# Ferrocenediyl-Bridged Triiron Complexes[†]

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The reaction of 2 equiv of $CpFe(CO)_2I$ and 1,1′-dilithioferrocene in the presence of 2 equiv of $PPh_3$ is an intermolecular version of the reaction of $CpFe(CO)_2I$ and $(\eta^5\text{-}C_5H_4Li)Fe(C_5H_4\text{-}PPh_2)$. In the three-component procedure, the $PPh_3$ substitution for iodide on $CpFe(CO)_2I$ is much faster than the nucleophilic Fc-addition at the Fe-center or at a CO ligand of $CpFe(CO)_2I$. This one-pot reaction proceeds through $[CpFe(CO)_2PPh_3^+]$ and yields $CpFe(CO)(PPh_3)[\mu,C{:}\eta^5\text{-}C(O)C_5H_4]Fe[\mu,\eta^5{:}\eta^4\text{-}5\text{-}exo\text{-}(1'\text{-}C_5H_4)C_5H_5]Fe(CO)_2(PPh_3)$ (**4**) in 50% yield, with the 1,1′-dilithioferrocene participating twice in the nucleophilic Fc-additions: at the Cp-ring and at a CO ligand of $[CpFe(CO)_2PPh_3^+]$. Complex **4** is a ferrocenediyl-bridged tri-Fe complex with three different Fe-centers: a metallocene Fe(II), a square-pyramidal pentacoordinate Fe(0), and a half-sandwich acyl-Fe(II). It has been found that, in the second Fc-additions, the pathway from $(\eta^5\text{-}C_5H_4Li)Fe[\mu,\eta^5{:}C\text{-}C_5H_4C(O)]FeCp(CO)(PPh_3)$ (**9**) to **4** proceeds normally, but the pathway from **9** to $Fe[(\mu,\eta^5{:}C\text{-}C_5H_4)C(O)FeCp(CO)(PPh_3)]_2$ (**5**) has been turned off. The preference of Fc-addition for **9** onto the Cp-ring of $[CpFe(CO)_2PPh_3^+]$ could be reasoned by a localization of the $Li^+$ cation in **9**.

## Introduction

Since its discovery half a century ago,[1] ferrocene, an electron-rich molecule, has displayed a variety of intriguing physical and chemical properties. Complexes with a ferrocenyl group (Fc) directly bonded to a metal are known, among which lithioferrocenes provide key intermediates for further elaboration.[2] The reaction between metal halides and FcLi,[3] the ferrocenyl transfer from $Fc_2Hg$,[4] and the thermal or photoinduced decarbonylation of ferrocenoyl complexes[5] are inter alia useful methods for the preparation of ferrocenyl derivatives.

The ring-opening reaction of $PhP(\eta^5\text{-}C_5H_4)_2Fe$ with PhLi provides a monoanionic ferrocenediyl nucleophile, $(\eta^5\text{-}C_5H_4Li)Fe(C_5H_4PPh_2)$, with a pendant $PPh_2$ ligand on the other Cp-ring.[6] When followed by a reaction with an electrophile, $CpFe(CO)_2I$, the reaction produces $CpFe(CO)_2(\mu,\eta^1{:}\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh_2)$, $CpFe(CO)[\mu,C{:}\eta^5\text{-}C(O)C_5H_4]Fe(\mu,\eta^5{:}P\text{-}C_5H_4PPh_2)$, and $CpFe(CO)(\mu,\eta^1{:}\eta^5\text{-}C_5H_4)Fe(\mu,\eta^5{:}P\text{-}C_5H_4PPh_2)$.[7] This reaction involves the nucleophilic Fc-addition at the Fe-center of $CpFe(CO)_2I$, with migratory insertion and CO de-insertion at later stages to yield products in series (Scheme 1).[8]

As a comparative study, it would be of interest to examine the reaction of 2 equiv of $CpFe(CO)_2I$ and 1,1′-dilithioferrocene in the presence of 2 equiv of $PPh_3$ in detail. This reaction is an intermolecular version of the above reaction between $CpFe(CO)_2I$ and $(\eta^5\text{-}C_5H_4Li)Fe(C_5H_4PPh_2)$. As we report here, we have found that under three-component conditions, the substitution of the iodide of $CpFe(CO)_2I$ by $PPh_3$ is much faster than nucleophilic Fc-addition at the Fe-center or at a CO ligand of $CpFe(CO)_2I$. The reaction proceeds through an intermediate, $[CpFe(CO)_2PPh_3^+]$, and results in the interesting ferrocenediyl-bridged tri-Fe complex $CpFe(CO)(PPh_3)[\mu,C{:}\eta^5\text{-}C(O)C_5H_4]Fe[\mu,\eta^5{:}\eta^4\text{-}5\text{-}exo\text{-}(1'\text{-}C_5H_4)C_5H_5]Fe(CO)_2(PPh_3)$ in 50% yield, with the 1,1′-dilithioferrocene participating twice in the nucleophilic Fc-additions: at the Cp-ring and at a CO ligand of $[CpFe(CO)_2PPh_3^+]$.

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[†] Dedicated to the memory of Prof. Kalman Burger.

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(8) The pathway for the replacement of the dangling $PPh_2$ for iodide in $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ followed by the anionic carbon addition onto one of the CO ligands could not be ruled out. In this pathway, the secondary reactions are the CO de-insertion to liberate phosphine or CO.

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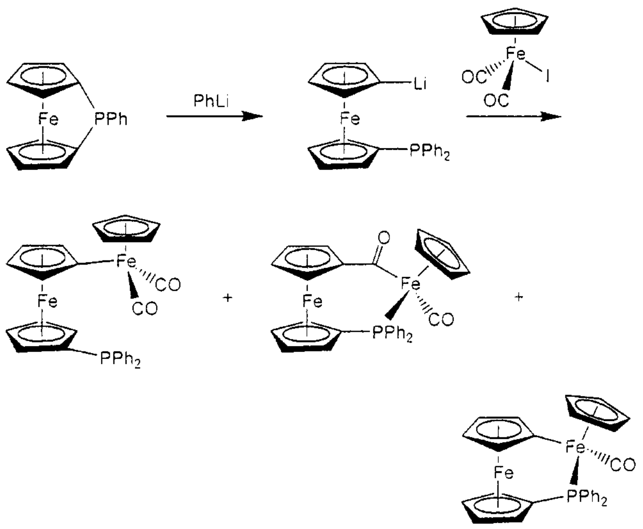
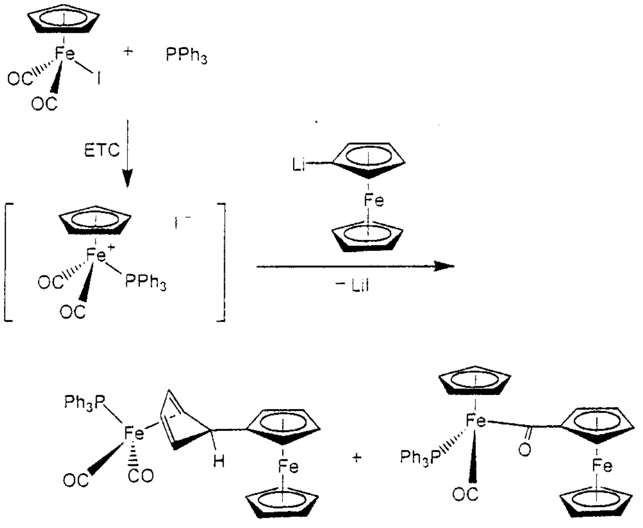
**Scheme 1**



**Scheme 2**



1 (25 %, Cp-alkylation) 2 (47 %, CO-alkylation)

## Results and Discussion

**Monoanionic Nucleophilic Fc-Additions.** The reaction with monoanionic CpFe($\eta^5$-$C_5H_4Li$) was studied first. An equimolar mixture of $CpFe(CO)_2I$ and $PPh_3$ in THF at low temperature was treated dropwise with a stoichiometric amount of CpFe($\eta^5$-$C_5H_4Li$). During the addition, the color of the solution gradually changed from black to orange, along with the formation of a yellow precipitate that redissolved by the end of the reaction. $PPh_3$ was incorporated into the products. Two isomeric compounds were isolated corresponding to nucleophilic Fc-addition at the Cp-ring, CpFe[$\mu,\eta^5$:$\eta^4$-5-*exo*-(1′-$C_5H_4$)$C_5H_5$]$Fe(CO)_2(PPh_3)$ (**1**; 24.8%), and to nucleophilic Fc-addition at the CO ligand, CpFe[$\mu,\eta^5$:*C*-$C_5H_4C(O)$]FeCp(CO)($PPh_3$) (**2**; 47.1%), as shown in Scheme 2.

