

The protonation of $Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF$ (**4**) is complicated by side reactions, one of which appears to involve attack of the diphenylphosphido bridge. The side reactions are more competitive in acetone than they are in tetrahydrofuran. Solvent polarity and ion pairing may play an important role. Attack at phosphorus is implicated by the formation of significant quantities of $Fe_2(PPh_2)_2(CO)_5(PHPh_2)$ (**2d**). The $PHPh_2$ ligand presumably arises by protonation at phosphorus.

Reaction of $Fe_2(PPh_2)_2(CO)_6^{2-}$ with Alkylating Agents. Additional Mechanistic Aspects. In the reaction of $Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF$ (**4**) with alkylating agents (eq 8), iodides react much more rapidly than do bromides, which react more rapidly than do chlorides. The reactivity of tosylates falls between that of bromides and chlorides. Relative substrate reactivities as a function of the alkyl group are allyl, benzyl > methyl > primary > secondary.

The possible intermediacy of free alkyl radicals produced by electron transfer in the reaction of primary halides with the dianion **4** was examined. The free radical which results upon abstraction of a bromine atom from 6-bromo-1-hexene is known to cyclize to methylcyclopentane radical at a rate of approximately 10^5 s^{-1}.[38] The ^1H NMR spectrum of the material resulting from the addition of 1 equiv of 6-bromo-1-hexene to $Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF$ (**4**) is consistent with acyl complex **6g**, in which the hexenyl group is uncyclized. No resonances corresponding to the methylcyclopentane acyl complex were observed. Furthermore, a GLC analysis of the crude reaction mixture indicated that no significant quantity of methylcyclopentane (<1%) was present.

A related experiment was conducted with a primary iodide. The free radical which results from the abstraction of an iodine atom from cyclopropylcarbinyl iodide rearranges to the 1-butenyl radical at a rate of 1.3 × 10^8 s^{-1} at 25 °C.[39] The ^1H NMR spectrum of the reaction mixture following the addition of 1 equiv of cyclopropylcarbinyl iodide to $Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF$ (**4**) in acetone-d_6 indicates an essentially quantitative yield of acyl complex **6h**, in which the $CH_2C_3H_5$ group has not rearranged. Only traces of signals were observed in the region of the spectrum characteristic of olefinic protons.

From the foregoing results, one may conclude that if a radical path is at all competitive in the reaction of complex **4** with primary substrates, the resulting radicals must be captured by iron at a rate much faster than 10^5 s^{-1} (X = Br) or 10^8 s^{-1} (X = I), that is, at a rate approaching that of diffusion-control.

In the reaction of secondary halides with $Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF$ (**4**), electron transfer is competitive with acyl formation. For example, in the reaction of the dianion **4** with an equimolar quantity of isopropyl iodide, approximately 50% of **4** is converted to isobutyryl complex **6c**, while approximately 30% of **4** is oxidized to the parent complex **1**. In the reaction of 2-iodooctane, octanes and hexadecanes were detected by GLC, consistent with the formation of intermediate octyl radicals, the products of reduction of the halide.

Reaction of $Fe_2(PPh_2)_2(CO)_5[C(O)R]^-$ with Proton. Protonation of acyl complexes **6** affords aldehyde in essentially

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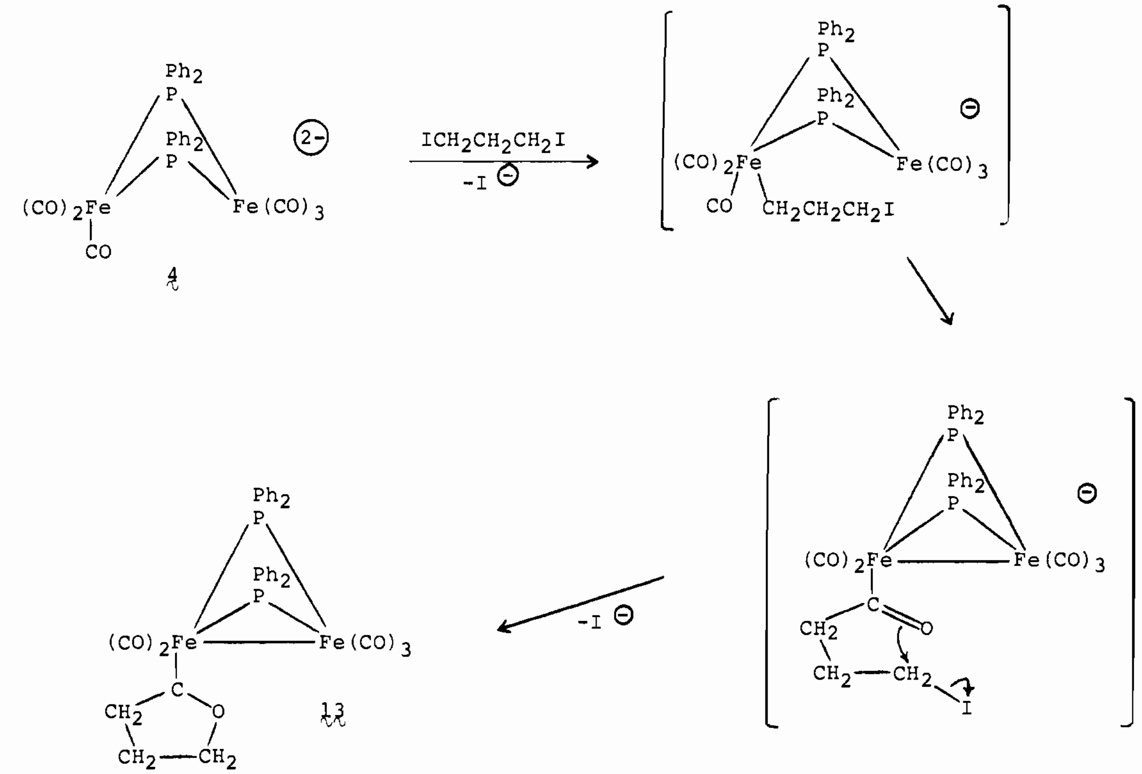
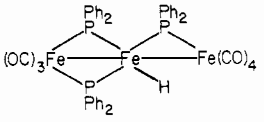


Figure 4. Mechanism of formation of carbene complex $Fe_2(PPh_2)_2(CO)_5(\overline{CCH_2CH_2CH_2O})$ (**13**).

quantitative yield, together with several iron carbonyl complexes, which presumably derive from a coordinately unsaturated intermediate complex (eq 11). The parent complex

$$\underset{\mathbf{6}}{NaFe_2(PPh_2)_2(CO)_5[C(O)R]\cdot 2THF} + CF_3CO_2H \xrightarrow[-CF_3CO_2Na]{THF} RCHO + \text{“}Fe_2(PPh_2)_2(CO)_5\text{”} \rightarrow \text{products} \quad (11)$$

$Fe_2(PPh_2)_2(CO)_6$ (**1**) and $Fe_2(PPh_2)_2(CO)_5(PHPh_2)$ (**2d**) are isolated from the reaction mixture in yields of approximately 50% and 10%, respectively. A third product of reaction 11 is one to which we assign the novel structure shown below (**12**).



