

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ with Anionic Bidentate Phosphine Ligands $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{NHLi})$ or $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{OLi})$

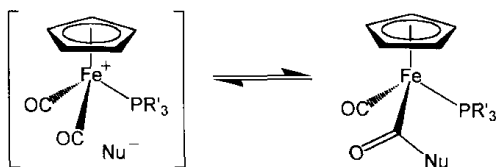
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The *o*-substituted hybrid phenylphosphines, $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{NH}_2)$ and $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{OH})$, could be deprotonated with LDA or *n*-BuLi to yield $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{NHLi})$ and $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{OLi})$, respectively. When added to a solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ at room temperature, these two lithiated reagents produce a chelated neutral complex **1** $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{C}(\text{O})\text{NH}(o\text{-C}_6\text{H}_4)\text{PPh}_2\text{-C}, P\text{-}\eta^2]$ for the former and mainly a zwitterionic complex **2**, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^+(\text{CO})_2[\text{PPh}_2(o\text{-C}_6\text{H}_4\text{O}^-)]$ for the latter. Complex **1** could easily be protonated and then decarbonylated to give **4** $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\{\text{NH}_2(o\text{-C}_6\text{H}_4)\text{PPh}_2\text{-N}, P\text{-}\eta^2\}^+]$. Complexes **1** and **4-I** have been crystallographically characterized with X-ray diffraction.

INTRODUCTION

Metal-bound carbon monoxide is generally reactive towards nucleophiles. Neutral metal carbonyls accept strong nucleophiles such as alkyllithium reagents to produce anionic metal acyl complexes. Many of these acylate complexes are stable enough for isolation and for further manipulation. Cationic $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)^+]$ reacts readily with anionic oxygen and sulfur nucleophiles to form carboxyalkyl and thiocarboxyalkyl compounds of the type $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{C}(\text{O})\text{Nu})(\text{PPh}_3)]$ where Nu = OMe, OPh, SMe, SPh. These neutral metalloester or metallothioester compounds are very interesting because they could coexist with corresponding cationic salts of the type $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)^+][\text{Nu}^-]$ (Scheme I).

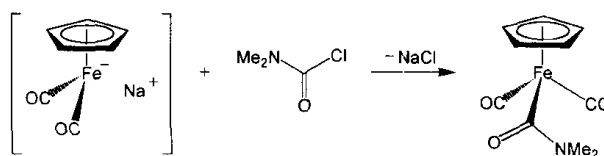
Scheme I



From the IR spectroscopic results, the thiocarboxyalkyl compounds are likely ionic thiolate salts whereas the carboxyalkyl compounds are more likely neutral metalloesters, especially for Nu = OMe.¹ For Nu = OPh, the conversion from $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{C}(\text{O})\text{OPh})(\text{PPh}_3)]$ to $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)^+][\text{OPh}^-]$ is extensive and seems to be a major pathway leading to the degradation of the carboxyphenyl complexes. This paper reports the use of bidentate P,O-anion $[\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{O}^-)]$, replacing $[\text{OPh}^-]$ and PPh_3 , in order to keep the oxygen nucleophile in close proximity of the CO ligand and hence avoid the degradation, taking advantage of the chelating effect.

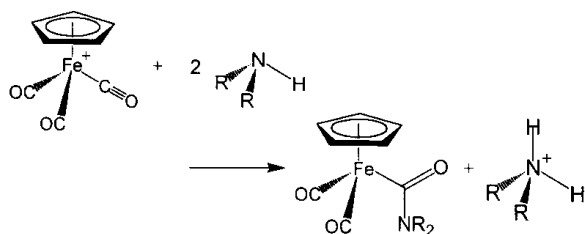
The first known (carbamoyl)iron complex was prepared by King in 1963 (Scheme II).² Later Angelici et al. reported the reaction of amines with $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$ to result in $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{O})\text{NHR})]$ via a reversed polarity.³

Scheme II



An amine attacks metal carbonyls, particularly the more reactive cationic ones, to produce carbamoyl complexes after the deprotonation by amine itself, as shown in Scheme III, which represents by far the most general method of preparation. Although NH_3 and primary and secondary alkylamines react smoothly, aniline and other aromatic amines have not yet been observed to undergo similar reactions.⁴ $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)^+]$ was also found to react with primary and secondary alkylamines, under more forcing conditions (e.g., with *xs* K_2CO_3), to give (carbamoyl)iron compounds of the type $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{C}(\text{O})\text{NHR})(\text{PPh}_3)]$.⁵ The chance of incorporating an aromatic amine into the metal carbamoyl species could be increased when coordinating P, N atoms are tethered. Following this strategy, this paper reports

Scheme III



also the rare preparation of the metal carbamoyl complex containing an anilide group.

EXPERIMENTAL

General

All manipulations were performed under an atmosphere of pre-purified nitrogen with standard Schlenk techniques, and all solvents were distilled from an appropriate drying agent.⁶ IR spectra were recorded in CH₃CN or CH₂Cl₂ using CaF₂ optics on a Perkin-Elmer 882 spectrophotometer. The ¹H NMR and ³¹P NMR spectra were obtained on Bruker AC200/AC300 spectrometers, with ¹H chemical shifts reported in δ values, downfield positive, relative to the residual solvent resonance of CDCl₃ (δ 7.24) or CD₃CN (δ 1.93) and ³¹P chemical shifts using 85% H₃PO₄ as an external standard (δ 0.00). Micro-analytical data were obtained with the use of a Perkin-Elmer 240C elemental analyzer independently operated by the Institute of Chemistry, Academia Sinica. All reagents were obtained from commercial sources and used without further purification. (η⁵-C₅H₅)Fe(CO)₂I,⁷ PPh₂(*o*-C₆H₄NH₂),⁸ PPh₂(*o*-C₆H₄OH)⁸ and PPh₂(*o*-C₆H₄OMe)⁹ were prepared according to the literature procedures.