The $^1H$ NMR data of **1** contain three peaks for the five ring protons of a $\eta^4$-5-*exo*-substituted cyclopentadiene skeleton, in an integrated ratio of 2:1:2 and progressively toward upfield for inner-diene H-atoms, the *endo* H-atom, and the outer-diene H-atoms ($\delta$ 2.49, 3.46, and 5.09). In the $^1H$ NMR spectrum, the ferrocenyl skeleton exhibits two peaks of equal intensity ($\delta$ 3.78, 2H; $\delta$ 3.87, 2H) and one Cp resonance ($\delta$ 4.01, 5H). The two IR $\nu_{CO}$ absorption bands at 1967 and 1908 cm$^{-1}$ of equal intensity and one $^{31}P$ NMR peak at $\delta$ 74.1 are consistent with those of other similar $\eta^4$-Fe complexes.[9] Hence, the molecular skeleton of **1** is readily deduced to be a Fc-group connected to the methine carbon of a 5-*exo*-substituted cyclopentadiene which is $\eta^4$-bonded to $Fe(CO)_2(PPh_3)$. On the other hand, the IR $\nu_{CO}$ absorption bands at 1915 (carbonyl CO) and 1583 (keto CO) cm$^{-1}$ and one $^{31}P$ NMR peak at $\delta$ 76.4 for complex **2** are typical of an iron−acyl complex, CpFe(CO)C(O)R-($PPh_3$).[10] The Fe-atom is chiral. As apparent from the $^1H$ and $^{13}C$ NMR spectra, complex **2** has four proton signals ($\delta$ 4.16, 4.20, 4.34, 4.55) and four carbons signals ($\delta$ 68.3, 68.6, 68.8, 69.7) for the substituted cyclopentadienyl ring protons and the C2−C5 carbon atoms, indicative of their magnetic nonequivalence. In the $^1H$ spectrum, there are two Cp resonances ($\delta$ 3.97, 4.43, 5H × 2) for **2**.

In our earlier studies, the presence of $PPh_3$ in the reaction of $CpFe(CO)_2X$ (X = Cl, Br, I) and RLi (R = Me, *n*-Bu, *s*-Bu, Ph) at low temperature did indeed give an overall three-component transformation to yield ($\eta^4$-$RC_5H_5$)$Fe(CO)_2PPh_3$, which effectively changes the ($\eta^5$-$C_5H_5$) to metal bonding mode in $CpFe(CO)_2X$ to a ($\eta^4$-$RC_5H_5$) to metal bonding in ($\eta^4$-$RC_5H_5$)$Fe(CO)_2PPh_3$ with the Fe-center concurrently reduced from Fe(II) to Fe(0).[9] The array of collected products includes

the Cp-alkylation product ($\eta^4$-$RC_5H_5$)$Fe(CO)_2PPh_3$,

the CO-alkylation product CpFe(CO)C(O)R($PPh_3$),

the reduction−dimerization product $[CpFe(CO)_2]_2$, and

the product of $PPh_3$ substitution for CO, CpFe(CO)-($PPh_3$)X.

The last two products either are found in trace amounts or are not observable at all, and the CO-alkylated CpFe(CO)C(O)R($PPh_3$) is at most minor. This similar pattern has been observed for all three half-sandwich iron halides and a range of lithiated alkyl and aryl nucleophiles. We also noted that the C-based nucleophiles (alkyl and aryl) add onto the Cp-ring,[10] and the O- and N-based nucleophiles add at CO.[11] As an example, the reaction with PhLi yields a branch ratio of 71:4, favoring the Cp-ring phenylation product. Nonetheless, CpFe($\eta^5$-$C_5H_4Li$) is different from these C-based nucleophiles and has exhibited a product ratio of ca. 1:2, preferring the CO-alkylation product. Apparently, the interaction of the Cp carbons and Fe-center in ferrocene shifts the anion toward acting as a non-C-based nucleophile. The nature of such an interaction is not yet understood.

Scheme 2 also shows the two-stage nature of the three-component preparation of compounds **1** and **2**. The initial drops of CpFe($\eta^5$-$C_5H_4Li$) act as a reducing agent

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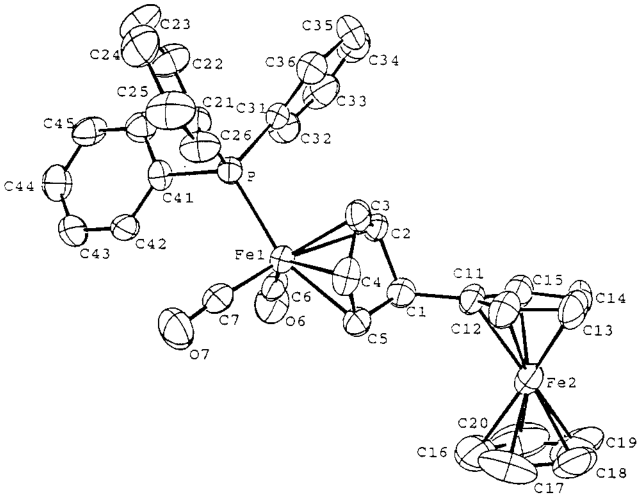

**Figure 1.** Molecular plot of ($\eta^5$-$C_5H_5$)Fe[$\mu$,$\eta^5$:$\eta^4$-5-*exo*-(1′-$C_5H_4$)$C_5H_5$]Fe(CO)$_2$(PPh$_3$) (**1**) with the atomic numbering sequence. The thermal ellipsoids are drawn at the 50% probability level with H atoms omitted for clarity. Selected bond lengths (Å): Fe1−P 2.225(3), Fe1−C2 2.126(9), Fe1−C3 2.043(9), Fe1−C4 2.044(9), Fe1−C5 2.095(9), Fe1−C6 1.744(11), Fe1−C7 1.751(11), C6−O6 1.145(13), C7−O7 1.163(14), C1−C11 1.515(13), P−C21 1.848(10), P−C31 1.827(10), P−C41 1.845(9). Selected bond angles (deg): P−Fe1−C6 97.3(3), P−Fe1−C7 94.8(3), C6−Fe1−C7 102.2(5), Fe1−C6−O6 178.1(5), Fe1−C7−C11 119.5(4), C7−C11−Fe2 124.7(4).

to initiate an electron-transfer chain catalysis[12] of the replacement of iodide on CpFe(CO)$_2$I by PPh$_3$. The cation [CpFe(CO)$_2$(PPh$_3$)$^+$] is rapidly obtained in this reaction (as a yellow precipitate that redissolves along the reaction coordinate).[13] The initiator function of CpFe($\eta^5$-$C_5H_4Li$)[14] is a perfect match with its properties because the concerned electron-transfer chain catalysis is reductive in nature: a carbanion is known to function inter alia as a reductant.[15] The stoichiometric CpFe($\eta^5$-$C_5H_4Li$) then acts as a normal nucleophile to add onto the Cp-ring or one of the CO ligands of the cation. As a Lewis acid, the cation is much more electrophilic than neutral CpFe(CO)$_2$I toward CpFe($\eta^5$-$C_5H_4Li$). Therefore, mixing three components is equivalent to performing the reaction of [CpFe(CO)$_2$(PPh$_3$)$^+$][I$^-$] with CpFe($\eta^5$-$C_5H_4Li$).

**X-ray Structures of 1 and 2.** The molecular structure of **1** with the atom numbering scheme is shown in Figure 1. To our knowledge, this is the first 5-*exo*-(ferrocenyl)cyclopentadiene skeleton characterized by X-ray diffraction. Complex **1** has one solvated $CH_2Cl_2$ molecule in the crystal. The bonding geometry around Fe1 can be described as a pseudo-square-pyramid with C6≡O6 at the apical position, PPh$_3$ in the basal plane *trans* to one of the double bonds, and C7≡O7 *trans* to the second double bond. The bulky ferrocenyl group is *exo* to the cyclopentadiene ring and located away from PPh$_3$. The C2-, C3-, C4-, and C5-atoms of cyclopentadiene are coplanar within 0.005 Å. The distance between C1 and the diene plane of C2−C5 is 0.582(2) Å, and the plane of C2−C1−C5 is tilted 35.3(8)° away from Fe toward the other side of the diene plane. The planes of C1 and C11−C15 [deviation within 0.025 Å] and C11, C1, Fe1, C6, and O6 [deviation within 0.015 Å] are perpendicular to the diene, the angles being 90.8(3)° and 90.0(4)°, respectively. The interplanar angle between them is 31.6(4)°. A very similar geometry has been observed in ($\eta^4$-PhCH$_2$C$_5$H$_5$)Fe(CO)$_2$(PPh$_3$),[16] ($\eta^4$-PhC$_5$H$_5$)Fe(CO)$_2$(PPh$_3$), ($\eta^4$-BuC$_5$H$_5$)Fe(CO)$_2$(PPh$_3$), and ($\eta^4$-MeC$_5$H$_5$)Fe(CO)$_2$(PMePh$_2$). The Fe1−P bond length is 2.225(3) Å, which is comparable to the average Fe(0)−P length [2.242(34) Å]. The ferrocenyl Cp-rings are virtually eclipsed by a small staggered angle of 2.9°.

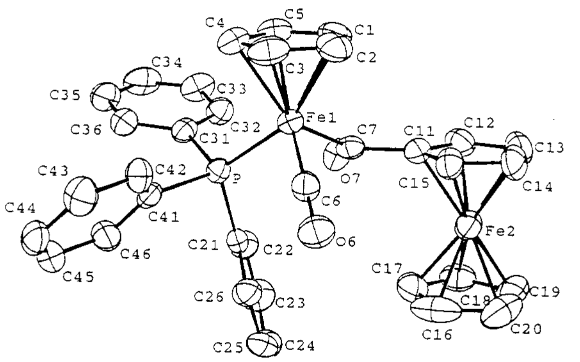

**Figure 2.** Molecular plot of ($\eta^5$-$C_5H_5$)Fe[$\mu$,$\eta^5$:*C*-$C_5H_4$C(O)]-Fe(CO)(PPh$_3$)($\eta^5$-$C_5H_5$) (**2**) with the atomic numbering sequence. The thermal ellipsoids are drawn at the 50% probability level with H atoms omitted for clarity. Selected bond lengths (Å): Fe1−P 2.202(2), Fe1−C1 2.121(5), Fe1−C2 2.111(5), Fe1−C3 2.126(6), Fe1−C4 2.132(5), Fe(1)−C5 2.114(5), Fe1−C6 1.722(5), Fe1−C7 1.963(5), C6−O6 1.160(7), C7−O7 1.223(6), C7−C11 1.509(7), P−C21 1.834(5), P−C31 1.848(5), P−C41 1.846(5). Selected bond angles (deg): P−Fe1−C6 91.1(2), P−Fe1−C7 93.4(2), C6−Fe1−C7 92.0(2), Fe1−C6−O6 178.1(5), Fe1−C7−O7 Fe1−C7−C11 119.5(4), C7−C11−Fe2 124.7(4).