12

Complex **12** exhibits absorption bands at 2038, 1996, 1965, and 1947 cm^{-1}, frequencies characteristic of terminal metal–hydrogen and terminal metal–carbonyl vibrations. The ^1H NMR spectrum of complex **12** displays a doublet of triplets (d t) centered at −21.06 ppm (J_d = 37.5 Hz, J_t = 30.0 Hz), which is consistent with the presence of a metal-bound hydrogen atom magnetically coupled to three phosphorus atoms, two of which are equivalent and different from the third. Furthermore, a complete elemental analysis (except oxygen) and a molecular weight determination are in good agreement with the proposed formulation.

Reactions of lithium acyl complexes **8** with protonic acids give similar results.

Reaction of $Fe_2(PPh_2)_2(CO)_5[C(O)R]^-$ with Alkylating Agents. Binuclear acyl complexes **6**, which are the result of monoalkylation of the dianion **4**, do not further react with electrophiles other than proton at an appreciable rate. However, dialkylation of the dianion is possible if the second equivalent of the alkylating agent is delivered internally. The reaction of $Na_2Fe_2(PPh_2)_2(CO)_6\cdot 5THF$ (**4**) with 1,3-diiodopropane in equimolar ratios affords binuclear carbene complex **13** in high yield. A plausible mechanism for the reaction is outlined in Figure 4. Attack of the dianion at one of the two equivalent electrophilic centers in $ICH_2CH_2CH_2I$, followed by alkyl migration, leads to an intermediate acyl complex, as observed in the *mono*alkylation reactions of eq 8. Intramolecular O-alkylation of the acyl results in the observed alkoxy carbene complex **13**. By analogy, we expect that the aldehyde generated upon protonation of acyl complexes **6** (eq 11) results from decomposition of an intermediate hydroxycarbene complex.

The coupling of allylic and benzylic substrates, yielding biallyl and bibenzyl, respectively, is effected by $Na_2Fe_2(PPh_2)_2(CO)_6\cdot 5THF$ (**4**) (eq 12). Rapid reaction of the first

$$Na_2Fe_2(PPh_2)_2(CO)_6\cdot 5THF + 2RX \rightarrow \underset{\mathbf{1}}{Fe_2(PPh_2)_2(CO)_6} + R{-}R + 2\ NaX \quad (12)$$

$$R = CH_2CH{=}CH_2;\ X = Br,\ OSO_2C_6H_4CH_3$$
$$R = CH_2Ph;\ X = Br$$

equivalent of substrate affords an isolable, intermediate acyl complex **6** and is followed by slow reaction of the second equivalent, resulting in biallyl (100%) and bibenzyl (50%) and the parent complex **1**. The second step may proceed via a free radical mechanism.

Reaction of $Fe_2(PPh_2)_2(CO)_5[C(O)R]^-$ with Phosphines and Carbon Monoxide. The reaction of $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_3]\cdot 2THF$ (**6a**) and $P(CH_3)_2Ph$ at 100 °C affords phosphine complexes **2b** (8%) and **3b** (27%). The related reaction of acetyl complex **6a** with carbon monoxide (40 psi) at room temperature slowly yields the parent complex **1** as the primary product. The fate of the acetyl ligand was not determined. These reactions effectively correspond to substitution of an acyl ligand with phosphine or CO. We are aware of no other examples of such a reaction.

Reduction of $Fe_2(PPh_2)_2(CO)_5[C(O)R]^-$. The cyclic voltammogram of $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_3]\cdot 2THF$ (**6a**) exhibits a single, reversible reduction wave at −1.62 V vs. the silver wire reference electrode. Anodic and cathodic waves are of equal height, with a peak-to-peak separation of 75 mV (scan rate 20 mV/s). Scans in the presence of $Fe_2(PPh_2)_2$-

$(CO)_6$ (**1**) indicate that the reduction potential of acetyl complex **6a** falls 680 mV more cathodic than that of the parent complex **1**. $Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF$ (**4**) was isolated in 65% yield following reduction of acetyl complex **6a** with an excess of sodium dispersion in tetrahydrofuran. The fate of the methyl group was not determined.

Experimental Section

General Data. Unless otherwise noted, all reactions and manipulations were performed under a nitrogen atmosphere in Schlenk-type glassware or in an inert-atmosphere glovebox.[40] Nitrogen (Liquid Carbonic, 99.99%) was further purified by passage through a BASF copper catalyst and activated Linde 3A molecular sieves. The glovebox (Vacuum Atmospheres Co.) was equipped with an MO-40 Dri-Train capable of maintaining an atmosphere of <1 ppm of O_2 and H_2O. The atmosphere of the box was monitored with a solution of diethylzinc in heptane (which fumes above 5 ppm of O_2) and with a punctured 25-W light bulb.

Infrared spectra were recorded on a Perkin-Elmer Model 457 or Model 621 grating spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian T-60 or XL-100 instrument at the normal probe temperature of 35 °C. Chemical shifts are reported relative to tetramethylsilane (δ 0.0). Most elemental analyses were carried out by the Stanford Microanalytical Laboratory, Department of Chemistry, Stanford University, Stanford, CA. Elemental analyses of highly air-sensitive samples were carried out by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were obtained in a Mel-Temp apparatus and are uncorrected, unless otherwise noted.

Tetrahydrofuran was distilled under nitrogen either from calcium hydride or sodium/benzophenone. Acetonitrile was distilled under nitrogen from calcium hydride. Benzene was distilled under nitrogen from Red-al, a 70% solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene (Aldrich). 1-Methyl-2-pyrrolidinone (NMP) was distilled from calcium hydride following 3 days of heating at reflux (85.0–87.5 °C at 13–14 mmHg). All other solvents, unless otherwise noted, were of reagent grade, purchased commercially, and used as supplied.

Column chromatography was carried out using 60–200 mesh, type 62 grade silica gel, purchased from W. R. Grace, and activity grade I neutral alumina, purchased from Woelm. The silica gel was dried for at least 12 h at 100 °C prior to use. Thin-layer chromatography was performed on silica gel or alumina plates, purchased from Analtech, Inc.

Commercial benzoyl chloride, dimethylphenylphosphine, diphenylchlorophosphine, diphenylmethylphosphine, and triethyl phosphite were distilled under nitrogen prior to use. Acetic acid was distilled from CrO_3 and acetic anhydride. Trifluoroacetic acid was distilled from P_2O_5. 6-Bromo-1-hexene was distilled prior to use. All other commercially available alkyl halides were passed through a short column of neutral activity I alumina and then stored in the dark over copper turnings. Methyl tosylate was distilled bulb-to-bulb in vacuo.