Preparation of (η⁵-C₅H₅)Fe(CO)[C(O)NH(*o*-C₆H₄)PPh₂-C,*P*-η²] **1**

Under N₂ atmosphere, PPh₂(*o*-C₆H₄NH₂) (300 mg, 1.1 mmol) was dissolved in THF (20 mL) and kept stirring at 0 °C. To this solution was slowly added *n*-BuLi (0.7 mL 1.6 M in *n*-hexane, 1.1 mmol) or LDA (0.75 mL 1.5 M in cyclohexane, 1.1 mmol). The solution was then allowed to return to room temperature and kept stirring for 30 min. This solution was then added dropwise into a round-bottomed flask containing (η⁵-C₅H₅)Fe(CO)₂I (304 mg, 1 mmol) in THF (20 mL) at 0 °C. The cold bath was taken away to allow the temperature of the mixture to rise to room temperature. A yellow colored solution formed. After the reaction mixture was stirred for 1 h, the solvent was reduced to a small quantity un-

der vacuum. Chromatographic purification of the residue on a short column of silica gel or alumina with CH₂Cl₂ as an eluent yielded a crude product that was recrystallized from CH₂Cl₂/*n*-hexane to give 350 mg of **1** as fine, yellow crystals, yield 77%.

1: IR (CH₂Cl₂) ν_{CO} 1940 (s), 1543 (s) cm⁻¹; ³¹P{¹H} NMR (CDCl₃) δ 71.5 (s); ¹H NMR (CDCl₃) δ 7.6-6.5 (m, 14H, Ph), 4.66 (s, 5H, Cp); ¹³C{¹H} NMR (CDCl₃) δ 219.1 (d, J_{PC} = 26 Hz, CO), 213.3 (d, J_{PC} = 39 Hz, CONH), 144.8 (d, J_{PC} = 12 Hz, CONHC), 134.9 (d, J_{PC} = 49 Hz, *ipso* Ph), 133.6 (d, J_{PC} = 43 Hz, *ipso* Ph), 132.9 (s, Ph), 132.8 (s, Ph), 132.7 (s, Ph), 132 (s, Ph), 130.4 (s, Ph), 129.3 (s, Ph), 128.7 (s, Ph), 128.6 (s, Ph), 120.9 (d, J_{PC} = 7 Hz, Ph), 118 (d, J_{PC} = 7 Hz, Ph), 117.3 (d, J_{PC} = 52 Hz, *ipso* Ph), 86.8 (s, Cp). Anal. Calcd. for C₂₅H₂₀FeNO₂P: C, 66.22; H, 4.45; N, 3.09. Found: C, 65.50; H, 4.31; N, 2.96.

Preparation of (η⁵-C₅H₅)Fe⁺(CO)₂[PPh₂(*o*-C₆H₄O)] **2** and [(η⁵-C₅H₅)Fe(CO)₂PPh₂(*o*-C₆H₄OMe)] [PF₆] **3**

Under N₂ atmosphere, PPh₂(*o*-C₆H₄OH) (330 mg, 1.2 mmol) and 0.5 mL TMEDA were dissolved in THF (20 mL) that was kept stirring at 0 °C. To this solution was slowly added *n*-BuLi (0.75 mL 1.6 M in *n*-hexane, 1.2 mmol) or LDA (0.8 mL 1.5 M in cyclohexane, 1.2 mmol). The solution was then allowed to return to room temperature and kept stirring for 30 min. This mixture was then added dropwise into a round-bottomed flask containing (η⁵-C₅H₅)Fe(CO)₂I (304 mg, 1 mmol) in THF (20 mL) at 0 °C. The cold bath was taken away to allow the temperature of the mixture to rise to room temperature. After the reaction mixture was further stirred for 2 h, 20 mL of *n*-hexane was added to give yellow precipitates. The reaction mixture was allowed to stand still before cannula-removal of the organic solvents. The precipitates were washed with Et₂O (20 mL × 3) to give powders of LiI and yellow zwitterionic complex **2**. Excess MeI in THF (20 mL) was then added to the mixture at room temperature. The yellow precipitates gradually formed in about 30 min. The mixture was kept stirring for 1 h then a CH₃CN solution (30 mL) containing NH₄PF₆ (1 g) was introduced. After the complete dissolution, a large quantity of H₂O was added to the solution to yield again yellow precipitates, which were filtered and washed with H₂O (20 mL × 3) and Et₂O (20 mL × 3), resulting in 275 mg of **3**, yield 45%. Compound **2** was also purified by passing a CH₂Cl₂ solution of crude **2** through a short SiO₂ column, followed by recrystallization from CH₂Cl₂/*n*-hexane, to get a yellow powder which, due to decomposition, hasn't been isolated as an analytically pure sample.

2: IR (CH₂Cl₂) ν_{CO} 2066 (s), 2012 (s) cm⁻¹; ³¹P{¹H} NMR (CDCl₃) δ 53.8; ¹H NMR (CDCl₃) δ 7.6-6.8 (m, 14H,

Ph), 5.15 (s, 5H, Cp). Also a minor form, (less than 10%, estimated from peak intensity integration in ^1H and ^{31}P NMR): IR (CH_2Cl_2) ν_{CO} 1959, 1609 cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 80.1; ^1H NMR (CDCl_3) δ 7.6-6.8 (Aryl), δ 4.51 (Cp).

3: IR (CH_3CN) ν_{CO} 2058 (s), 2013 (s) cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) δ 54.7; ^1H NMR (CD_3CN) δ 7.6-6.8 (m, 14H, Ph), 5.22 (s, 5H, Cp), 3.7 (s, OMe); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN) δ 211.8 (d, $J_{\text{PC}} = 24$ Hz, CO), 89.5 (s, Cp), 56.0 (s, OCH₃). Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{F}_6\text{FeO}_3\text{P}_2$: C, 50.81; H, 3.61. Found: C, 49.92; H, 3.56.