The molecular structure of **2** with an atom numbering scheme is shown in Figure 2. There are very few examples of ferrocenoyl derivatives directly bonded to another transition metal via the keto C-atom.[17] Thermal and photochemical decarbonylation often leads to ferrocenyl derivatives. Complex **2** adopts a three-legged piano-stool geometry, and the Fe atom exists in a distorted octahedral environment with the Cp-ring occupying the *fac* sites and three legs being orthogonal.[18] PPh$_3$ is located away from the ferrocenyl moiety, in which the Cp-rings are essentially eclipsed with a staggered angle of 6.5°. The Fe1−P bond length is 2.202(2) Å. The torsion angle of P−Fe1−C7−C11 is −154.6(3)°. The acyl CO-group points away from the carbonyl CO-group to minimize the dipole−dipole repulsion

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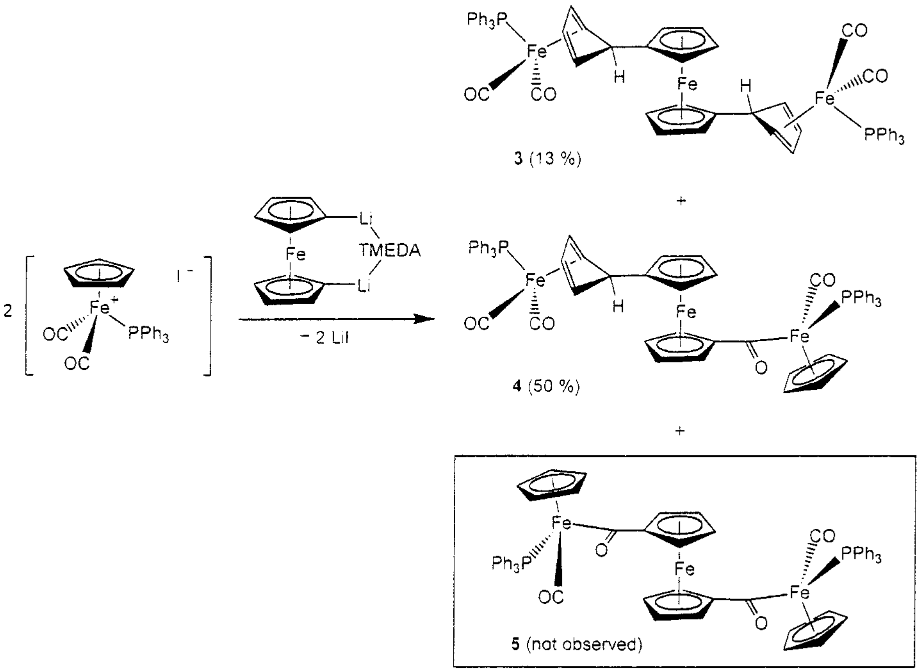
**Scheme 3**



where the torsion angle of C6−Fe1−C7−O7 is 124.7(4)°. The P−Fe1−C7−C11 value is among the largest reported,[8a] apparently due to steric repulsion. Other structural parameters compare well with the published ones.

**Reaction of 2 equiv of $CpFe(CO)_2I$ and 1,1′-Dilithioferrocene in the Presence of 2 equiv of $PPh_3$.** As obtained from the reaction between $CpFe(CO)_2I$ and FcLi in the presence of $PPh_3$, the product ratio for **1**:**2** was 1:2. The reaction of 2 equiv of $CpFe(CO)_2I$ and 1 equiv of 1,1′-dilithioferrocene in the presence of 2 equiv of $PPh_3$ would give 1,1′-ferrocenediyl-disubstituted products in a statistical manner, provided that the two Fc-additions react independently. That is, a ratio of 1:4:4 could be predicted for the three possible tri-Fe complexes Fe{[$\mu$,$\eta^5$:$\eta^4$-5-*exo*-(1′-$C_5H_4$)$C_5H_5$]Fe$(CO)_2(PPh_3)$}$_2$ (**3**), $CpFe(CO)(PPh_3)$[$\mu$,*C*:$\eta^5$-C(O)$C_5H_4$]Fe[$\mu$,$\eta^5$:$\eta^4$-5-*exo*-(1′-$C_5H_4$)$C_5H_5$]Fe$(CO)_2$(P $Ph_3$) (**4**), and Fe[($\mu$,$\eta^5$:*C*-$C_5H_4$)C(O)Fe(CO)$(PPh_3)$Cp]$_2$ (**5**).

However, with 2 equiv of $CpFe(CO)_2I$ and 2 equiv of $PPh_3$ in the mixture and $(\eta^5\text{-}C_5H_4Li)_2Fe$(TMEDA) replacing FcLi to participate in the above three-component reaction, only **3** (13%) and **4** (50%) were obtained, as shown in Scheme 3. Compound **5**, which was expected to be produced in a quantity similar to that of **4**, was not observed at all. We believe that there is a molecular self-assembly process going on upon reaction of $(\eta^5\text{-}C_5H_4Li)_2Fe$(TMEDA) which did not occur with FcLi.

Complex **3** reveals spectroscopic features very similar to those of **1** without the singlet Cp resonance [IR $\nu_{CO}$ 1967, 1908 cm$^{-1}$; $^1$H $\delta$ 2.43 (4H), 3.36 (2H), 5.05 (4H) for $\eta^4$-5-*exo*-substituted cyclopentadiene, $\delta$ 3.61 (4H), 3.72 (4H) for the monosubstituted cyclopentadienyl ring; $^{31}$P $\delta$ 74.1]. The molecular skeleton of **3** is thus a ferrocenediyl group linking two identical $\eta^4$-Fe$(CO)_2(PPh_3)$ fragments. Complex **4** mainly shows a combination of the spectroscopic features of **1** and **2**, leaving out the singlet Cp resonance of the ferrocene skeleton. Its IR spectrum reveals three $\nu_{CO}$ absorption bands at 1967, 1909 (overlapped), and 1583 cm$^{-1}$. Its $^{31}$P NMR spectrum exhibits two resonances at $\delta$ 74.7 and 77.4. The $^1$H NMR and $^{13}$C NMR spectra clearly indicate a magnetic nonequivalence in the molecule [eight proton signals and eight carbon signals (C2−C5)] of the 1,1′-disubstituted ferrocenediyl moiety. Four $^1$H NMR chemical shifts ($\delta$ 2.42, 2.46; $\delta$ 5.02, 5.07) and four $^{13}$C NMR chemical shifts ($\delta$ 56.0, 56.9; $\delta$ 82.3, 82.5) have been assigned to the inner and the outer diene protons and carbons of the cyclopentadiene ligand. The significant distinction is due to the chiral Fe-center of the iron−acyl end. In **1**, the inner and the outer diene protons and carbons of cyclopentadiene show only one peak each. A similar remote chiral influence was noticed in [CpFe(CO)C(O)Me]($\mu$,$\eta^1$:$\eta^1$-dppe)[($\eta^4$-5-*exo*-Me$C_5H_5$)Fe$(CO)_2$].[19] The molecular connectivity of **4** is a ferrocenediyl-bridged tri-Fe complex, one end in the form of ($\eta^4$-5-*exo*-R$C_5H_5$)Fe$(CO)_2(PPh_3)$ and the other end in the form of $CpFe(CO)(PPh_3)C(O)R$, R = ferrocenediyl. Structurewise, **4** is very interesting with three Fe-centers in three different environments: the $\eta^4$-Fe is a pentacoordinate Fe(0), the ferrocenediyl-Fe is an Fe(II) metallocene, and the acyl-Fe is a hexacoordinate Fe(II).

**Mössbauer Study.** Table 1 lists the Mössbauer parameters of the three Fe-centers, as obtained at 80 K, on a constant-acceleration apparatus. The ferrocenyl-Fe in **1**−**4** and **7** is low-spin Fe(II) with isomer shifts $\delta$ ranging from 0.45 to 0.48 mm/s and quadrupole splitting $\Delta E_Q$ ranging from 2.48 to 2.56 mm/s, in agreement with the literature values, e.g., $\delta$ 0.45 mm/s, $\Delta E_Q$ 2.38 mm/s in $Cp_2Fe$, $\delta$ 0.45 mm/s, $\Delta E_Q$ 2.39 mm/s in ferrocenyl-fullerene, $\delta$ 0.42 mm/s, $\Delta E_Q$ 2.56 mm/s in $(\eta^5\text{-}C_5Me_5)_2Fe$,[20] and $\delta$ 0.468 mm/s, $\Delta E_Q$ 2.37 mm/s in oxidized ferrocenyl(phenyl)phosphine.[21] In **4**, the $\eta^4$-Fe, a distorted square-pyramidal Fe(0), has been assigned to the

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[19] Luh, L.-S.; Liu, L.-K. *Organometallics* **1995**, *14*, 1514.