The following reagents were prepared as previously described: allyl tosylate,[44] bis(triphenylphosphin)iminium chloride,[42] cyclopropylcarbinyl iodide,[43] 1,3-diiodopropane,[43] ethyl tosylate,[44] isopropyl tosylate,[44] $Na_2Fe(CO)_4{\cdot}1.5C_4H_8O_2$,[10] $Na_2Fe_2(CO)_8$,[11] neopentyl iodide,[45] and neopentyl tosylate.[44]

All other reagents were of reagent grade, purchased commercially, and used as supplied.

Bis[μ-(diphenylphosphido)]-bis[tricarbonyliron(I)], $Fe_2(PPh_2)_2(CO)_6$ (1). To a suspension of $Na_2Fe(CO)_4{\cdot}1.5C_4H_8O_2$ (34.6 g, 0.100 mol) in 1.5 L of THF was added dropwise $Fe(CO)_5$ (13.5 mL, 0.100 mol). The CO evolved was released through a mercury bubbler. After the resulting red suspension stirred for 1 h, Ph_2PCl (37.4 mL, 0.200 mol) was added dropwise. The resulting orange-brown suspension was stirred for 1 h.

The following manipulations were carried out in air. The solvent was removed under reduced pressure. The residue was extracted with benzene and filtered until washings were nearly colorless. Silica gel of 60–200 mesh (100 g) was added to the combined filtrates and the solvent removed under reduced pressure. The residue was added to the top of a column (10 × 90 cm) packed with 1.4 kg of 60–200 mesh silica gel. Elution with 3:1 hexane:benzene resulted in several bands. The major, yellow band ($R_f = 0.4$) was collected and filtered through a M frit. Reduction of the volume of the filtrate to 150 mL of cooling to 5 °C resulted in large orange crystals (42.7 g, 59%). An integrated, 100-MHz ^1H NMR spectrum of the crystallized material in acetone-d_6 with a known volume of CH_2Cl_2, added as an internal standard, revealed the presence of 1.0 molecule of C_6H_6 solvate per molecule of $Fe_2(PPh_2)_2(CO)_6$. The C_6H_6 solvate was efficiently removed by heating in vacuo at 65 °C for 4 h. The resulting yellow powder was stored in the dark: mp = 186–188 °C dec (corrected); IR (C_6H_6 solution) ν_{CO} 2055, 2015, 1992, 1960 cm^{-1}. The mass spectrum of **1** was identical with that previously reported.[46]

Ligand Substitution Reactions. (A) $Fe_2(PPh_2)_2(CO)_5[P(CH_3)_2Ph]$ (2b) and $Fe_2(PPh_2)_2(CO)_4[P(CH_3)_2Ph]_2$ (3b). A solution of **1** (0.991 g, 1.52 mmol) and $P(CH_3)_2Ph$ (5.2 mL, 36 mmol) in 25 mL of cyclohexane was placed in a quartz reaction vessel. Irradiation for 24 h with a 140-W Hanovia lamp, equipped with a quartz arc tube, resulted in a deep red colored solution and precipitate.

The following manipulations were carried out in air. The precipitate was collected by filtration and recrystallized from hot benzene/hexane, affording dark red crystals of **3b**, which were washed with hexane and dried in vacuo (0.88 g, 67%): IR (C_6H_6 solution) 1950, 1915, 1885, 1870 (sh); ^1H NMR (C_6D_6) δ 1.51 (d, J = 8 Hz, 12 H), 6.7, 7.0, 7.4, 7.7 (m, 30 H). Anal. Calcd for $C_{44}H_{42}Fe_2O_4P_4$: C, 60.71; H, 4.86; Fe, 12.8; P, 14.2. Found: C, 61.46; H, 4.95; Fe, 11.9; P, 13.2.

The filtrate obtained upon filtration of the crude reaction mixture was concentrated and then chromatographed on silica gel, with the use of an eluant of 1:1 benzene:hexane. The major red band was collected and reduced in volume to approximately 5 mL. Addition of 15 mL of hexane and cooling to 5 °C resulted in red crystals of **2b** (0.25 g, 22%): IR (C_6H_6 solution) ν_{CO} 2020, 1965, 1945 (sh), 1905 cm^{-1}; ^1H NMR (C_6D_6) δ 1.32 (d, J = 8 Hz, 6 H), 6.7, 7.0, 7.5 (m, 25 H). Anal. Calcd for $C_{37}H_{31}Fe_2O_5P_3$: C, 58.45; H, 4.11; Fe, 14.7; P, 12.22. Found: C, 58.87; H, 4.22; Fe, 13.8; P, 12.13.

This procedure was employed in the following three cases.

(B) $Fe_2(PPh_2)_2(CO)_5[P(OCH_2CH_3)_3]$ (2a): IR (THF solution) ν_{CO} 2030, 1970, 1945, 1920 cm^{-1}; ^1H NMR (C_6D_6) δ 1.00 (t, J = 7 Hz, 9 H), 3.9 (m, 6 H), 6.8, 7.7 (m, 20 H). Anal. Calcd for $C_{35}H_{35}Fe_2O_8P_3$: C, 53.33; H, 4.48; Fe, 14.2. Found: C, 53.45; H, 4.49; Fe, 13.8.

(C) $Fe_2(PPh_2)_2(CO)_4[P(OCH_2CH_3)_3]_2$ (3a): IR (THF solution) ν_{CO} 1990, 1940, 1905 cm^{-1}; ^1H NMR (C_6D_6) δ 1.07 (t, J = 7 Hz, 18 H), 4.1 (m, 12 H), 6.9, 7.8 (m, 20 H). Anal. Calcd for $C_{40}H_{50}Fe_2O_{10}P_4$: C, 51.86; H, 5.44; Fe, 12.1. Found: C, 51.98; H, 5.31; Fe, 11.0.

(D) $Fe_2(PPh_2)_2(CO)_4[P(CH_3)Ph_2]_2$ (3c): IR (THF solution) ν_{CO} 1955, 1925, 1890 (split) cm^{-1}; ^1H NMR (C_6D_6) δ 1.28 (d, J = 8 Hz, 6 H), 6.5–8.0 (m, 40 H).

No attempt was made to isolate the monosubstituted derivative [**2**, L = $P(CH_3)Ph_2$].