Alternative Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PPh}_2(o\text{-C}_6\text{H}_4\text{OMe})][\text{PF}_6]$, **3**

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ (304 mg, 1 mmol) and $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{OMe})$ (292 mg, 1 mmol) were dissolved in THF (20 mL) and maintained at -78 °C. Addition of tracing $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$ or *n*-BuLi then removal of the cold bath resulted in a large quantity of yellow precipitates during the slow warming of the solution to 0 °C. At this stage, Et_2O containing trace H_2O was added to the mixture. Filtration, washing the precipitates with Et_2O (20 mL \times 3), addition of excess NH_4PF_6 in CH_3CN to the precipitates, and then a vigorous stirring of the resultant mixture for 30 min followed by addition of sufficient H_2O yielded yellow precipitates. Filtration then washing the precipitates with H_2O (20 mL \times 3) and Et_2O (20 mL \times 3) produced 540 mg of **3**, yield 88%.

Reaction of **1** with Strong Acids

Under N_2 atmosphere, complex **1** (453 mg, 1 mmol) was dissolved in CH_2Cl_2 (30 mL) and kept stirring at 0 °C. To this solution was slowly added HBF_4 (0.2 mL 48 wt. % in H_2O , 1.5 mmol) before the solution was allowed to return to room temperature. The solution was further stirred for 30 min. It was then added dropwise into a round-bottomed flask containing $(\text{O})\text{NMe}_3$ (150 mg, 2 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The cold bath was taken away to allow the temperature of the mixture to rise to room temperature. After the reaction mixture was further stirred for 1 h, 20 mL of hexane was added to form red brown precipitates. Filtration, washing the precipitates with H_2O (30 mL \times 3) and Et_2O (30 mL \times 3), followed by addition of a CH_3CN solution (20 mL) containing NH_4PF_6 (2 g) re-dissolved the precipitates. The solution was kept stirring for 10 min. Sufficient H_2O was then added to give precipitates, which were filtered and washed with H_2O (30 mL \times 3) and Et_2O (30 mL \times 3), affording 377 mg of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{PPh}_2(o\text{-C}_6\text{H}_4\text{NH}_2)][\text{PF}_6]$ **4-PF₆**, yield 66%.

4-PF₆: IR (CH_2Cl_2) ν_{CO} 1977 (s) cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) δ 82 (s); ^1H NMR (CD_3CN) δ 7.8-7.2 (m, 14H, Ph), 5.26 (m, 2H, NH_2), 4.78 (d, $J_{\text{PH}} = 1.6$ Hz, 5H, Cp); $^{13}\text{C}\{^1\text{H}\}$

NMR (CD_3CN) δ 218.1 (d, $J_{\text{PC}} = 26$ Hz, CO), 150.5 (d, $J_{\text{PC}} = 20$ Hz, CNH_2), 136.8 (d, $J_{\text{PC}} = 46$ Hz, *ipso* Ph), 134.6 (d, $J_{\text{PC}} = 11$ Hz, Ph), 133.1 (s, Ph), 132.8 (s, Ph), 132.5 (s, Ph), 132.2 (d, $J_{\text{PC}} = 11$ Hz, Ph), 131.7 (d, $J_{\text{PC}} = 45$ Hz, *ipso* Ph), 131.6 (s, Ph), 130.9 (d, $J_{\text{PC}} = 55$ Hz, *ipso* Ph), 129.9 (d, $J_{\text{PC}} = 11$ Hz, Ph), 129.1 (d, $J_{\text{PC}} = 5$ Hz, Ph), 126.1 (d, $J_{\text{PC}} = 8$ Hz, Ph), 82.9 (s, Cp). Anal. Calcd. for $\text{C}_{24}\text{H}_{21}\text{F}_6\text{FeNOP}_2$: C, 50.43; H, 3.71; N, 2.45. Found: C, 51.26; H, 3.58; N, 2.32.

Alternative Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{PPh}_2(o\text{-C}_6\text{H}_4\text{NH}_2)][\text{I}]$, **4-I**

Under N_2 atmosphere, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ (304 mg, 1.0 mmol) and $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{NH}_2)$ (300 mg, 1.1 mmol) were dissolved in toluene (40 mL) that was then refluxed for 6 h with stirring. The solution was cooled down to room temperature when red brown precipitates were formed. The precipitates were filtered then recrystallized twice from a $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ solution to result in **4-I**, 480 mg, yield 87%.

X-ray Structure Analysis

The crystals of **1** and **4-I** suitable for X-ray diffraction analysis were grown from $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ by a slow evaporation method. A summary of crystal data and refinement details for **1** and **4-I** is given in Table 1. Diffraction intensities were measured with background counts made for half the total scan time on each side of peak. Three standard reflections, re-measured after every hour, showed no significant decrease in intensity during data collection. Data were corrected for Lorentz-polarization and absorption (empirical Ψ corrections). The structure was solved by direct methods MULTAN.¹⁰ Calculations and full matrix least-squares refinements were performed utilizing the NRCVAX program package.¹¹ All non-H atoms were refined with anisotropic thermal parameters with all hydrogen atoms fixed ($\text{C-H} = 1.00$ Å) at anisotropic convergence stage. For **4-I** 1.5 CH_2Cl_2 , the 0.5 solvate molecule is disordered in which a weighted scattering factor (50% - 50% Cl and C) was assumed for atom labeled as Z. Scattering factor curves of I, Fe, Cl, P, F, O, N, C, and H were taken from the International Tables.¹² Final fractional coordinates for **1** and **4-I** are given in Tables 2 and 3, with respective molecular plots in Figs. 1 and 2.