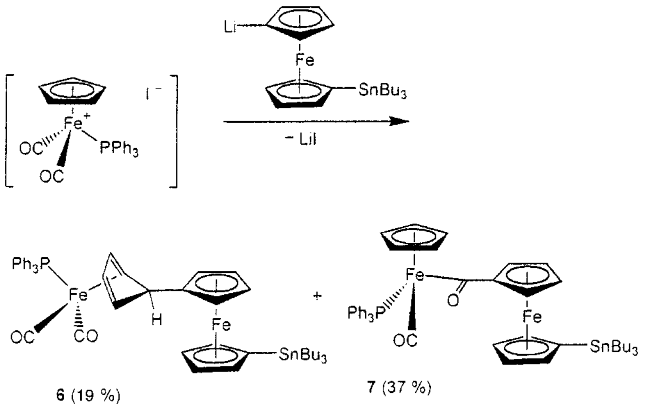
[20] Vertes, A.; Klencsar, Z.; Gal, M.; Kuzmann, E. *Fullerene Sci. Technol.* **1997**, *5*, 97.

[21] Durfey, D. A.; Kirss, R. U.; Frommen, C.; Feighery, W. *Inorg. Chem.* **2000**, *39*, 3506.

**Table 1. Mössbauer Parameters of the Fe-Centers in 1−4 and 7**

| | ferrocenyl-Fe(II) | | | ($\eta^4$-*exo*-$RC_5H_5$) Fe(0) | | | acyl-Fe(II) | | |
|---|---|---|---|---|---|---|---|---|---|
| compd | $\delta$ (mm/s) | $\Delta E_Q$ (mm/s) | | $\delta$ (mm/s) | $\Delta E_Q$ (mm/s) | | $\delta$ (mm/s) | $\Delta E_Q$ (mm/s) | |
| **1** | 0.48 | 2.48 | 45% | 0.09 | 1.49 | 55% | | | |
| **2** | 0.45 | 2.51 | 47% | | | | 0.19 | 1.51 | 53% |
| **3** | 0.45 | 2.56 | 34% | 0.08 | 1.55 | 66% | | | |
| **4** | 0.46 | 2.56 | 32% | 0.06 | 1.62 | 34% | 0.20 | 1.68 | 34% |
| **7** | 0.45 | 2.51 | 48% | | | | 0.20 | 1.67 | 52% |

**Scheme 4**



parameters of $\delta$ 0.06 mm/s and $\Delta E_Q$ 1.62 mm/s, whereas the half-sandwich acyl-Fe has been assigned to the parameters of $\delta$ 0.20 mm/s and $\Delta E_Q$ 1.68 mm/s. The whole set of Mössbauer parameters is self-explanatory in the table. If the $\eta^4$-Fe is indeed Fe(0), then it accounts for the smaller isomer shift value of the corresponding doublet, since the higher is the (s-type) electronic density on the Fe-atom and the lower is the observed isomer shift.

**Stepwise Reactions.** To further understand how the second-stage Fc-addition proceeds in the reaction of ($\eta^5$-$C_5H_4Li)_2$Fe(TMEDA), the Cp-ring without substitution in **1** and **2** must be lithiated. The transmetalation reaction of a $SnBu_3$-group by lithium, originally developed by Seyferth in organic synthesis, was employed.[22] In a stepwise manner, ($\eta^5$-$C_5H_4SnBu_3)_2$Fe permits an unsymmetrical functionalization of the ferrocene skeleton. Thus, ($\eta^5$-$C_5H_4SnBu_3)_2$Fe was treated with slightly greater than 1 molar equiv of *n*-BuLi and then introduced dropwise to the equimolar mixture of $CpFe(CO)_2I$ and $PPh_3$ in THF at −78 °C, using the same procedure as that used in the FcLi reaction. The reaction is shown in Scheme 4. It gave the Cp-ring addition isomer ($\eta^5$-$C_5H_4SnBu_3$)Fe[$\mu$,$\eta^5$:$\eta^4$-5-*exo*-(1′-$C_5H_4$)$C_5H_5$]Fe$(CO)_2(PPh_3)$ (**6**; 19%) and the CO-addition isomer ($\eta^5$-$C_5H_4SnBu_3$)Fe[$\mu$,$\eta^5$:*C*-$C_5H_4$C(O)]FeCp$(PPh_3)$(CO) (**7**; 37%). The product ratio is similar to that of the FcLi result. The $\eta^4$-Fe moieties of **1** and **6** are virtually spectroscopically identical [IR $\nu_{CO}$ 1967, 1908 $cm^{-1}$; $^1$H NMR $\delta$ 2.50, 3.49, 5.08 ($\eta^4$-*exo*-$RC_5H_5$); $^{31}$P NMR $\delta$ 74.0]. So are the Fe−acyl moieties of **2** and **7** [IR $\nu_{CO}$ 1914, 1583 $cm^{-1}$; $^1$H NMR $\delta$ 4.42 Cp; $^{31}$P NMR $\delta$ 76.4]. The results suggest that the $SnBu_3$ substituent on **6** and **7** does not have a significant electronic impact.

Compounds **6** and **7** were transmetalated to ($\eta^5$-$C_5H_4$Li)Fe[$\mu$,$\eta^5$:$\eta^4$-5-*exo*-(1′-$C_5H_4$)$C_5H_5$]Fe$(CO)_2(PPh_3)$ (**8**) and ($\eta^5$-$C_5H_4$Li)Fe[$\mu$,$\eta^5$:*C*-$C_5H_4$C(O)]FeCp(CO)$(PPh_3)$ (**9**), respectively, and each of them was transferred to the 1:1 mixture of $CpFe(CO)_2I$ and $PPh_3$ using a cannula. The reaction of **8** produced **3** (22%) and **4** (27%), whereas that of **9** yielded only **4** (53%) and no **5**. These results are shown in Schemes 5 and 6, respectively.

It is clear that, in the second Fc-additions, the pathway from **9** to **4** proceeds normally, but the pathway from **9** to **5** has been turned off. The preference of Fc-addition onto the Cp-ring could be rationalized in terms of a localization of the $Li^+$ cation in **9**. The drawing of **9** in Scheme 6 is in accordance with the molecular structure **2** (Figure 2), with the proton at C17 substituted by the $Li^+$ cation. In the close proximity of this Li-atom are the keto O-atom and carbonyl O-atom of the iron−acyl attached to the other Cp-ring. These supramolecular attractions create a resultant arrangement, which gives more than just a steric barrier for the reaction. When the electrophile [$CpFe(CO)_2PPh_3{}^+$] approaches **9** from its carbonyl CO end, the negative end of the CO dipole has a strong interaction with this $Li^+$ cation. The disturbance is so large that the orientation necessary between the nucleophilic carbanion of **9** and the antibonding orbital of the carbonyl of the electrophile could not be reached. And hence the Fc-addition at CO does not occur. On the other hand, when the electrophile [$CpFe(CO)_2PPh_3{}^+$] approaches **9** from its Cp-ring, the Cp-ring plane could be in a parallel position to the ferrocenyl Cp of **9**. The carbon atom of the Cp-ring in the electrophile is also preactivated to react with **9** according to the $S_N1$ mechanism. [CpFe$(CO)_2PPh_3{}^+$] has been reported to react with the bulky anion [$C(SiMe_3)_2(SiMe_2H)^-$] very effectively.[23]

In addition to the major products shown in Schemes 3−6, we found that there was an array of minor products, e.g., in the reaction employing 1,1′-dilithioferrocene:

the reduction−dimerization product $[CpFe(CO)_2]_2$ (4.5%),

the single Fc-addition products **1** (14%) and **2** (15%), and

the protonation product ferrocene (8.6%).

Similarly in the reaction of **8**, the minor products were $[CpFe(CO)_2]_2$ (11%) and **1** (37.3%), and in the reaction of **9**, $[CpFe(CO)_2]_2$ (13%) and **2** (13.3%). In reactions employing **8** and **9**, **1** and **2** were formed presumably when $H_2O$ was added to **8** and **9**. The presence of **8** and **9** at the end of the reaction is also consistent with a large steric barrier for the second-stage Fc-addition. In the reaction employing ($\eta^5$-$C_5H_4$Li)Fe($\eta^5$-$C_5H_4SnBu_3$), the minor products $[CpFe(CO)_2]_2$ (2%), **1** (8.4%), **2**

