114 *J. Am. Chem. Soc.* **1998,** *120,* 114−123

Functionalization of $Cp_4Fe_4(CO)_4$: Contrasts and Comparisons with Ferrocene

Mark D. Westmeyer, Mark A. Massa, Thomas B. Rauchfuss,* and Scott R. Wilson

Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Received July 28, 1997

Abstract: Thermolysis of a xylene solution of $Cp_2Fe_2(CO)_4$ and PPh_3 yields primarily $Cp_4Fe_4(CO)_4$ (**1**) together with smaller amounts of $(C_5H_4Ph)Cp_3Fe_4(CO)_4$ and $Cp_3Fe_3(CO)_3(PPh_2)$. Cluster **1** can be alkylated and arylated by using organolithium reagents to give the derivatives $(C_5H_4R)Cp_3Fe_4(CO)_4$. This reaction is competitive with reduction of **1** by the organolithium reagent. A more versatile method for functionalizing **1** involves its deprotonation with lithium diisopropylamide (LDA) followed by treatment with electrophiles to give $(C_5H_4X)Cp_3Fe_4(CO)_4$ (X = $C(OH)HCH_3$, CO_2H, CHO, SPh, PPh_2). An excess of LDA gave increased amounts of the di- and even trifunctionalized derivatives $(C_5H_4X)_xCp_{4-x}Fe_4(CO)_4$ ($x = 2, 3$). Treatment of $(C_5H_4\text{-}CHO)Cp_3Fe_4(CO)_4$ with the lithiated cluster gave the double cluster $[(C_5H_4)Cp_3Fe_4(CO)_4]_2CHOH$. The use of the cluster as a ligand was demonstrated by the synthesis of the adducts $(C_5H_4PPh_2ML_n)Cp_3Fe_4(CO)_4$, where $ML_n = RuCl_2$(cymene), $IrCl(1,5\text{-}C_8H_{12})$. Single-crystal X-ray diffraction was employed to characterize $[(C_5H_4)Cp_3Fe_4(CO)_4]_2CHOH$ and $(C_3H_4PPh_2)Cp_3Fe_4(CO)_4RuCl_2$(cymene).

Introduction

There is increasing interest in metal-containing compounds bearing ligands with functionality *not* available for coordination to the central metal. Such external functionality is important in the control of steric properties of other bonding sites, in surface binding (i.e. catalyst anchoring), and in molecular recognition.[1] The use of such external functionality in coordination compounds is to some extent guided by knowledge of metal-containing enzymes wherein the protein superstructure serves as the ultimate functional group.[2] In contrast to mononuclear complexes, externally functionalized metal cluster compounds have been examined mainly in the context of the polyoxometalates.[3] This study focuses on functionalized *organometallic* clusters; the breadth of this class of compounds in terms of the range of metals and nuclearity suggests that fundamental studies in this area will ultimately prove fruitful. Previous studies on functional organometallic clusters are illustrated by work on the methylidyne clusters $RCCo_3(CO)_9$, which have functionality on the R groups, and studies on triiron phosphinidine clusters.[4] Few clusters however have been functionalized through cyclopentadienyl (Cp) ligands.[5] Cp functionalization is of interest based on considerations of scope and practicality: many Cp-containing clusters are known and the metal−Cp linkage is extremely robust.

The functionalization of metal cyclopentadienyl compounds, while an old field, continues to be actively pursued. Ferrocenes dominate the area,[6] but other cyclopentadienyl complexes, especially monometallic compounds, have been functionalized.[7,8] Advances in Cp functionalization have strongly contributed to the area of organometallic polymers, because polymerization processes are contingent on reactive functionalities such as vinyl, silylene, and persulfido.[9,10] Electroactive phosphine-functionalized metallocenes exhibit catalytic selectivity that depends on the redox state. There are two basic strategies for functionalization of metal Cp compounds, the first being the complexation of prefunctionalized Cp precursors, e.g. $C_5H_4CO_2Me^-$.[11] A second strategy involves the functionalization of metal-Cp compounds.[12] The use of prefunctionalized cyclopentadienyl

---

[1] Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim; 1995. Vögtle, F. *Supramolecular Chemistry*; Wiley: New York, 1991.

[2] An overview of bioinorganic chemistry: Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239.

[3] Leading references: Clegg, W.; Errington, R. J.; Fraser, K. A.; Holmes, S. A.; Schafer, A. *J. Chem. Soc., Chem. Commun.* **1995**, 455. Stark, J. L.; Young, V. G.; Maatta, E. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2547.

[4] Wei, C.; Haller, K. J.; Fehlner, T. P. *Inorg. Chem.* **1993**, *32*, 995. Bautista, M. T.; White, P. S.; Schauer, C. K. *J. Am. Chem. Soc.* **1994**, *116*, 2143.