RESULTS AND DISCUSSION

Electron transfer catalysis

With greatly enhanced reactivity of organometallic **17e** and **19e** radicals, the electron-transfer chain catalysis has been used in the preparation of organometallic complexes.^{13,14,15}

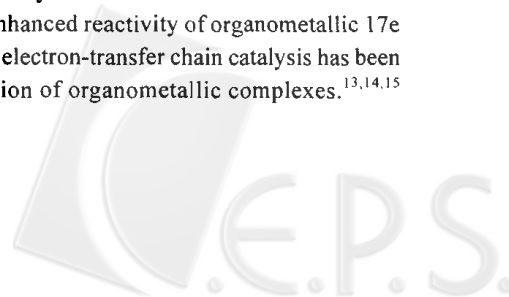


Table 1. Crystal Data and Refinement Details for **1** and **4-I**·1.5 CH₂Cl₂

Compound	1	4-I ·1.5 CH ₂ Cl ₂
Formula	C ₂₅ H ₂₀ FeNO ₂ P	C ₂₄ H ₂₁ FeINOP·1.5 CH ₂ Cl ₂
Fw	453.06	680.29
Space group	P-1	P 2 ₁ /c
a (Å)	8.5134(9)	10.564(1)
b (Å)	10.1064(8)	17.726(1)
c (Å)	12.123(1)	14.919(2)
α (deg)	89.516(9)	
β (deg)	85.500(9)	94.831(9)
γ (deg)	88.816(6)	
V (Å ³)	1039.6(2)	2783.7(5)
Z	2	4
F (000)	423.93	1347.86
D _{calc} (g cm ⁻³)	1.307	1.624
Temperature (K)	298	298
μ (cm ⁻¹)	0.82	2.01
λ(Mo Kα) (Å)	0.71073	0.71073
Crystal dimensions (mm)	0.37 × 0.20 × 0.31	0.25 × 0.18 × 0.30
2θ (max)	50.0	50.0
Diffractometer	Nonius CAD-4	Nonius CAD-4
Scan mode	θ/2θ	θ/2θ
Data range	-10 < h < 10 0 < k < 12 -14 < l < 14	-12 < h < 12 0 < k < 21 0 < l < 17
Unique reflections	3649	4892
Observations	3325, I ₀ > 2.5σ(I ₀)	3787, I ₀ > 2.5σ(I ₀)
Absorption corrections	Yes	Yes
Transmission factors	0.7585-0.8305	0.8945-0.9999
Total atoms	50	57
Parameters	272	307
Weights	Counting-statistics	Counting-statistics
Weight modifier	0.0001	0.0001
R	0.030	0.047
R _w	0.048	0.066
Goodness of fit	3.13	3.42
Max Δ/σ	0.0001	0.130
D-map highest peak (e Å ⁻³)	0.290	1.320
deepest hole (e Å ⁻³)	-0.290	-0.940

Stweigart et al. reported that the phosphine substitution for CO on $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$ proceeds with the 17e-19e pathway after electrochemical or chemical initiation.¹⁶ We noted that the reaction of 1:1 $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}/\text{PPh}_3$, after a reductive initialization with a diluted lithiated reagent or $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$, follows also the 17e-19e pathway and instantaneously gives precipitates of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)^+][\Gamma^-]$, Γ^- being selectively replaced by PPh_3 (Scheme IV). If one equiv of *n*-BuLi is used, the first drop of *n*-BuLi acts as the initiating reductant and the thereafter stoichiometric *n*-BuLi acts as a normal nucleophile, resulting in a Cp-ring butylation on $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)^+]$ to give (*exo*- η^4 -BuC₅H₅)-Fe(CO)₂(PPh₃).¹⁷

In Scheme IV, the redox coupling followed by the ligand exchange coupling completes a cycle of the electron transfer chain catalytic reaction. The Fe-I bond is the weakest bond (i.e., HOMO) around the Fe-center. In a 19e radical, the extra electron is placed in the Fe-I antibonding orbital. Thus, when a ligand exchange reaction occurs on the 19e Fe-center, if compared to the 16e or 18e Fe-center, the barrier is greatly reduced to approximately one half of Fe-I bond energy. The large decrease in barrier justifies the enhanced reactivity with the 17e-19e pathway.

The 1:1 mixture of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}/\text{PPh}_2(o\text{-C}_6\text{H}_4\text{OH})$ or of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}/\text{PPh}_2(o\text{-C}_6\text{H}_4\text{NH}_2)$, upon treatment of 1 equiv of *n*-BuLi, didn't give similar cationic

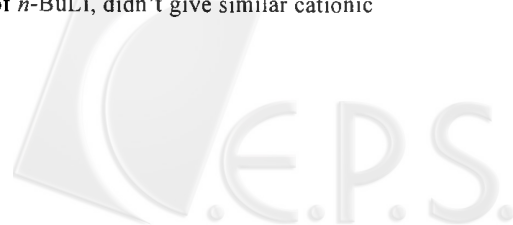


Table 2. Final Fractional Coordinates and Equivalent Isotropic Displacement Coefficients (\AA^2) for non-H Atoms of **1**

Atom	x	y	z	Biso
Fe	0.63686(4)	0.68643(3)	0.84661(3)	2.32(2)
P	0.7938(1)	0.7825(1)	0.7231(0)	2.39(2)
O6	0.6192(3)	0.4436(2)	0.7258(2)	4.8(1)
O7	0.8135(2)	0.5906(2)	1.0181(1)	3.3(1)
N	0.9579(2)	0.5680(2)	0.8606(2)	3.1(1)
C1	0.4857(4)	0.8518(3)	0.8529(3)	5.2(1)
C2	0.5627(4)	0.8444(4)	0.9480(4)	5.9(2)
C3	0.5184(5)	0.7280(5)	1.0013(3)	7.1(2)
C4	0.4172(5)	0.6658(3)	0.9362(5)	6.9(2)
C5	0.3979(4)	0.7430(4)	0.8460(3)	6.0(2)
C6	0.6294(3)	0.5407(2)	0.7730(2)	2.9(1)
C7	0.8186(3)	0.6115(2)	0.9170(2)	2.5(1)
C11	0.9582(3)	0.6747(2)	0.6764(2)	2.6(1)
C12	1.0150(3)	0.5809(2)	0.7501(2)	2.8(1)
C13	1.1453(3)	0.4997(3)	0.7144(2)	3.7(1)
C14	1.2139(3)	0.5098(3)	0.6092(3)	4.4(1)
C15	1.1569(4)	0.6000(3)	0.5355(2)	4.3(1)
C16	1.0310(3)	0.6808(3)	0.5688(2)	3.5(1)
C21	0.8860(3)	0.9311(2)	0.7715(2)	2.9(1)
C22	1.0210(3)	0.9179(3)	0.8267(2)	3.5(1)
C23	1.0875(4)	1.0271(3)	0.8714(2)	4.5(1)
C24	1.0193(4)	1.1506(3)	0.8618(3)	5.3(2)
C25	0.8840(5)	1.1649(3)	0.8090(3)	6.0(2)
C26	0.8173(4)	1.0563(3)	0.7639(3)	4.8(2)
C31	0.7124(3)	0.8343(2)	0.5934(2)	3.1(1)
C32	0.7855(3)	0.9301(3)	0.5242(2)	4.3(1)
C33	0.7357(4)	0.9546(4)	0.4208(3)	5.5(2)
C34	0.6115(4)	0.8854(4)	0.3848(2)	5.3(2)
C35	0.5343(4)	0.7941(3)	0.4532(2)	4.5(1)
C36	0.5854(3)	0.7682(3)	0.5573(2)	3.4(1)