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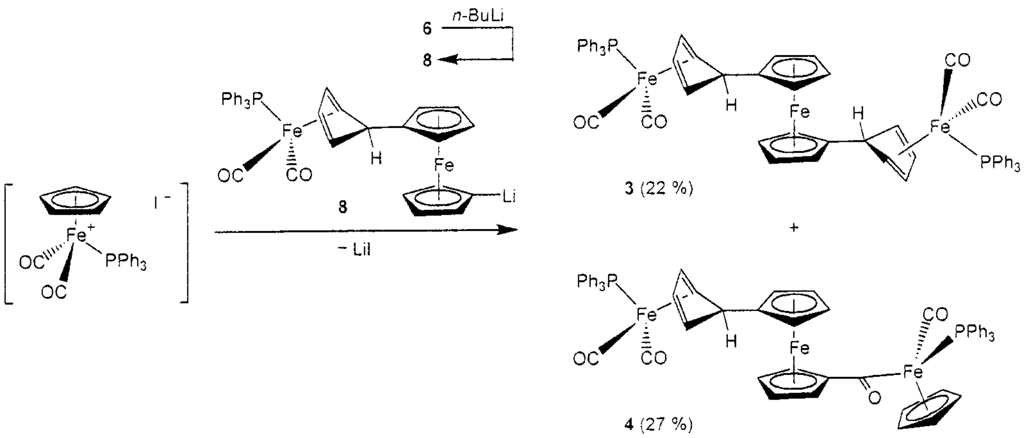
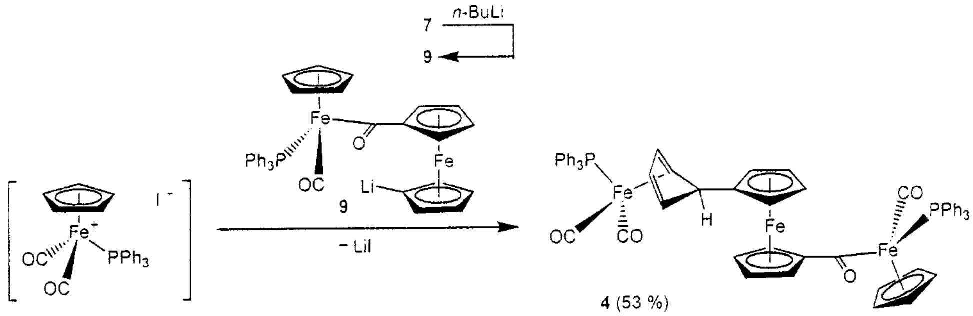
[22] (a) Helling, J. F.; Seyferth, D. *Chem. Ind. (London)* **1961**, 1568. (b) Seyferth, D.; Hofmann, H. P.; Burton, R.; Helling, J. F. *Inorg. Chem.* **1962**, *1*, 227. (c) Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 3583. (d) Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1962**, *84*, 361. (e) Seyferth, D.; Vaughn, L. G. *J. Am. Chem. Soc.* **1964**, *86*, 883.

[23] Liu, L.-K.; Luh, L.-S. *Organometallics* **2000**, *19*, 374.

**Scheme 5**



**Scheme 6**



(7.6%), **4** (3.6%), and ferrocene (6.4%) were observed. The presence of **1**, **2**, and **4** was believed to be due to the 20% excess of *n*-BuLi used in the transmetalation. In all of the reactions, noticeable amounts of $[CpFe(CO)_2]_2$ were observed, suggesting that the reductive process involved with $[CpFe(CO)_2PPh_3^+]$ and/or $[CpFe(CO)_2I]$ competes with the Fc-addition.

**Alternative Route to 3.** We have found that **3** could be prepared in an alternative way upon building the $\eta^4$-Fe arm first and then the ferrocene core. $C_5H_5Li$ is readily generated by deprotonation of $C_5H_6$ using *n*-BuLi. $C_5H_5Na$ is available from commercial sources. The reactivities of these two nucleophiles in the three-component reaction are similar. The Cp anion is aromatic during the three-component reaction. After the addition, it becomes a cyclopentadiene and is no longer aromatic, however. The $C_5H_5M$ (M = Na, Li) reaction gave two unseparated, isomeric $\eta^4$-Fe products (in about a 1:1 ratio, total yield 60%). One is $[\eta^4\text{-5-}exo\text{-}(1'\text{-}C_5H_5)C_5H_5]Fe(CO)_2PPh_3$ (**10a**), and the other is $[\eta^4\text{-5-}exo\text{-}(2'\text{-}C_5H_5)C_5H_5]Fe(CO)_2PPh_3$ (**10b**). The difference is only at the site of substitution on the cyclopentadiene that is not attached to Fe. There was no spectroscopic evidence for the third possible isomer $[\eta^4\text{-5-}exo\text{-}(5'\text{-}C_5H_5)C_5H_5]Fe(CO)_2PPh_3$ (**10c**). Compound **10c** is believed to be the immediate product that rearranges to **10a,b** by proton shifts on the cyclopentadiene. There was no observation of the CO-alkylation product either. Thus, the Cp anion is different from Fc anions and acts as a normal C-based nucleophile, preferring the Cp-ring alkylation in the three-component reaction.

The reaction of $C_5H_5M$ and $CpFe(CO)_2I$ in the presence of $PPh_3$ yielded the interesting extra bis($\eta^4$-Fe) products $(1',3'\text{-}C_5H_4)[(C_5H_5\text{-5-}exo\text{-}\eta^4)Fe(CO)_2PPh_3]_2$ (**11a**) and $(1',4'\text{-}C_5H_4)[(C_5H_5\text{-5-}exo\text{-}\eta^4)Fe(CO)_2PPh_3]$ (**11b**) in about a 1:1 ratio (total yield 16%). The 1′,2′-isomer was not observed, attributed to crowdedness. The reaction mechanism producing **11a,b** involves the addition of the Cp anion, which adds to the Cp-ring of $[CpFe(CO)_2PPh_3^+]$ to yield **10a,b**. These compounds are deprotonated on the cyclopentadiene that is not attached to Fe by the free Cp anion to form the conjugate base $[\eta^4\text{-5-}exo\text{-}(C_5H_4^-)C_5H_5]Fe(CO)_2PPh_3$ (**12**). The acid−base equilibrium is very quickly established (Scheme 7). Thus, also as a C-based nucleophile, **12** produces **11a,b**. At the same time, the Cp anion produces **10a,b** during later stages of the reaction. To compensate for this problem, the quantity of $C_5H_5M$ was increased to 3 equiv to maximize the yield of **10a,b**.

Indeed, **12** could be generated by treatment of pure **10a,b** with *n*-BuLi. When **12** reacted with $[CpFe(CO)_2PPh_3^+][I^-]$, the products were **11a,b**. When **12** reacted with $FeCl_3$ following a literature procedure,[24] the product was **3** (38.5%, not optimized, Scheme 8).

## Conclusion

The reaction of 1,1′-dilithioferrocene with the mixture of $CpFe(CO)_2I$ and $PPh_3$ is a one-pot operation in which overall two types of Fc-additions result in **4**, a ferrocenediyl-bridged tri-Fe complex. Complex **4** has been created with three different Fe-centers: a metallocene Fe(II), a square-pyramidal pentacoordinate Fe(0), and a half-sandwich acyl-Fe(II).

## Experimental Section

All manipulations were performed under an atmosphere of prepurified nitrogen with standard Schlenk techniques, and

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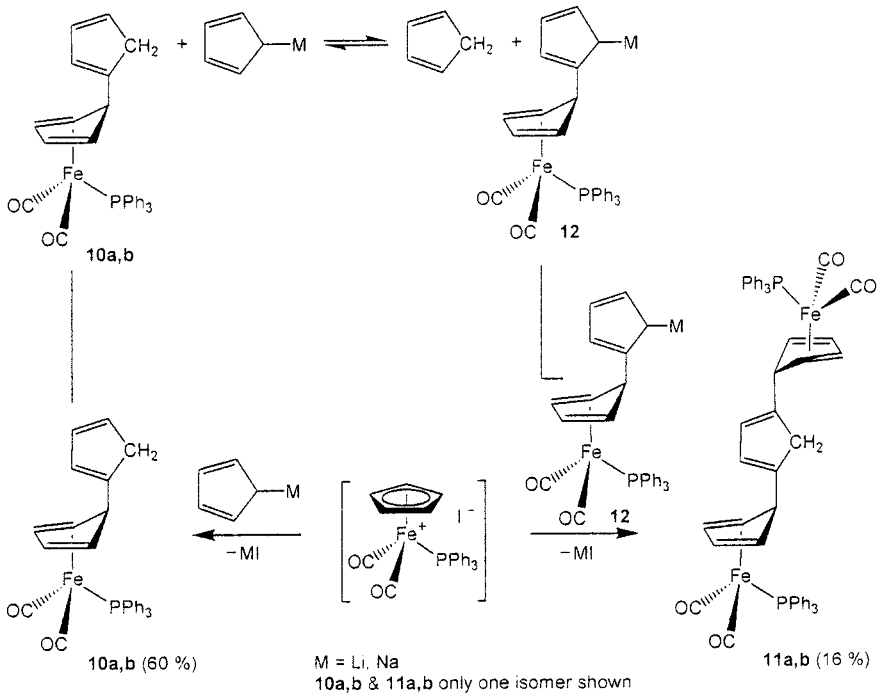
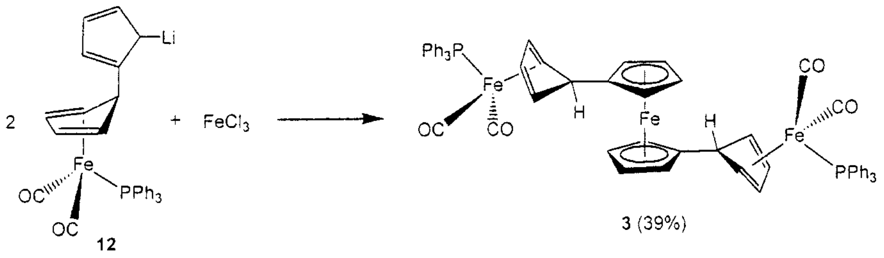
[24] Chung, T.-M.; Chung, Y. K. *Organometallics* **1992**, *11*, 2822.