(E) $Fe_2(PPh_2)_2(CO)_5(PHPh_2)$ (2d). Complex **2d** was isolated as a side product in the preparation of **1**. Spectral data: IR (THF solution) ν_{CO} 2025, 1975, 1948, 1925 cm^{-1}; ^1H NMR (C_6D_6) δ 5.93 (d of t, J_{PH} = 354 Hz, J_{P_2H} = 9 Hz, 1 H), 6.6, 6.9, 7.6 (m, 30 H). Anal. Calcd for $C_{41}H_{31}Fe_2O_5P_3$: C, 60.92; H, 3.87; Fe, 13.8; P, 11.5. Found: C, 61.56; H, 4.02; Fe, 13.2; P, 10.8, 10.6. Molecular weight for **2d**: calcd, 808; found, 775, 837 (by osmometry in $CHCl_3$).

$Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF$ (4). To a dry mixture of **1** (4.16 g, 6.40 mmol) and 50% sodium dispersion (0.552 g, 12.0 mmol) was added 40 mL of THF. The resulting red solution was stirred overnight. Slow addition of 75 mL of heptane with stirring afforded red crystals. After the mother liquor was decanted, the crystals were washed with 4 × 40 mL of heptane, dried in vacuo, and stored in an inert-atmosphere box (5.4 g, 85%): IR (THF solution) ν_{CO} 1930 (sh), 1905, 1845, 1825 (sh), 1800 cm^{-1}; ^1H NMR [$(CD_3)_2CO$] δ 1.8 (m, 20 H), 3.7 (m, 20 H), 7.0, 8.1 (m, 20 H). Anal. Calcd for $C_{50}H_{60}Fe_2Na_2O_{11}P_2$: C, 56.83; H, 5.72; Fe, 10.57; Na, 4.35; P, 5.86. Found: C, 56.66; H, 5.50; Fe, 10.77; Na, 4.32; P, 5.94.

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$(NaCRYPT)_2Fe_2(PPh_2)_2(CO)_6$ (5). To a dry mixture of **4** (100 mg, 0.0946 mmol) and 2,2,2-cryptand (71 mg, 0.19 mmol) was added 2 mL of NMP. Diffusion of hexane vapor into the solution resulted in several crops of red crystals, which were washed with THF and dried upon standing: IR (KBr pellet, mixed under a nitrogen atmosphere) ν_{CO} 1920 (sh), 1895, 1835, 1800 cm^{-1}. Anal. Calcd for $C_{66}H_{92}Fe_2N_4Na_2O_{18}P_2$: C, 54.70; H, 6.40; Fe, 7.71; N, 3.87; Na, 3.17. Found: C, 54.44; H, 6.59; Fe, 7.58; N, 3.90; Na, 3.03.

Reaction of $Na_2Fe_2(PPh_2)_2(CO)_6 \cdot 5THF$ (4) with Dioxygen. A 0.2 M solution of **4** in THF was bubbled for a few seconds with dioxygen. An infrared spectrum of the resulting solution was superimposable with that of **1** in the region of 2400–1600 cm^{-1}. Thin-layer chromatography revealed a single component with an R_f value equal to that of **1**.

The uptake of dioxygen by NMP solutions of **4** was measured with use of the apparatus described previously by Calderazzo and Cotton.[47] Four independent measurements were conducted. In one case, 4.00 mL of a solution of 193 mg (0.183 mmol) of **4** in 8.00 mL of NMP consumed 3.17 mL (0.142 mmol) of dioxygen. Hence, the uptake occurred in a molar ratio of O_2:**4** = 1.55. The values of O_2:**4** measured in the other three experiments were 1.28, 1.68, and 1.53.

A solution of **4** (0.500 g, 0.473 mmol) in 4 mL of THF was bubbled with dioxygen for 10 min. After removal of the solvent under reduced pressure, 5.00 mL of H_2O (pH 6.01), distilled from $KMnO_4$ in air, was added to the residue. The resulting yellow suspension was titrated with 0.100 N HCl, with use of a Fisher Model 140A Accumet pH meter. An equivalence point occurred at pH 7.7–8.1 upon addition of 0.78–0.80 equiv of acid. A second equivalence point occurred at pH 3.6–4.2 upon addition of another 0.74–0.92 equiv of acid. Following the titration, the suspension was filtered. The resulting solid was washed with copious amounts of H_2O and dried in vacuo at 65 °C, affording $Fe_2(PPh_2)_2(CO)_6$ as a yellow powder of mp 182–184 dec (0.30 g, 98%). The solution infrared spectra and analytical TLC properties of the product and an authentic sample of **1** were identical. (The following control experiment was conducted. The solvent of a solution of **1** (0.50 g, 0.77 mmol) in 3–4 mL of THF was removed under reduced pressure. Following the addition of 5.00 mL H_2O (pH 5.80), the resulting suspension was titrated with 0.100 N HCl. No equivalence point was observed.)

Preparation of Acyl Complexes 6. (A) $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_3] \cdot 2THF$ (6a). To a solution of **4** (1.00 g, 0.946 mmol) in 10 mL of THF was added via syringe CH_3I (63 µL, 1.0 mmol). After 10 min of stirring, the reaction mixture was filtered. Slow addition of hexane afforded red crystals, which were washed with 3 × 1 mL of hexane and then dried in vacuo (0.72 g, 91%): IR (THF solution) ν_{CO} 1995, 1940, 1905 (sh), 1885 (sh) cm^{-1}, ν_{acyl} 1570 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 2.25 (s, 3 H) (the expected phenyl and THF resonances were also observed); ^{13}C NMR spectral data appear in Table I. Anal. Calcd for $C_{39}H_{39}Fe_2Na_2O_8P_2$: C, 56.27; H, 4.72; Fe, 13.4; Na, 2.76. Found: C, 56.09; H, 4.95; Fe, 14.2; Na, 2.7.

This procedure was employed in the following seven cases. Reaction with CH_3OTs required about 1 week.

(B) $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_2CH_3] \cdot 2THF$ (6b): IR (THF solution) ν_{CO} 1995, 1940, 1905 (sh), 1890 (sh) cm^{-1}, ν_{acyl} 1570 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 0.50 (t, J = 7 Hz, 3 H), 2.70 (q, J = 7 Hz, 2 H). The expected phenyl and THF resonances were also observed. Complete reaction of ethyl iodide, bromide, and tosylate required a few seconds, 1–2 days, and 1–2 weeks, respectively.

(C) $NaFe_2(PPh_2)_2(CO)_5[C(O)CH(CH_3)_2] \cdot 2THF$ (6c): IR (THF solution) ν_{CO} 2000, 1945, 1915 (sh), 1880 (sh) cm^{-1}, ν_{acyl} 1565 cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 0.77 (d, J = 7 Hz, 6 H), 2.8 (septet, J = 7 Hz, 1 H). The expected phenyl and THF resonances were also observed. Complete reaction of isopropyl iodide and tosylate required a few seconds and 1–2 weeks, respectively.