yellow precipitates nor η^4 -Fe products at all. That is, in the reaction of 1:1 (η^5 -C₅H₅)Fe(CO)₂I/(*o*-substituted hybrid phenylphosphines) in THF at -78 °C, the 17e-19e pathway similar to that shown in Scheme IV was off. Even if the temperature of the reaction was raised to room temperature, one could not identify in the mixture the Cp-ring butylation products (*exo*- η^4 -BuC₅H₅)Fe(CO)₂PPh₂(*o*-C₆H₄NH₂) or (*exo*- η^4 -BuC₅H₅)Fe(CO)₂PPh₂(*o*-C₆H₄OH). One could obtain complexes **1** or **2** this way, albeit at much lower yields than those obtained following the procedure described in the experimental section.

Apparently, a system containing radical acceptor reactants, e.g., those with an amino or a hydroxyl group, turns off the 17e-19e pathway. Depending on the situations, *n*-BuLi is known to be a reductant, a nucleophile, and a base.¹⁸ It is apparently that its character as a base is the most important one when amino or hydroxyl groups are present in the mixture. The acid-base equilibrium is quickly established, leaving be-

Table 3. Final Atomic Fractional Coordinates and Equivalent Isotropic Displacement Coefficients (\AA^2) for non-H Atoms of **4-1**·1.5 CH₂Cl₂

Atom	x	y	z	Biso
I	0.12246(5)	0.59531(3)	0.12448(3)	6.22(3)
Fe	0.05257(7)	0.32310(5)	0.14809(5)	3.77(3)
P	0.2507(1)	0.3044(1)	0.1982(1)	3.46(6)
N	0.1245(5)	0.4000(3)	0.0660(3)	4.3(2)
O6	0.0468(5)	0.2093(3)	0.0083(3)	6.2(2)
C1	-0.0986(6)	0.2739(4)	0.2053(5)	5.6(3)
C2	-0.0177(7)	0.3050(5)	0.2714(5)	6.3(4)
C3	-0.0065(7)	0.3828(6)	0.2566(6)	7.2(4)
C4	-0.0869(8)	0.3993(4)	0.1772(7)	7.1(4)
C5	-0.1452(6)	0.3324(5)	0.1465(5)	6.0(4)
C6	0.0512(5)	0.2536(4)	0.0641(4)	4.3(3)
C11	0.3354(6)	0.3489(3)	0.1097(4)	3.9(3)
C12	0.4643(6)	0.3451(4)	0.0984(4)	5.2(3)
C13	0.5117(7)	0.3787(5)	0.0262(5)	6.2(4)
C14	0.4346(8)	0.4174(4)	-0.0343(5)	5.9(4)
C15	0.3070(7)	0.4228(4)	-0.0243(4)	5.4(3)
C16	0.2566(6)	0.3895(3)	0.0497(4)	3.9(3)
C21	0.3115(6)	0.2080(3)	0.2132(4)	4.2(3)
C22	0.4408(6)	0.1936(4)	0.2332(4)	4.9(3)
C23	0.4860(7)	0.1204(4)	0.2407(5)	5.6(3)
C24	0.4054(8)	0.0621(4)	0.2302(5)	5.9(4)
C25	0.2757(8)	0.0752(4)	0.2120(5)	6.0(4)
C26	0.2290(6)	0.1482(3)	0.2043(4)	4.8(3)
C31	0.3049(5)	0.3512(3)	0.3026(4)	3.6(2)
C32	0.3180(6)	0.3115(4)	0.3838(4)	4.4(3)
C33	0.3479(7)	0.3482(5)	0.4637(4)	5.6(4)
C34	0.3647(7)	0.4258(5)	0.4633(5)	6.1(4)
C35	0.3524(6)	0.4658(4)	0.3851(5)	5.4(3)
C36	0.3212(6)	0.4280(4)	0.3036(4)	4.6(3)
C	0.298(2)	0.7959(8)	0.0747(8)	16(1)
Z*	0.969(1)	0.0231(7)	0.0222(9)	14.5(9)
Cl1	0.3147(3)	0.8214(2)	-0.0311(2)	9.9(2)
Cl2	0.3352(2)	0.8609(2)	0.1583(2)	9.5(1)
Cl3*	0.9488(5)	0.0494(3)	0.1071(5)	10.8(3)

* Z is a special atom with 50%-50% scattering factors of Cl and C. Cl3 is with an occupancy factor of 0.5.

hind the redox reaction and the nucleophilic addition.