**Scheme 7**



**Scheme 8**



all solvents were distilled from an appropriate drying agent.[25] Infrared spectra were recorded in CH$_2$Cl$_2$ using CaF$_2$ optics on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. The $^1$H and $^{13}$C NMR spectra were obtained on the Brucker AC-200/AC-300 spectrometers, in which chemical shifts were reported in $\delta$ values relative to the residual solvent resonance of CDCl$_3$ ($^1$H, $\delta$ 7.24; $^{13}$C, $\delta$ 77.0). The $^{31}$P NMR spectra were obtained on the Brucker AC-200/AC-300 spectrometers using 85% H$_3$PO$_4$ as an external standard ($^{31}$P, $\delta$ 0.00). Mass spectra were obtained on a VG system, model 70-250S, spectrometer. Microanalytical data were obtained with the use of a Perkin-Elmer 240C elemental analyzer independently operated by the Institute of Chemistry, Academia Sinica. Mössbauer spectra were obtained at $T = 80$ K with a Wissel spectrometer in constant-acceleration mode. Isomer shift values are given with respect to α-iron. The typical estimated error of the Mössbauer parameters is ±0.02 mm/s. CpFe(CO)$_2$I,[26] CpFe($\eta^5$-C$_5$H$_4$SnBu$_3$),[27] ($\eta^5$-C$_5$H$_4$Li)$_2$Fe(TMEDA),[28] and ($\eta^5$-C$_5$H$_4$SnBu$_3$)$_2$Fe[29] were prepared according to literature procedures. All reagents were obtained from commercial sources and used without further purification.

**Reaction of CpFe(CO)$_2$I and CpFe($\eta^5$-C$_5$H$_4$Li) in the Presence of PPh$_3$.** A solution of CpFe($\eta^5$-C$_5$H$_4$SnBu$_3$) (1.6 g, 3.4 mmol) in THF (30 mL) was treated with *n*-BuLi (1.6 M in *n*-hexane, 2.2 mL, 3.5 mmol) at −78 °C. After being stirred for 30 min, the resulting solution of CpFe($\eta^5$-C$_5$H$_4$Li) was cannula-transferred dropwise into the mixture of CpFe(CO)$_2$I (0.912 g, 3.0 mmol) and PPh$_3$ (0.786 g, 3.0 mmol) in THF (100 mL) at −78 °C. During addition, the color of the solution gradually changed from black to orange, accompanied by the formation of a yellow precipitate that redissolved by the end of the addition. After it had been stirred overnight, the solution was quenched with water (200 mL) and then extracted with Et$_2$O (100 mL × 2). The combined organic layer was dried over MgSO$_4$ before being evaporated to dryness under vacuum. The oily residue was purified through a SiO$_2$ chromatography column with 1:10 EtOAc/hexane as eluent, followed by removal of the solvents, to give, according to the order of appearance, the colorless SnBu$_4$, the yellow ferrocene (0.048 g), the yellow **1** (0.46 g, 25%), the purple [CpFe(CO)$_2$]$_2$ (0.032 g, 6.0%), and the orange **2** (0.88 g, 47%).

**1**: IR (CH$_2$Cl$_2$, cm$^{-1}$) 1967 (s), 1908 (s); $^1$H NMR (CDCl$_3$) $\delta$ 2.49 (br, 2H, $-$CH=C*H*CHC$_5$H$_4-$), 3.46 (br, 1H, $-$CH=CHC*H*C$_5$H$_4-$), 3.78, 3.87 (br, 2H × 2, C$_5$H$_4$), 4.01 (s, 5H, C$_5$H$_5$), 5.09 (br, 2H, $-$C*H*=CHCHC$_5$H$_4-$), 7.31−7.45 (m, 15H, Ph); $^{13}$C NMR (CDCl$_3$) $\delta$ 54.6 (s, $-$CH=CH*C*HC$_5$H$_4-$), 55.7 (s, $-$CH=*C*HCHC$_5$H$_4-$), 66.1, 70.0 (s, C$_5$H$_4$), 68.0 (s, C$_5$H$_5$), 82.0 (s, $-$*C*H=CHCHC$_5$H$_4-$), 95.3 (s, C$_5$H$_{4,ipso}$), 128.1, 128.3, 129.7, 132.9, 133.1, 136.0, 136.5 (m, Ph), 219.5 (d, $^2J_{PC} = 12.4$ Hz, CO); $^{31}$P NMR (CDCl$_3$) $\delta$ 74.1 (s); MS (*m*/*z*) M$^+$ 624 (parent

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(26) (a) Dombek, B. D.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, 345. (b) Meyer, T. J.; Johnson, E. C.; Winterton, N. *Inorg. Chem.* **1971**, *10*, 1673. (c) *Inorg. Synth.* **1971**, *12*, 36. (d) *Inorg. Synth.* **1963**, *7*, 110.

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(29) Dodo, T.; Suzuki, H.; Takiguchi, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 288.

ion). Anal. Calcd for $C_{35}H_{29}Fe_2O_2P$: C, 67.34; H, 4.68. Found: C, 67.44; H, 4.87.

**2**: IR ($CH_2Cl_2$, cm$^{-1}$) 1915 (s), 1583 (m); $^1$H NMR ($CDCl_3$) $\delta$ 3.97, 4.43 (s, 5H × 2, $C_5H_5$), 4.16, 4.20, 4.34, 4.55 (br, 1H × 4, $C_5H_4$), 7.31−7.52 (m, 15H, Ph); $^{13}$C NMR ($CDCl_3$) $\delta$ 68.3, 68.6, 68.8, 69.7 (s × 4, $C_5H_4$), 69.2, 85.3 (s, $C_5H_5$ × 2), 97.3 (s, $C_5H_{4,ipso}$), 127.9, 128.0, 129.5, 133.6, 136.5, 137.1 (m, Ph), 221.3 (d, $^2J_{PC} = 33$ Hz, CO), 270.3 (d, $^2J_{PC} = 22$ Hz, C(O)$C_5H_4$); $^{31}$P NMR ($CDCl_3$) $\delta$ 76.4 (s); MS (*m*/*z*) M$^+$ 624 (parent ion). Anal. Calcd for $C_{35}H_{29}Fe_2O_2P$: C, 67.34; H, 4.68. Found: C, 67.43; H, 4.86.

**Reaction of CpFe(CO)$_2$I and ($\eta^5$-C$_5$H$_4$Li)$_2$Fe(TMEDA) in the Presence of PPh$_3$.** The mixture of CpFe(CO)$_2$I (0.77 g, 2.5 mmol) and PPh$_3$ (0.65 g, 2.5 mmol) was dissolved in THF (100 mL) at −78 °C. ($\eta^5$-C$_5$H$_4$Li)$_2$Fe(TMEDA) (0.395 g, 1.26 mmol) in THF (50 mL) was then added dropwise via a dropping funnel. During the addition, the color of the solution gradually changed from black to orange, accompanied by the formation of a yellow precipitate that redissolved by the end of the reaction. After complete addition, the solution was warmed to room temperature and stirred overnight before the mixture was quenched with water (200 mL) and extracted with Et$_2$O (100 mL × 2). The combined organic layer was dried over MgSO$_4$ and then evaporated to dryness under vacuum. The oil-like residue was purified by SiO$_2$ column chromatography with 1:10 to 1:3 EtOAc/hexane as eluent to give, after solvent removal, according to the order of appearance, yellow ferrocene (0.02 g, 8%), yellow **1** (0.11 g, 14%), yellow Fe{[$\mu,\eta^5:\eta^4$-(5-*exo*-C$_5$H$_4$)C$_5$H$_5$]Fe(CO)$_2$(PPh$_3$)}$_2$ (**3**; 0.17 g, 13%), purple [CpFe(CO)$_2$]$_2$ (0.02 g, 4%), orange **2** (0.12 g, 15%), and orange CpFe(CO)(PPh$_3$)[$\mu$,*C*:$\eta^5$-C(O)C$_5$H$_4$]Fe[$\mu,\eta^5:\eta^4$-(5-*exo*-C$_5$H$_4$)C$_5$H$_5$]Fe(CO)$_2$(PPh$_3$) (**4**; 0.67 g, 50%).

**3**: IR ($CH_2Cl_2$, cm$^{-1}$) 1967 (s), 1908 (s); $^1$H NMR ($CDCl_3$) $\delta$ 2.43 (br, 2H, $-CH{=}C\mathit{H}CHC_5H_4-$), 3.36 (br, 1H, $-CH{=}CHC\mathit{H}C_5H_4-$), 3.61, 3.72 (br, 2H × 2, $C_5H_4$), 5.05 (br, 2H, $-C\mathit{H}{=}CHCHC_5H_4-$), 7.36−7.41 (m, 15H, Ph); $^{13}$C NMR ($CDCl_3$) $\delta$ 54.5 (s, $-CH{=}CH\mathit{C}HC_5H_4-$), 55.9 (s, $-CH{=}\mathit{C}HCHC_5H_4-$), 66.3, 67.3 (s, $C_5H_4$), 82.0 (s, $-\mathit{C}H{=}CHCHC_5H_4-$), 95.1 (s, $C_5H_{4,ipso}$), 128.1, 128.3, 129.6, 132.9, 133.1, 135.9, 136.6 (m, Ph), 219.5 (d, $^2J_{PC} = 14$ Hz, CO); $^{31}$P NMR ($CDCl_3$) $\delta$ 74.1 (s); MS (*m*/*z*) M$^+$ 1062 (parent ion). Anal. Calcd for $C_{60}H_{48}Fe_3O_4P_2$: C, 67.82; H, 4.55. Found: C, 67.57; H, 4.70.