(D) $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_2C(CH_3)_3] \cdot 2THF$ (6d): ^{1}H NMR [$(CD_3)_2CO$] δ 0.72 (s, 9 H), 2.75 (s, 2 H). The expected phenyl and THF resonances were also observed. Complete reaction of neopentyl iodide required a few seconds.

(E) $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_2Ph] \cdot 2THF$ (6e): IR (THF solution) ν_{CO} 1995, 1945, 1920 (sh), 1905 (sh), 1885 (sh) cm^{-1}, ν_{acyl} 1565 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 3.97 (s, 2 H). The expected phenyl and THF resonances were also observed. Anal. Calcd for $C_{45}H_{43}Fe_2NaO_8P_2$: C, 59.49; H, 4.77; Fe, 12.30; Na, 2.53. Found: C, 59.22; H, 4.59; Fe, 12.04; Na, 2.66. Benzyl bromide was employed (vide infra).

(F) $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_2CH{=}CH_2] \cdot 2THF$ (6f): IR (THF solution) ν_{CO} 2000, 1945, 1905 (sh), 1885 (sh) cm^{-1}, ν_{acyl} 1570 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 3.48 (d, J = 7 Hz, 2 H), 4.7 (m, 2 H), 5.6 (m, 1 H). The expected phenyl and THF resonances were also observed. Anal. Calcd for $C_{41}H_{41}Fe_2NaO_8P_2$: C, 57.37; H, 4.81; Fe, 13.01; Na, 2.68. Found: C, 57.24; H, 4.81; Fe, 13.09; Na, 2.80. Allyl bromide and tosylate were employed (vide infra).

(G) $NaFe_2(PPh_2)_2(CO)_5[C(O)(CH_2)_4CH{=}CH_2] \cdot 2THF$ (6g): IR (THF solution) ν_{CO} 1995, 1940, 1920 (sh), 1900 (sh), 1880 (sh) cm^{-1}, ν_{acyl} 1570 cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 1.2 (m, 6 H), 2.80 (t, J = 7 Hz, 2 H), 2.9 (m, 2 H), 5.7 (m, 1 H). The expected phenyl and THF resonances were also observed. Complete reaction of 6-bromo-1-hexene required 2–3 days.

(H) $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_2C_3H_5] \cdot 2THF$ (6h): IR (THF solution) ν_{CO} 1995, 1945, 1900 (sh), 1880 (sh) cm^{-1}, ν_{acyl} 1565 cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ −0.3 to +0.9 (m, 5 H), 2.67 (d, J = 7 Hz, 2 H). The expected phenyl and THF resonances were also observed. Complete reaction of cyclopropylcarbonyl iodide required a few seconds.

$PPNFe_2(PPh_2)_2(CO)_5[C(O)CH_3]$ (7). To a solution of **4** (165 mg, 0.156 mmol) in 5 mL of acetone was added via syringe CH_3I (10 µL, 0.16 mmol). After the resulting red solution stirred for 15 min, PPNCl (96 mg, 0.178 mmol) was added. The mixture was stirred for 15 min and then filtered. Addition of Et_2O and hexane to the filtrate and cooling to −22 °C afforded red crystals: IR (THF solution) ν_{CO} 1990, 1940, 1920 (sh), 1900 (sh), 1870 (sh) cm^{-1}, ν_{acyl} 1587 cm^{-1}. Anal. Calcd for $C_{67}H_{53}Fe_2NO_6P_4$: C, 66.85; H, 4.44; Fe, 9.28; N, 1.16. Found: C, 66.44; H, 4.61; Fe, 9.30; N, 1.08.

$LiFe_2(PPh_2)_2(CO)_5[C(O)CH_3] \cdot 3THF$ (8a). To a solution of **1** (0.893 g, 1.37 mmol) in 20 mL of THF was added via syringe 1.8 M CH_3Li in Et_2O (0.76 mL, 1.4 mmol). After the resulting red solution stirred for 30 min, the solvent was removed under reduced pressure. The residue was dissolved in a minimum volume of THF and filtered. Slow addition of hexane afforded red crystals, which were washed with hexane and then dried upon standing (1.01 g, 83%): IR (THF solution) ν_{CO} 2000, 1950, 1920 (sh), 1890 cm^{-1}, ν_{acyl} 1545 cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 1.8 (m, 12 H), 2.27 (s, 3 H), 3.7 (m, 12 H), 6.9, 7.5 (m, 20 H). Anal. Calcd for $C_{43}H_{47}Fe_2LiO_9P_2$: C, 58.13; H, 5.33; Fe, 12.57; Li, 0.78. Found: C, 58.01; H, 5.44; Fe, 12.27; Li, 0.71.

$LiFe_2(PPh_2)_2(CO)_5[C(O)Ph] \cdot 3THF$ (8b). The procedure described above was employed. Spectral data: IR (THF solution) ν_{CO} 2000, 1945, 1920 (sh), 1886 cm^{-1}, ν_{acyl} 1525 cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 1.8 (m, 12 H), 3.7 (m, 12 H), 6.7–7.7 (m, 25 H). Anal. Calcd for $C_{48}H_{49}Fe_2LiO_9P_2$: C, 60.65; H, 5.20; Fe, 11.75; Li, 0.73. Found: C, 60.46; H, 5.22; Fe, 11.9, 11.6; Li, 0.8.

$NaHFe_2(PPh_2)_2(CO)_6 \cdot xTHF$ (9). To a solution of **4** (0.500 g, 0.473 mmol) in 3 mL of THF was added via syringe CH_3CO_2H (29 µL, 0.51 mmol). After 2 h of stirring, the resulting red suspension was filtered. Diffusion of hexane vapor into the filtrate afforded a deep red oil, which was washed with hexane and dried upon standing. The infrared spectrum of **9** appears in Figure 3.

$PPNHFe_2(PPh_2)_2(CO)_6$ (10). To a solution of **4** (0.500 g, 0.473 mmol) in 5 mL of acetone was added via syringe CH_3CO_2H (27 µL, 0.473 mmol). After 10 min of stirring, a solution of PPNCl (0.270 g, 0.470 mmol) in 5 mL of acetone was added. After being stirred overnight, the resulting red suspension was filtered. The solvent was removed from the filtrate under reduced pressure and the residue dissolved in a minimum volume of THF and chromatographed on 60–200 mesh silica gel. Elution with benzene afforded **1** (0.126 g, 41%) and then **2d** (74 mg, 19%). Elution with THF afforded **10** as a red band. Removal of the solvent under reduced pressure resulted in a red oil: ^{1}H NMR (THF-d_8) δ −20.3 (t, J = 42.5 Hz), 7.0–7.7 (m); ^{31}P NMR-^{1}H decoupled (THF-d_8) δ 74.7 (s), 179.2 (s). The infrared spectrum of **10** appears in Figure 3.