Differentiation between reactivity of PPh₂(*o*-C₆H₄OH) and PPh₂(*o*-C₆H₄NH₂)

As shown in Fig. 1, the X-ray structure of neutral complex **1** is a cyclometallacarbamoyl complex containing an anilide group. The IR spectrum of **1** reveals two ν_{CO} stretching bands: one for the carbonyl group at 1940 cm^{-1} and the other for the keto group at 1543 cm^{-1} . The ³¹P NMR (CDCl₃) spectrum of **1** shows one peak at δ 71.5. For comparison, the non-cyclic, (alkylcarbamoyl)iron counterpart [(η^5 -C₅H₅)-Fe(CO)(C(O)NHC₆H₁₁)(PPh₃)] exhibits IR ν_{CO} stretching

bands at 1910 and 1561 cm^{-1} and ^{31}P NMR (CDCl_3) signal at δ 77.2.⁵

In the literature only a recently published $(\text{CO})_2\text{FeC}(\text{O})\text{NPhCH}_2(\text{C}_5\text{Me}_4\text{-}\eta^5)$ **5** is also a carbamoyl complex with an anilide group.¹⁹ Complex **5** has a chelate ring in the structure, which is the same as that of **1**. The rareness of carbamoyl complexes with an anilide group is suggestive that aniline or aromatic amines do not undergo the reaction shown in Scheme III; the reverse reaction occurs more naturally. The chelate in **1** and **5** stabilizes the anilide carbamoyl structure kinetically because if the ring opens, the tether assists the reformation.

On the thermodynamic side, the chelate in **5** also allows the anilide N-atom to become more sp^2 hybridized, on the basis of unusually short N-CO length, 1.406(3) Å, and the significant shift of IR $\nu(\text{keto})$ stretching band to 1580 cm^{-1} .¹⁹

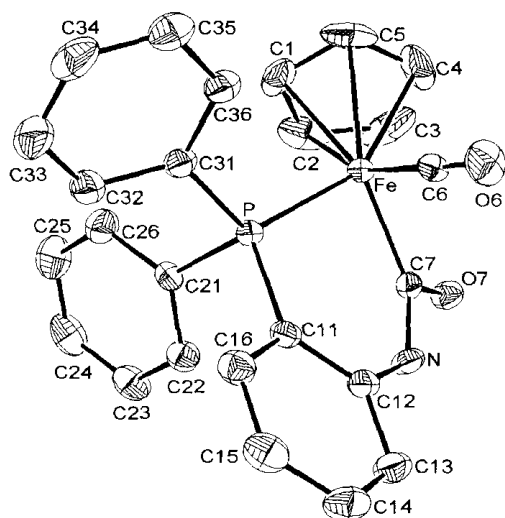


Fig. 1. ORTEP molecular plot of **1**. The thermal ellipsoids for non-H atoms are plotted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Fe-P, 2.1642(7); Fe-C1, 2.086(3); Fe-C2, 2.080(3); Fe-C3, 2.100(3); Fe-C4, 2.101(3); Fe-C5, 2.102(3); Fe-C6, 1.733(3); Fe-C7, 1.961(2); P-C11, 1.813(2); P-C21, 1.831(3); P-C31, 1.836(2); O6-C6, 1.149(3); O7-C7, 1.240(3); N-C7, 1.387(3); N-C12, 1.395(3). Selected bond angles ($^\circ$): P-Fe-C6, 94.5(8); P-Fe-C7, 90.15(7); C6-Fe-C7, 88.4(1); Fe-P-C11, 111.59(8); C7-N-C12, 131.7(2); Fe-C6-O6, 177.6(2); Fe-C7-O7, 121.5(2); Fe-C7-N, 124.8(2); O7-C7-N, 113.6(2); P-C11-C12, 119.1(2); N-C12-C11, 124.2(2); N-C12-C13, 116.7(2).

The structural parameters of **1** have suggested even further delocalization of its anilide N-atom. The bond distance of N-C7 and N-C12 are 1.387(3) and 1.395(3) Å, respectively, and the IR $\nu(\text{keto})$ stretching band is at 1543 cm^{-1} , attributed to the nature of a 6-membered ring and the presence of a P-donor atom with empty d-orbital. Whereas in **5** the structure is a 5-membered ring and there is no P-donor atom attached to the Fe-center.

More than 90% of complex **2** reveals in IR two equally intense ν_{CO} stretching bands at 2066, 2012 cm^{-1} . Equal intensities are indicative that the two CO vectors are 90° apart. The relatively high ν_{CO} wave numbers are indicative that the CO ligands are coordinated to a cationic Fe-center and subject to a weak back bonding from Fe accordingly. This major form of **2** exhibits in ^1H NMR a singlet δ 5.15 (5H) for Cp protons and peaks ranging δ 7.6-6.8 (14H) for aryl protons, and in ^{31}P NMR a peak at δ 53.8 for the phosphine ligand coordinated to Fe. There is also a minor form of **2** (less than 10%, estimated from peak intensity integration in ^1H and ^{31}P NMR) with spectroscopic data as follows: ν_{CO} at 1959, 1609 cm^{-1} , ^1H