**4**: IR ($CH_2Cl_2$, cm$^{-1}$) 1967 (s), 1909 (s), 1583 (m); $^1$H NMR ($CDCl_3$) $\delta$ 2.42, 2.46 (br, 1H × 2, $-CH{=}C\mathit{H}CHC_5H_4-$), 3.36 (br, 1H, $-CH{=}CHC\mathit{H}C_5H_4-$), 3.57, 3.60, 3.62, 3.72, 4.00, 4.03, 4.21, 4.34 (b, 1H × 8, $C_5H_4$ × 2), 4.39 (s, 5H, $C_5H_5$), 5.02, 5.07 (b, 1H × 2, $-C\mathit{H}{=}CHCHC_5H_4-$), 7.31−7.50 (m, 30H, Ph); $^{13}$C NMR ($CDCl_3$) $\delta$ 55.0 (s, $-CH{=}CH\mathit{C}HC_5H_4-$), 56.0, 56.9 (s × 2, $-CH{=}\mathit{C}HCHC_5H_4-$), 67.5, 69.2, 69.4, 69.5, 70.0 (s, $C_5H_4$ × 2), 82.3, 82.5 (s × 2, $-\mathit{C}H{=}CHCHC_5H_4-$), 85.5 (s, $C_5H_5$), 96.1, 97.9 (s, $C_5H_{4,ipso}$ × 2), 128.4, 128.5, 129.6, 129.8, 133.3, 133.4, 134.2, 136.7, 137.1, 137.5, 138.0 (m, Ph), 219.9 (d, $^2J_{PC} = 14.5$ Hz, CO), 220.3 (d, $^2J_{PC} = 13.6$ Hz, CO), 221.8 (d, $^2J_{PC} = 33$ Hz, CO), 265.7 (d, $^2J_{PC} = 20.6$ Hz, C(O)$C_5H_4$); $^{31}$P NMR ($CDCl_3$) $\delta$ 74.7 (s), 77.4 (s); MS (*m*/*z*) M$^+$ 1062 (parent ion). Anal. Calcd for $C_{60}H_{48}Fe_3O_4P_2$: C, 67.82; H, 4.55. Found: C, 68.12; H, 4.69.

**Reaction of CpFe(CO)$_2$I and ($\eta^5$-C$_5$H$_4$SnBu$_3$)Fe($\eta^5$-C$_5$H$_4$Li) in the Presence of PPh$_3$.** At −78 °C, ($\eta^5$-C$_5$H$_4$-SnBu$_3$)$_2$Fe (3.82 g, 5.0 mmol) in THF (50 mL) was treated with *n*-BuLi (1.6 M in hexane, 3.75 mL, 6.0 mmol) and the reaction mixture was stirred for 1 h. The resulting lithiated solution of ($\eta^5$-C$_5$H$_4$SnBu$_3$)Fe($\eta^5$-C$_5$H$_4$Li) was then transferred under nitrogen via a cannula dropwise to the mixture of CpFe(CO)$_2$I (1.52 g, 5.0 mmol) and PPh$_3$ (1.31 g, 5.0 mmol) in THF (100 mL) at −78 °C. After complete addition, the orange solution was warmed to room temperature and then stirred overnight before it was quenched with water (100 mL) and extracted with Et$_2$O (100 mL × 2). The combined organic layer was dried over MgSO$_4$ and then evaporated to dryness under vacuum. Purification by SiO$_2$ column chromatography with 1:9 EtOAc/hexane as eluent gave, after solvent removal, according to the order of appearance, SnBu$_4$, orange oil CpFe($\eta^5$-C$_5$H$_4$SnBu$_3$), yellow ferrocene (0,06 g, 6.4%), yellow **1** (0.26 g, 8.4%), orange ($\eta^5$-C$_5$H$_4$SnBu$_3$)Fe[$\mu,\eta^5:\eta^4$-(5-*exo*-C$_5$H$_4$)C$_5$H$_5$]Fe(CO)$_2$(PPh$_3$) (**6**; 0.88 g, 19%), orange ($\eta^5$-C$_5$H$_4$SnBu$_3$)Fe[$\mu,\eta^5$:*C*-C$_5$H$_4$C(O)]FeCp(CO)(PPh$_3$) (**7**; 1.69 g, 37%), purple [CpFe(CO)$_2$]$_2$ (0.02 g, 1%), orange **2** (0.24 g, 7.6%), and orange **4** (0.19 g, 3.6%).

**6**: IR ($CH_2Cl_2$, cm$^{-1}$) 1967 (s), 1908 (s); $^1$H NMR ($CDCl_3$) $\delta$ 0.83−1.59 (m, 27H, Bu), 2.50 (br, 2H, $-CH{=}C\mathit{H}CHC_5H_4-$), 3.47 (br, 1H, $-CH{=}CHC\mathit{H}C_5H_4-$), 3.73, 3.76, 3.80, 4.16 (br, 2H × 4, $C_5H_4$ × 2), 5.08 (br, 2H, $-C\mathit{H}{=}CHCHC_5H_4-$), 7.30−7.45 (m, 15H, Ph); $^{13}$C NMR ($CDCl_3$) $\delta$ 10.2, 10.7, 27.4, 29.2 (s, Bu), 54.6 (s, $-CH{=}CH\mathit{C}HC_5H_4-$), 55.7 (s, $-CH{=}\mathit{C}HCHC_5H_4-$), 66.0, 67.1, 70.7, 74.4 (s, $C_5H_4$ × 2), 82.0 (s, $-\mathit{C}H{=}CHCHC_5H_4-$), 95.1 (s, $C_5H_{4,ipso}$), 128.1, 128.2, 129.6, 132.9, 133.0, 136.0, 136.5 (m, Ph), 219.5 (d, $^2J_{PC} = 14$ Hz, CO); $^{31}$P NMR ($CDCl_3$) $\delta$ 74.0 (s); MS (*m*/*z*) M$^+$ 913 (parent ion). Anal. Calcd for $C_{47}H_{55}Fe_2O_2PSn$: C, 61.81; H, 6.07. Found: C, 61.63; H, 6.03.

**7**: IR ($CH_2Cl_2$, cm$^{-1}$) 1914 (s), 1583 (m); $^1$H NMR ($CDCl_3$) $\delta$ 0.85−1.61 (m, 27H, Bu), 3.83, 3.96, 4.00, 4.01, 4.06, 4.29, 4.50 (br, 1H × 8, $C_5H_4$ × 2), 4.42 (s, 5H, $C_5H_5$), 7.31−7.52 (m, 15H, Ph); $^{13}$C NMR ($CDCl_3$) $\delta$ 10.2, 13.7, 27.4, 29.3 (s, Bu), 68.1, 68.7, 69.0, 69.5, 72.8, 73.1, 74.8, 75.0 (s, $C_5H_4$ × 2), 85.2 (s, $C_5H_5$), 97.0, 97.1 (s, $C_5H_{4,ipso}$ × 2), 127.8, 128.0, 129.5, 132.8, 133.1, 133.5, 133.7, 136.3, 137.2 (m, Ph), 221.2 (d, $^2J_{PC} = 33$ Hz, CO), 270.2 (d, $^2J_{PC} = 21$ Hz, C(O)$C_5H_4$); $^{31}$P NMR ($CDCl_3$) $\delta$ 76.4 (s); MS (*m*/*z*) M$^+$ 913 (parent ion). Anal. Calcd for $C_{47}H_{55}Fe_2O_2PSn$: C, 61.81; H, 6.07. Found: C, 62.40; H, 6.00.

**Reaction of CpFe(CO)$_2$I and 8 in the Presence of PPh$_3$.** At −78 °C, complex **6** (0.913 g, 1.0 mmol) in THF (30 mL) was treated with *n*-BuLi (1.6 M in hexane, 0.75 mL, 1.2 mmol) and the reaction mixture was stirred for 1 h. The resulting lithiated solution of ($\eta^5$-C$_5$H$_4$Li)Fe[$\mu,\eta^5:\eta^4$-(5-*exo*-C$_5$H$_4$)C$_5$H$_5$]Fe(CO)$_2$-(PPh$_3$) (**8**) was transferred under nitrogen via a cannula dropwise to the mixture of CpFe(CO)$_2$I (0.304 g, 1.0 mmol) and PPh$_3$ (0.262 g, 1.0 mmol) in THF (50 mL) at −78 °C. After complete addition, the orange solution was warmed to room temperature and then stirred overnight before the mixture was quenched with water (100 mL) and extracted with Et$_2$O (50 mL × 2). The combined organic layer was dried over MgSO$_4$ and then evaporated to dryness under vacuum. The oil-like residue was purified by SiO$_2$ column chromatography with 1:9 EtOAc/hexane as eluent, followed by removal of the solvents to give, according to the order of appearance, SnBu$_4$, yellow **1** (0.23 g, 37%), purple [CpFe(CO)$_2$]$_2$ (0.02 g, 11%), yellow **3** (0.24 g, 22%), and orange **4** (0.28 g, 27%).

**Reaction of CpFe(CO)$_2$I and 9 in the Presence of PPh$_3$.** At −78 °C, complex **7** (1.60 g, 1.75 mmol) in THF (30 mL) was treated with *n*-BuLi (1.6 M in hexane, 1.31 mL, 2.1 mmol) and stirred for 1 h. The resulting lithiated solution of ($\eta^5$-C$_5$H$_4$Li)-Fe[$\mu,\eta^5$:*C*-C$_5$H$_4$C(O)]FeCp(CO)(PPh$_3$) (**9**) was then transferred under nitrogen via a cannula dropwise to the mixture of CpFe(CO)$_2$I (0.532 g, 1.75 mmol) and PPh$_3$ (0.459 g, 1.75 mmol) in THF (50 mL) at −78 °C. After complete addition, the orange solution was warmed to room temperature and then stirred overnight before it was quenched with water (100 mL) and extracted with ether (50 mL × 2). The combined organic layer was dried over MgSO$_4$ and then evaporated to dryness under vacuum. The oil-like residue was purified by SiO$_2$ column chromatography with 1:8 EtOAc/hexane as eluent to give, after solvent removal, according to the order of appearance, orange oil SnBu$_4$, purple [CpFe(CO)$_2$]$_2$ (0.04 g, 13%), orange **2** (0.15 g, 13%), and orange **4** (0.98 g, 53%).