$LiHFe_2(PPh_2)_2(CO)_6 \cdot xTHF$ (11). To a solution of **4** (0.500 g, 0.473 mmol) in 10 mL of THF was added LiCl (50 mg, 1.2 mmol). After 8 h of stirring, the resulting suspension was filtered. To the filtrate was added via syringe CF_3CO_2H (37 µL, 0.48 mmol). After 30 min of stirring, the resulting suspension was filtered. Following removal of the solvent from the filtrate under reduced pressure, the residue was triturated with hexane until washings were colorless. The residue was then dissolved in a minimum volume of THF. Vapor diffusion of hexane into the solution afforded a red oil, which was washed with

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hexane and dried upon standing. The infrared spectrum of **11** appears in Figure 3.

Reaction of $NaHFe_2(PPh_2)_2(CO)_6$ (9) with Proton. To a flask equipped with a rubber septum and containing a solution of **4** (50 mg, 0.047 mmol) in 10 mL of THF was added *2* equiv of CF_3CO_2H (8.0 μL, 0.10 mmol). An immediate reaction occurred, with evolution of a colorless gas and with a change in the reaction mixture from a red solution to a turbid, yellow suspension. Dihydrogen was detected in the gaseous phase by GLC, using a column packed with 15% $MnCl_2$ on Alcoa F_1 68–100 mesh alumina at −78 °C. The presence of dihydrogen was confirmed by coinjection of an authentic sample. An infrared spectrum of the crude THF solution was identical with that of **1** in the region of 2400–1600 cm^{-1}. Analytical TLC (conducted on 250 μ silica gel plates with an eluant of 1:1 benzene:hexane) of 1 aliquot of the crude THF solution revealed one major spot with R_f equal to that of an authentic sample of **1**.

Reaction of $NaHFe_2(PPh_2)_2(CO)_6$ (9) with Benzoyl Chloride. To a solution of **4** (300 mg, 0.284 mmol) in 0.850 mL of THF was added 1 equiv of CH_3CO_2H (16.2 μL, 0.284 mmol). After 2 h of stirring, the mixture was filtered, and to the filtrate was added benzoyl chloride (34 μL, 0.293 mmol). After 2 days of stirring, a 100-μL aliquot of the reaction mixture was removed, and to it was added 5.0 μL of n-$C_{12}H_{26}$ as an internal standard. GLC analysis, using a 7-ft column packed with 10% OV101 on Supelcon AW DMCS at 110 °C, revealed benzaldehyde (0.127 mmol, 45%). The presence of PhCHO was confirmed by coinjection of an authentic sample onto both the OV101 column and a 12-in. column packed with 7% Carbowax 20M on Chromosorb WAW.

An infrared spectrum of the crude THF solution exhibited an absorption band at 1700 cm^{-1}, the position of ν_{CO} in PhCHO. Bulb-to-bulb distillation of an aliquot of the crude reaction mixture at room temperature, followed by GLC of the distillate, revealed the presence of benzaldehyde.

The presence of **1** was demonstrated as described above.

Reaction of $NaHFe_2(PPh_2)_2(CO)_6$ (9) with Carbon Tetrachloride. To a solution of **4** (50 mg, 0.047 mmol) in 0.300 mL of NMP was added 1 equiv of CH_3CO_2H (2.8 μL, 0.049 mmol). After a few minutes of stirring, CCl_4 (4.8 μL, 0.050 mmol) was added via syringe. After stirring overnight, a 150-μL aliquot of the reaction mixture was removed, and to it was added 5.0 μL of n-C_6H_{14} as an internal standard. GLC analysis, using a 7-ft. column packed with 3% BDS on Chromosorb WAW at 20 °C, revealed chloroform (0.037 mmol, 78%). The presence of $CHCl_3$ was confirmed by coinjection of an authentic sample. The presence of **1** was demonstrated as described above.

Reaction of $Na_2Fe_2(PPh_2)_2(CO)_6{\cdot}5THF$ (4) with 2 Equiv of CF_3CO_2D. To a flask equipped with a rubber septum and containing a solution of **4** (0.400 g, 0.379 mmol) in 8 mL of protio THF was added 2 equiv of CH_3CO_2D (59 μL, 0.77 mmol). An immediate reaction occurred, with evolution of a colorless gas and with a change in the reaction mixture from a red solution to a turbid, yellow suspension. HD and D_2 were detected in the gaseous phase by GLC, using a column packed with 15% $MnCl_2$ on Alcoa F_1 68–100 mesh alumina at −196 °C. No H_2 was detected. The presence of HD and D_2 was confirmed by coinjection of authentic samples. Integration of peak areas indicated that $D_2/(D_2 + HD) = 0.88$. The presence of **1** was demonstrated as described above. Note: A ^1H NMR spectrum (neat) of the CF_3CO_2D (with a known volume of C_6H_6 injected as an internal standard) indicated that the sample was >97 atom % D.

Reaction of Acyl Complexes 6 and 8 with Protonic Acids. All of these reactions were conducted similarly. A representative example follows.

Reaction of $LiFe_2(PPh_2)_2(CO)_5[C(O)CH_3]{\cdot}3THF$ (8a) with Trifluoroacetic Acid. (A) Characterization of the Aldehyde. To a solution of **8a** (150 mg, 0.169 mmol) in 300 μL of acetone-d_6, in a 5-mm NMR tube equipped with a rubber septum, was added via syringe CF_3CO_2H (15 μL, 0.19 mmol). An immediate reaction was observed. In addition to the expected phenyl, THF and acetone-d_{0-5} resonances, only a doublet (J = 3 Hz) at δ 2.03 and a quartet (J = 3 Hz) at δ 9.67 (resonances characteristic of CH_3CO) were observed in the ^1H NMR spectrum of the resulting solution. Integration of the spectrum indicated that acetaldehyde was present in >90% yield.

(B) Characterization of the Iron-Containing Products. To a solution of **8a** (5.4 g, 6.1 mmol) in 100 mL of acetone was added via syringe CF_3CO_2H (0.475 mL, 6.16 mmol). After 15 min of stirring, the solvent was removed under reduced pressure. The residue was extracted with 4 × 30 mL of benzene. To the filtered extracts was added, with stirring, 6 g of 60–200 mesh silica gel. After 30 min, the solvent was removed under reduced pressure. The resulting dry residue was added to the top of a column (4.5 × 50 cm) packed with 60–200 mesh silica gel. Elution with 4:1 hexane:benzene (drop rate ≃ 2.5 mL/min) afforded several bands.

The leading yellow band was collected and filtered. The solvent was removed under reduced pressure, affording **1** as yellow crystals, which were dried in vacuo at 65 °C (1.91 g, 48%). The solution infrared spectra and analytical TLC properties of the product and an authentic sample of **1** were identical.