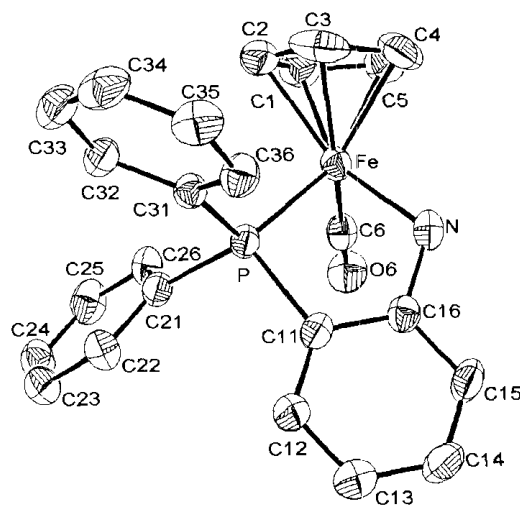
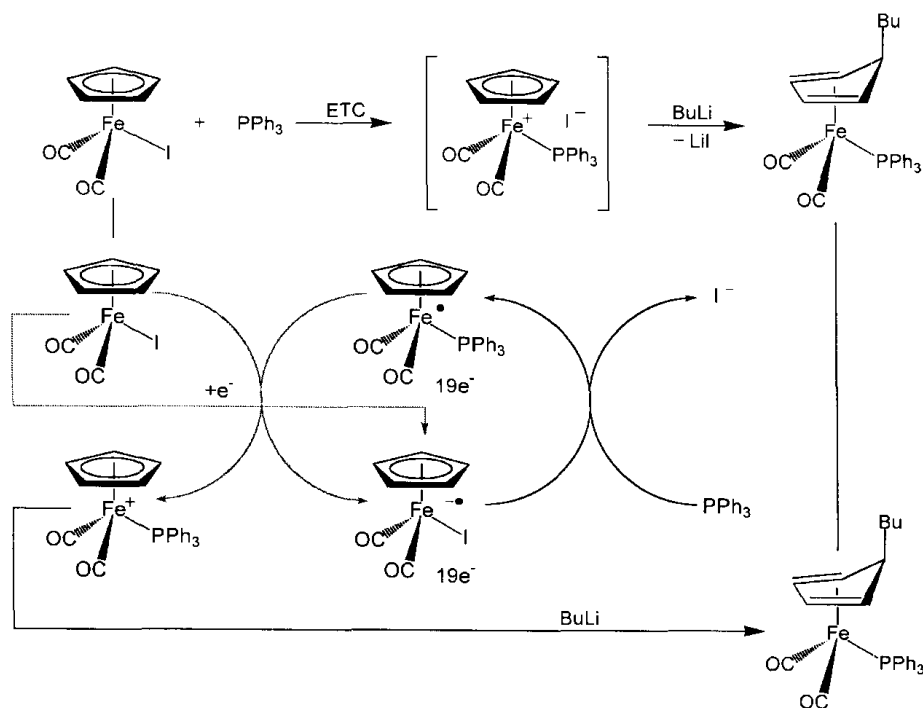


Fig. 2. ORTEP molecular plot of cation **4**. The thermal ellipsoids for non-H atoms are plotted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Fe-P, 2.188(2); Fe-N, 2.022(5); Fe-C1, 2.066(7); Fe-C2, 2.066(7); Fe-C3, 2.074(7); Fe-C4, 2.072(7); Fe-C5, 2.094(7); Fe-C6, 1.756(7); P-C11, 1.834(6); N-C16, 1.449(8); O6-C6, 1.143(8). Selected bond angles ($^\circ$): P-Fe-N, 84.9(1); P-Fe-C6, 95.1(2); N-Fe-C1, 151.3(3); Fe-C6-O6, 177.9(5); Fe-P-C11, 101.5(2); Fe-P-C21, 119.9(2); Fe-P-C31, 116.6(2); N-C16-C11, 119.8(5); N-C16-C15, 121.1(5).

Scheme IV



NMR at δ 4.51 (Cp) and δ 7.6-6.8 (Aryl), and ^{31}P NMR at δ 80.1. As a comparison, the ionic form of the untethered complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)]^+[\text{OPh}]^-$ exhibits characteristically ν_{CO} at 2057, 2014 cm^{-1} and ^{31}P NMR at δ 63.4 whereas the neutral form $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{C}(\text{O})\text{OPh})(\text{PPh}_3)]$ exhibits ν_{CO} at 1952, 1602 cm^{-1} and ^{31}P NMR at δ 69.6.¹

The characteristic ν_{CO} stretching bands of the major form of **2** are different from those of the neutral compound **1**, at 1940, 1543 cm^{-1} , that are instead similar to those of the minor form of **2**. The two forms are in equilibrium. It is thus evident that the major form of **2** is a zwitterion with a cationic Fe-center and an anionic OArly group. The minor form of **2** is neutral with a 6-membered, cyclometallacarboxyalkyl ring with a weak C-OArly bond.²⁰

Complex **2** is unstable and decomposes slowly in the crystalline state. A further chemical derivatization has been performed to better understand the reactivity of **2**. Protonation of **2** with CF_3COOH leads to decomposition. When quenched with MeI, however, **2** could be converted to the more stable cationic complex **3**, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PPh}_2(o\text{-C}_6\text{H}_4\text{OMe})]^+$ that is alternatively prepared by reaction between $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ and $\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{OMe})$. $\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{OMe})$ does not have any active protons and hence behaves as a common phosphine with which the ETC replace-

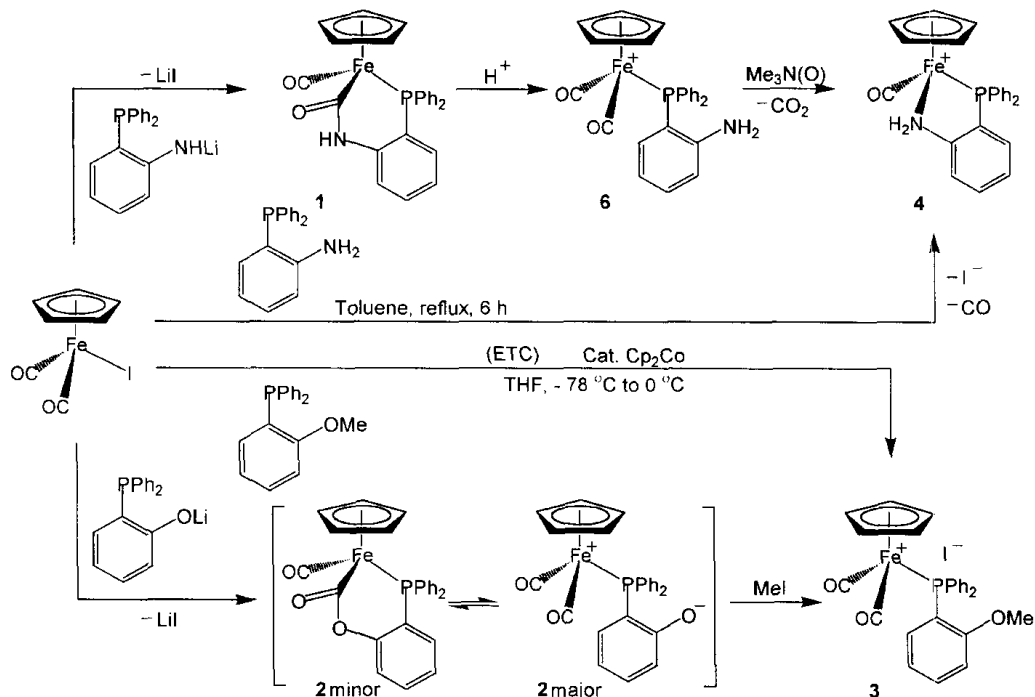
ment of $\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{OMe})$ for iodide on $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ has been performed. Indeed, the facile substitution reaction proceeds smoothly in THF at low temperature and during the warming of the solution from -78°C to 0°C , the reaction has already reached its completion.