**Reaction of CpFe(CO)$_2$I and C$_5$H$_5$Na in the Presence of PPh$_3$.** A 3 equiv sample of C$_5$H$_5$Na (15 mL, 2 M) was added dropwise to a solution of CpFe(CO)$_2$I (3.04 g, 10 mmol) and PPh$_3$ (2.62 g, 10 mmol) in 150 mL of THF at −78 °C. The color of the solution changed from black to orange-red during the addition. After being warmed to room temperature, the solution was quenched with water (200 mL) and extracted with diethyl ether (100 mL × 2). The organic layer was combined with the ether extracts, and this solution was dried over $MgSO_4$ and then evaporated to dryness under vacuum. The oily residue was purified by chromatography using a $SiO_2$ column with 1:7 EtOAc/hexane as the eluent. The following three bands separated in the order of appearance: unreacted $PPh_3$, yellow $[\eta^4\text{-5-}exo\text{-}(1'\text{-}C_5H_5)C_5H_5]Fe(CO)_2PPh_3$ and $[\eta^4\text{-5-}exo\text{-}(2'\text{-}C_5H_5)C_5H_5]Fe(CO)_2PPh_3$ (**10a,b**; 2.95 g, 60%), and yellow $(1',3'\text{-}C_5H_4)[(C_5H_5\text{-5-}exo\text{-}\eta^4)Fe(CO)_2PPh_3]_2$ and $(1',4'\text{-}C_5H_4)\text{-}[(C_5H_5\text{-5-}exo\text{-}\eta^4)Fe(CO)_2PPh_3]$ (**11a,b**; 0.75 g, 16%).

**10a**: IR ($CH_2Cl_2$, $cm^{-1}$) 1969 (s), 1913 (s); $^1H$ NMR ($C_6D_6$) $\delta$ 2.62 (br, 2H, $-CH{=}CHCH(C_5H_5)-$), 2.56 (br, 2H, $C_5H_5$), 3.87 (br, 1H, $-CH{=}CHCH(C_5H_5)-$), 4.92 (br, 2H, $-CH{=}CHCH(C_5H_5)-$), 5.81 (br, 1H, $C_5H_5$), 6.02 (d, 1H, $J_{HH} = 1.3$ Hz, $C_5H_5$), 6.27 (d, 1H, $J_{HH} = 1.9$ Hz, $C_5H_5$), 6.97−7.50 (m, 15H, Ph); $^{31}P$ NMR ($C_6D_6$) $\delta$ 73.8 (s). **10b**: $^1H$ NMR ($C_6D_6$) $\delta$ 2.43 (br, 2H, $-CH{=}CHCH(C_5H_5)-$), 2.56 (br, 2H, $C_5H_5$), 3.92 (br, 1H, $-CH{=}CHCH(C_5H_5)-$), 5.00 (br, 2H, $-CH{=}CHCH(C_5H_5)-$), 5.57 (br, 1H, $C_5H_5$), 6.04 (d, 1H, $J_{HH} = 1.2$ Hz, $C_5H_5$), 6.29 (d, 1H, $J_{HH} = 1.8$ Hz, $C_5H_5$), 6.97−7.50 (m, 15H, Ph). Anal. Calcd for $C_{30}H_{25}FeO_2P$ (mixture of **10a,b**): C, 71.44; H, 5.00. Found: C, 71.76; H, 5.08.

**11a**: IR ($CH_2Cl_2$, $cm^{-1}$) 1971 (s), 1911 (s); $^1H$ NMR ($C_6D_6$) $\delta$ 2.29 (br, 2H, $C_5H_4$), 2.52 (br, 4H, $-CH{=}CHCH(C_5H_5)-$), 3.80 (br, 2H, $-CH{=}CHCH(C_5H_5)-$), 4.90 (br, 4H, $-CH{=}CHCH(C_5H_5)-$), 5.57 (br, 2H, $C_5H_4$), 6.95−7.52 (m, 15H, Ph); $^{31}P$ NMR ($C_6D_6$) $\delta$ 73.8 (s). **11b**: $^1H$ NMR ($C_6D_6$) $\delta$ 2.16 (br, 2H, $C_5H_4$), 2.58 (br, 4H, $-CH{=}CHCH(C_5H_5)-$), 3.76 (br, 2H, $-CH{=}CHCH(C_5H_5)-$), 5.00 (br, 4H, $-CH{=}CHCH(C_5H_5)-$), 5.31 (br, 1H, $C_5H_4$), 5.60 (br, 1H, $C_5H_4$), 6.95−7.52 (m, 15H, Ph). Anal. Calcd for $C_{55}H_{44}Fe_2O_4P_2$ (mixture of **11a,b**): C, 70.08; H, 4.71. Found: C, 70.65; H, 5.07.

**Reactions of 12.** (a) *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol) was added dropwise via syringe to a yellow solution of a mixture of **10a,b** (1.52 g, 3.0 mmol) in 20 mL of THF at 0 °C. The color of the solution changed from yellow to orange-red. After being stirred for 1 h, the in situ generated lithium reagent was cannula-transferred to the suspension of $[CpFe(CO)_2PPh_3^+][I^-]$ in 50 mL of THF at −78 °C. The solution was then warmed to room temperature over 2 h. The resulting brown solution was quenched with water (200 mL) and extracted with diethyl ether (100 mL × 2). The organic layer, combined with the ether extracts, was dried over $MgSO_4$ and then evaporated to dryness under vacuum. The oily residue was purified by chromatography using a $SiO_2$ column with 1:2.5 $CH_2Cl_2$/hexane as eluent. The following three bands separated in the order of appearance: $PPh_3$, unreacted **10a,b**, and the yellow **11a,b** (1.25 g, 44%).

(b) A solution of **10a,b** (0.756 g, 1.5 mmol) in THF (20 mL) was treated with *n*-BuLi (1.6M in *n*-hexane, 1.0 mL, 1.6 mmol) at 0 °C. After the solution was stirred for 1 h, anhydrous $FeCl_3$ (0.146 g, 0.90 mmol) was added in one portion via an angled tube. The mixture was then refluxed for 15 h. The solvent was removed under vacuum to give a black residue, which was purified by $SiO_2$ column chromatography with 1:2 $CH_2Cl_2$/hexane as eluent to give yellow **3** (0.307 g, 38%) and some unidentified compounds.

**X-ray Structure Analysis.** Single crystals of **1** and **2** were grown by slow evaporation from $CH_2Cl_2$/hexane. The X-ray diffraction measurements were performed on a Nonius CAD-4 automated diffractometer, using graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.710\,69$ Å). Twenty-five high-angle reflections were used in a least-squares fit to obtain accurate cell constants. Diffraction intensities were collected up to $2\theta < 50°$ using the $\theta/2\theta$ scan technique, with background counts made for half the total scan time on each side of the peak. Three standard reflections, measured every hour, showed no significant decrease in intensity during data collection. The reflections with $I_o > 2.0\sigma(I_o)$ were judged as observations and were used for solution and structure refinement. Data were corrected for Lorentz-polarization factors. An empirical absorption correction based on series of $\Psi$ scans was applied to the data. The structure was solved by direct methods[30] and refined by a full-matrix least-squares routine[31] with anisotropic thermal parameters for all non-hydrogen atoms (weight $= 1/[\sigma(F_o)^2 + 0.0001(F_o)^2]$, $\sigma(F_o)$ from counting statistics). All hydrogen atoms were placed isotropically at idealized positions (C−H = 1.00 Å) and fixed in the calculation. Atomic scattering factor curves $f_o$, $\Delta f'$, and $\Delta f''$ of Fe, P, O, and C and $f_o$ of H were taken from the *International Tables for X-ray Crystallography*.[32]

Crystal data for **1**: yellow prism (0.38 × 0.19 × 0.13 mm), $C_{36}H_{31}Cl_2Fe_2O_2P$, fw = 709.21, monoclinic, space group $P2_1/c$, $a = 10.205(1)$ Å, $b = 14.914(1)$ Å, $c = 20.841(2)$ Å, $\beta = 90.29(1)°$, $V = 3171.8(4)$ Å$^3$, $Z = 4$, F(000) = 1460.29, $D_{calcd} = 1.485$ g cm$^{-3}$, $\mu = 1.17$ mm$^{-1}$, $hkl$ $-10 \le h \le +10$, $0 \le k \le +16$, $0 \le l \le +22$, $R = 0.051$, $R_w = 0.072$ for 2546 out of 4128 reflections.

Crystal data for **2**: orange prism (0.44 × 0.22 × 0.22 mm), $C_{35}H_{29}Fe_2O_2P$, fw = 624.27, monoclinic, space group $P2_1/c$, $a = 7.852(2)$ Å, $b = 34.484(4)$ Å, $c = 10.548(1)$ Å, $\beta = 103.62(2)°$, $V = 2775.6(9)$ Å$^3$, $Z = 4$, $F(000) = 1287.80$, $D_{calcd} = 1.494$ g cm$^{-3}$, $\mu = 1.13$ mm$^{-1}$, $hkl$ $-9 \le h \le +9$, $0 \le k \le +40$, $0 \le l \le +12$, $R = 0.040$, $R_w = 0.044$ for 2757 out of 4875 reflections.

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**Supporting Information Available:** For the structures of **1** and **2**, listing of crystallographic data, positional and thermal parameters, bond distances and angles, and torsion angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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