The second band, faint and brown in color, was discarded.

The third band, reddish brown in color, was collected and filtered. The solvent was removed under reduced rpessure, affording a rust-colored solid, which was dissolved in a minimum volume of 3:1 hexane:benzene and filtered. Slow evaporation of the filtrate resulted in **12** as red crystals, which were washed with a small volume of hexane and dried in vacuo (100–125 mg, 2%). In pure form, **12** is indefinitely air stable both in the solid state and in solution. However, decomposition on silica gel in air occurs at an appreciable rate. Spectral data: IR (C_6H_6 solution) ν_{CO} 2038, 1996, 1965, 1947 cm^{-1}; ^1H NMR (C_6D_6) δ −21.06 (d of t, J_{PH} = 37.5 Hz, J_{P_2H} = 30.0 Hz, 1 H), 6.5, 7.2, 8.0 (m, 30 H). Anal. Calcd for $C_{43}H_{41}Fe_3O_7P_3$: C, 56.12; H, 3.40; Fe, 18.2; P, 10.10. Found: C, 56.28; H, 3.52; Fe, 17.3; P, 10.24. Molecular weight of **12**: calcd, 920; found, 875 (by osmometry in C_6H_6).

The fourth band, orange in color, was collected and filtered. The solvent was removed under reduced pressure, affording **2d** as an orange solid, which was dried in vacuo at 65 °C (0.43 g, 9%). The solution infrared spectra and analytical TLC properties of the product and an authentic sample of **2d** were identical.

The several faint bands which trailed the fourth were discarded.

$Fe_2(PPh_2)_2(CO)_5(\overline{CCH_2CH_2CH_2O})$ (13). To a solution of **4** (0.500 g, 0.473 mmol) in 1 mL of acetone-d_6 was added via syringe $ICH_2CH_2CH_2I$ (54.5 μL, 0.474 mmol). A rapid reaction resulted in a red-orange solution and precipitate. After the solvent was removed under reduced pressure, the residue was crystallized from hexane in air, affording orange crystals (257 mg, 79%): IR (C_6H_6 solution) ν_{CO} 2025, 1975, 1940 (sh), 1920 (sh) cm^{-1}; ^1H NMR (C_6D_6) δ 0.5 (m, 2 H), 2.85 (m), 3.58 (t, J = 8 Hz, 2 H), 6.8, 7.6 (m, 20 H). Anal. Calcd for $C_{33}H_{26}Fe_2O_6P_2$: C, 57.26; H, 3.79; Fe, 16.1; P, 8.95. Found: C, 57.68; H, 3.95; Fe, 15.6; P, 8.45, 8.55.

Reaction of $Na_2Fe_2(PPh_2)_2(CO)_5[C(O)CH_2CH{=}CH_2]{\cdot}2THF$ (6f) with Allyl Bromide and Tosylate. To a solution of **4** (107 mg, 0.101 mmol) in 0.5 mL of NMP was added via syringe allyl bromide (20 μL, 0.23 mmol) and 10.0 μL of cyclohexane as an internal standard. Following a few minutes of stirring at room temperature, a GLC analysis of an aliquot of the crude reaction mixture, using a 7-ft column packed with 10% OV101 on Supelcon AW DMCS at 22 °C, revealed biallyl (0.102 mmol, 101%). The assignment of biallyl was confirmed by coinjection of an authentic sample onto both the OV101 column and a 7-ft column packed with 3% BDS on Chromosorb WAW at 25 °C. The GLC injector port temperature in all cases was ≃280 °C.

Following several hours of stirring at room temperature, an infrared spectrum of 1 aliquot of the reaction mixture in THF exhibited absorption bands characteristic of **6f**. Biallyl apparently formed in the hot injection port. The reaction of **4** with 2 equiv of allyl tosylate was carried out in a similar manner.

Reaction of $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_2Ph]{\cdot}2THF$ (6e) with Benzyl Bromide. (A) Experiment No. 1. To a solution of **4** (100 mg, 0.0946 mmol) in 0.5 mL of THF was added via syringe benzyl bromide (24 μL, 0.20 mmol) and 20 μL of n-$C_{13}H_{28}$ as an internal standard. Following 3.5 h of stirring at room temperature, an infrared spectrum of 1 aliquot of the reaction mixture in THF was nearly superimposable with that of **6e** in the region of 2400–1600 cm^{-1}. Following 5.5 h of stirring, a GLC analysis of an aliquot, using a 7-ft column packed with 10% OV101 on Supelcon AW DMCS at 185 °C, revealed bibenzyl (0.0447 mmol, 47%). The assignment of bibenzyl was confirmed by coinjection of an authentic sample onto both the OV101 column and a 7-ft column packed with 3% BDS on Chromosorb WAW at 182 °C.

Following 24 h of stirring, a second GLC analysis was conducted and found to be identical with that described above.

After 7 days of reaction time, an infrared spectrum of another aliquot exhibited strong absorption bands characteristic of **6e** and additional bands of medium intensity characteristic of **1**. A GLC analysis gave results identical with those described above.

After 28 days, an infrared spectrum of another aliquot was nearly superimposable with that of **1** in the region of 2400–1600 cm^{-1}. No absorption bands characteristic of **6e** were discernible. Biallyl was apparently formed in the hot (~280 °C) GLC injection port.

(B) Experiment No. 2. To a solution of **4** (190 mg, 0.180 mmol) in 0.50 mL of Me_2SO-d_6, in a 5-mm NMR tube equipped with a rubber septum, was added via syringe benzyl bromide (20 μL, 0.17 mmol). The ^1H NMR spectrum of the resulting red solution was identical with that of **6e**. An infrared spectrum of an aliquot of the reaction mixture in THF was identical with that of **6e** in the region of 2400–1600 cm^{-1}.

A second portion of benzyl bromide (24 μL, 0.20 mmol) was added to the tube through the septum, via syringe. The tube was then sealed under an atmosphere of nitrogen. The ^1H NMR spectrum of the resulting sample indicated the presence of **6e** and $PhCH_2Br$ in a molar ratio of approximately 1:1. No change was discernible by ^1H NMR after 20 h at room temperature. The sample was then heated in the dark at 80–100 °C. Over a period of 2 h, ^1H NMR spectra showed a gradual decrease in the intensities of singlets at δ 3.97 and 4.63, resonances characteristic of **6e** and $PhCH_2Br$, respectively. Concurrently, singlets appeared at δ 2.13 and 2.72 (resonances characteristic of toluene and bibenzyl, respectively) and gradually increased in intensity. After 2 h at 80–100 °C, no resonances characteristic of **6e** were detectable above noise, and only a trace of $PhCH_2Br$ was evident. Integration of the spectrum indicated the formation of bibenzyl in ~30% yield and toluene-$d_{0,1}$ in 35–50% yield.