Reaction of **1** with strong acids

Adding strong acids such as HCl or HBF_4 to **1** produces mixtures of cationic complexes **4** and **6** that are difficult to separate. Apparently, protonation at the anilide N-site produces a P, N ligand $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{NH}_2)$ that has a dangling N-donor available to proceed with the CO substitution. As shown in Scheme V, complex **4** is actually an entropy driven product after the dissociation of one of the CO ligands in **6**, followed by cyclization of the P, N ligand. In the experimental section, complex **6** has been totally converted to **4**, taking advantage of an oxidative decarbonylation effected by trimethylamine N-oxide.

The direct reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ and $\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{NH}_2)$ has been done in which the ETC pathway is apparently turned off and the conventional 16e-18e pathway is on: **4-I** could be produced by refluxing a mixture of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ and $\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{NH}_2)$ in toluene. The structure of **4-I** has been characterized by single-crystal X-ray

Scheme V



analysis. The difference in structural parameters between 1 and 4-I are mainly due to the change from a 6-membered cyclometallacarbamoyl skeleton to a 5-membered cycloammine skeleton. In 1, the fragment of P-C11-C12-N-C7 is planar [± 0.1 Å] with the Fe-atom placed away from the plane by 0.93(2) Å. The N-C12 length of 1.395(3) Å is short. In 2, the 5-membered ring is an envelope with an Fe-atom about 0.51(1) Å from the planar P-C11-C16-N fragment. The N-C16 bond length is 1.449(8) Å that is much longer and is more likely with an sp³ N-atom.

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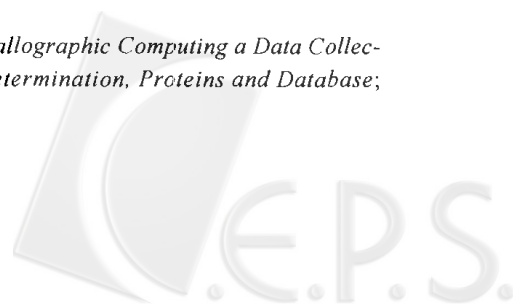
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Key Words

o-Substituted hybrid phosphine; Electron transfer chain catalysis; (Carbamoyl)iron complex; (Carboxyalkyl)iron complex.

REFERENCES

- Liu, L.-K.; Eke, U. B.; Mesubi, M. A. *Organometallics* **1995**, *14*, 3958.
- King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1918.
- Busetto, L.; Angelici, R. J. *Inorg. Chim. Acta* **1968**, *2*, 391.
- Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.
- Liao, Y.-H.; Liu, L.-K. Manuscript in preparation.
- Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U. K., 1981.
- (a) Dombek, B. D.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 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. (e) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15.
- Cooper, M. K.; Downes, J. M.; Duckworth, P. A.; Tiekink, E. R. T. *Aust. J. Chem.* **1992**, *45*, 595.
- Blin, J.; Braunstein, P.; Fischer, J.; Kickelbick, G.; Knorr, M.; Morise, X.; Wirth, T. *J. Chem. Soc., Dalton Trans.* **1999**, *13*, 2159.
- Main, P. In *Crystallographic Computing a Data Collection, Structure Determination, Proteins and Database*;



- Sheldrick, G. M.; Krueger, C.; Goddard, R., Eds.; Clarendon: Oxford, U. K., 1985; pp 206-215.
11. Gabe, E. J.; Le Page, Y.; Lee, F. L. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Database*; Sheldrick, G. M.; Krueger, C.; Goddard, R., Eds.; Clarendon: Oxford, U. K., 1985; pp 167-174.
12. Ibers, J. A.; Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, U. K. (current distributor D. Reidel, Dordrecht, The Netherlands), 1974; Vol. 4, Tables 2.2A and 2.3.1D.
13. Trogler, W. C., Ed. *Organometallic Radical Processes*; Elsevier: Amsterdam, 1990.
14. (a) Tyler, D. R. *Prog. Inorg. Chem.* **1988**, *36*, 125. (b) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189. (c) Baird, M. C. *Chem. Rev.* **1990**, *88*, 1217. (d) Tyler, D. R.; Mao, F. *Coord. Chem. Rev.* **1990**, *97*, 119. (e) Tyler, D. R. *Acc. Chem. Rev.* **1991**, *24*, 325.
15. Astruc, D. *Electron Transfer and Radical Process in Transition Metal Chemistry*; VCH: Weinheim, Germany, 1995.
16. Pevear, K. A.; Banaszak Holl, M. M.; Carpenter, G. B.; Rieger, A. L.; Rieger, P. H.; Stweigart, D. A. *Organometallics* **1995**, *14*, 512.
17. Liu, L.-K.; Luh, L.-S. *Organometallics* **1994**, *13*, 2816.
18. Liu, L.-K.; Liao, Y.-H.; Eke, U. B. *Organometallics* **1999**, *18*, 1154 and references within.
19. Manoj, K. K.-V.; Khan, M. A.; Nicholas, K. M. *Organometallics* **2000**, *19*, 3754.
20. Complex **2** was also observed in the reaction of NaH and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PPh}_2(o\text{-C}_6\text{H}_4\text{OH})]^+[\text{BF}_4]^-$, independently prepared from mixing $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ and AgBF_4 in THF/ CH_2Cl_2 followed by treatment with $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{OH})$.