The sealed tube was opened under a nitrogen atmosphere, and its contents were transferred to a second 5-mm tube. An infrared spectrum of 1 aliquot of the crude reaction mixture in THF was essentially superimposable with that of **1**. An analytical TLC analysis of the crude reaction mixture revealed the presence of **1**. The second NMR tube containing the bulk of the reaction mixture was equipped with a rubber septum. The presence of bibenzyl and toluene in the solution was confirmed by measuring ^1H NMR spectra before and after addition of authentic samples of the two.

Reaction of $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_3]\cdot 2THF$ (6a) with Dimethylphenylphosphine. A solution of **6a** (110 mg, 0.132 mmol) and $P(CH_3)_2Ph$ (25 μL, 0.17 mmol) in 250 μL of Me_2SO-d_6 was sealed under a nitrogen atmosphere in a 5-mm NMR tube. The ^1H NMR spectrum of the resulting mixture exhibited only reasonances characteristic of the two individual components. After the tube was heated in the dark for 1 h at 100 °C, the spectrum was devoid of a doublet at δ 1.25, a resonance characteristic of free $P(CH_3)_2Ph$. In addition, the singlet at δ 2.22, characteristic of **6a**, had significantly decreased in intensity. Several new resonances had appeared in the region δ 1.3–1.6.

In an inert-atmosphere glovebox, the sample was removed from the tube. An infrared spectrum of 1 aliquot of the crude reaction mixture in THF exhibited several absorption bands in the region of 2400–1400 cm^{-1}. Bands characteristic of unreacted **6a** were evident. The sample was filtered. Addition of 0.5 mL of THF to the filtrate resulted in red crystals of **3b** [20 mg, 27%, based on $P(CH_3)_2Ph$]. Infrared spectra (KBr pellet and THF solution) of the product were identical with those of **3b**. Anal. Calcd for $C_{44}H_{42}Fe_2O_4P_4$: C, 60.71; H, 4.86; Fe, 12.83. Found: C, 60.88; H, 5.21; Fe, 12.45.

The filtrate from the crystallization above was chromatographed in air on a 20 × 20 cm, 250-μ silica gel plate with an eluant of 1:1 benzene:hexane. The major red band was scraped from the plate, washed free of the silica with benzene, and filtered. The solvent of the resulting red filtrate was removed under reduced pressure, affording **2b** (8 mg, 8%, based on **6a**): ^1H NMR ($CDCl_3$) δ 1.56 (d, J = 8 Hz, 6 H), 6.4–7.8 (m, 25 H). The infrared spectrum of the product in THF was identical with that of **2b**.

Reaction of $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_3]\cdot 2THF$ (6a) with Carbon Monoxide. A 0.02 M solution of **6a** was stirred at room temperature under carbon monoxide at 40 psig. Infrared spectra of the crude reaction mixture, taken periodically over a period of 2 weeks, showed a gradual increase in the intensities of absorption bands characteristic of **1** and a gradual decrease in the intensities of absorption bands characteristic of **6a**.

Reaction of $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_3]\cdot 2THF$ (6a) with Sodium. To a solution of **6a** (50 mg, 0.060 mmol) in 3 mL of THF was added 50% sodium dispersion (8 mg, 0.2 mmol). After 2 h of stirring, the red mixture was filtered. Diffusion of hexane vapor into the filtrate resulted in crystals of **4**, which were washed with hexane and dried in vacuo (41 mg, 65%). The solution infrared spectra of the product and an authentic sample of **4** were identical. Treatment of a THF solution of the product with dioxygen (air) resulted in the formation of **1**.

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Registry No. 1, 19599-68-9; **2a**, 79190-80-0; **2b**, 79172-57-9; **2d**, 79172-58-0; **3a**, 79172-59-1; **3b**, 79172-60-4; **3c**, 79200-24-1; **4**, 79172-61-5; **5**, 72124-56-2; **6a**, 72275-07-1; **6b**, 79172-63-7; **6c**, 79172-82-0; **6d**, 79172-84-2; **6e**, 79172-86-4; **6f**, 79172-88-6; **6g**, 79172-90-0; **6h**, 79172-92-2; **7**, 72275-03-7; **8a**, 79200-26-3; **8b**, 72275-05-9; **9**, 79172-93-3; **10**, 79172-95-5; **11**, 79172-96-6; **12**, 79391-51-8; **13**, 79172-64-8; $Na_2Fe(CO)_4$, 14878-31-0; $Fe(CO)_5$, 13463-40-6; Ph_2PCl, 1079-66-9; Cf_3CO_2H, 76-05-1; benzoyl chloride, 98-88-4; CCl_4, 56-23-5; $ICH_2CH_2CH_2I$, 627-31-6; allyl bromide, 106-95-6; benzyl bromide, 100-39-0.

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Reaction of $(CH_3)_3L$ (L = N, P) with Chlorinated Compounds of *closo*-2,4-$C_2B_5H_7$: Net Displacement Reactions at Boron Atoms of *closo*-Carboranes

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Unlike the parent pentagonal-pyramidal *closo*-2,4-$C_2B_5H_7$, both 3-Cl-*closo*-2,4-$C_2B_5H_6$ and 5-Cl-*closo*-2,4-$C_2B_5H_6$ readily react with $(CH_3)_3L$ (L = N, P) to form 1:1 adducts. Removal of Cl^- from these two adducts, using BCl_3, produces the unique [3-$(CH_3)_3L$-*closo*-2,4-$C_2B_5H_6$]$^+$ and [5-$(CH_3)_3L$-*closo*-2,4-$C_2B_5H_6$]$^+$ cations, respectively. The reaction of $(CH_3)_3N$ with 1-Cl-*closo*-2,4-$C_2B_5H_6$ proceeds with more difficulty than with the other two B–Cl isomers, but once formed, the 1:1 adduct combines with BCl_3 to give the rearrangement product [3-$(CH_3)_3N$-*closo*-2,4-$C_2B_5H_6$]$^+$[BCl_4]$^-$.

Introduction

Reactivities of the small *closo*-carboranes toward $(CH_3)_3L$ (L = P or N) are known to follow the order 1,5-$C_2B_3H_5$ > 1,6-$C_2B_4H_6$ > 2,4-$C_2B_5H_7$. The smallest cage compound forms unstable adducts whereas 1,6-$C_2B_4H_6$ gives the well-characterized open cage dipolar 5-$(CH_3)_3L^+$-*nido*-2,4-$C_2B_4H_6^-$; the largest of the three, 2,4-$C_2B_5H_7$, does not react with $(CH_3)_3L$ at temperatures below the decomposition of either reagent but is readily cleaved by many secondary amines, R_2NH, to products such as $R_2NH\cdot BH_3$ and $[R_2NBHCH_3]_x$, x = 1, 2.[1-3]

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