[5] The subject of CpM clusters, per se, has not been reviewed. The scope of the area is indicated in: Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339.

[6] *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995.

[7] Functionalization of cyclopentadienyl transition metal complexes: Avey, A.; Weakley, T. J. R.; Tyler, D. R. *J. Am. Chem. Soc.* **1993**, *115*, 7706. Barlow, S.; O'Hare, D. *Organometallics* **1996**, *15*, 3885. Saha, A. K.; Hossain, M. M. *J. Organomet. Chem.* **1993**, *445*, 137. Katz, T. J.; Sudhakar, A.; Teasley, M. F.; Gilbert, A. M.; Geiger, W. E.; Robben, M. P.; Wuensch, M. *J. Am. Chem. Soc.* **1993**, *115*, 3182. Sünkel, K.; Blum, A. *Chem. Ber.* **1992**, *125*, 1605. Herberhold, M.; Biersack, M. *J. Organomet. Chem.* **1990**, *381*, 379. Sterzo, C. L.; Stille, J. K. *Organometallics* **1990**, *9*, 687. Balem, M. P.; Le Plouzennec, M.; Louër, M. *Inorg. Chem.* **1982**, *21*, 2573.

[8] Lorkovic, I. M.; Duff, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 3617.

[9] Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602 (*Angew. Chem.* **1996**, *108*, 1712). Compton, D. L.; Brandt, P. F.; Rauchfuss, T. B.; Rosenbaum, D. F.; Zukoski, C. F. *Chem. Mater.* **1995**, *7*, 2342 and references therein.

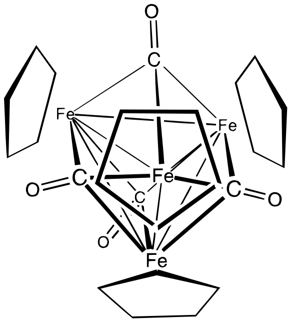
[10] Tyler, D. R. *J. Chem. Educ.* **1997**, *74*, 668.

[11] Functionalization of cyclopentadienyl ligands: Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1. Abbenhuis, H. C. L.; Burkardt, U.; Gramlich, V.; Togni, A.; Albinati, A.; Müller, B. *Organometallics* **1994**, *13*, 4481. Molander, G. A.; Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J. *Organometallics* **1996**, *15*, 3817. Herberich, G. E.; Fischer, A.; Wiebelhaus, D. *Organometallics* **1996**, *15*, 3106. Wright, M. E. *Organometallics* **1990**, *9*, 853. Lai, L.-L.; Dong, T.-Y. *J. Chem. Soc., Chem. Commun.* **1994**, 2347. Iftime, G.; Moreau-Bossuet, C.; Manoury, E.; Balavoine, G. G. A. *Chem. Commun.* **1996**, 527. Song, L.-C.; Shen, J.-Y.; Hu, Q.-M.; Liu, H.; Hung, X.-Y. *Polyhedron* **1996**, *15*, 2915.

S0002-7863(97)02557-2 CCC: $15.00

ligands is well suited for the metallocenes but it is less easily applied to clusters since the functional group can be incompatible with clusterification processes. These considerations led us to explore the functionalization of performed Cp−metal clusters, a theme that has not previously been examined. We selected $Cp_4Fe_4(CO)_4$ (**1**) because it has been well characterized in terms of its physical properties and it is prepared in one step from the readily available $[CpFe(CO)_2]_2$.[13,14] Additional advantages for this cluster are that it is electroactive, reversibly undergoing both reduction and oxidation, and it strongly absorbs visible light, which facilitates spectroscopic and chromatographic analysis.[15]

Our previous, brief study on the functionalization of **1** focused on its acylation under Friedel Crafts-like conditions.[16] Although we were able to acetylate the cluster, the yields were low. Under conditions when ferrocene is fully acylated, **1** is almost completely inert. This great difference in reactivity suggested that new approaches to the functionalization of **1** should exploit its potential reactivity toward basic or nucleophilic reagents.



1

Results

Nomenclature. We employ a numbering system that distinguishes derivatives of $Cp_4Fe_4(CO)_4$ based on the degree of substitution at the Cp groups. Thus derivatives where R replaces one H atom are labeled **2R**; derivatives where two H atoms are substituted (always on separate Cp rings) are labeled **3RR′** or **3R$_2$**, depending on whether the substituents are identical or not.

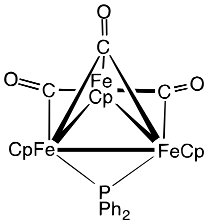
Preparation of $Cp_4Fe_4(CO)_4$. Compound **1** was prepared on a gram scale by the thermal reaction of a *m*-xylene solution of $Cp_2Fe_2(CO)_4$ and triphenylphosphine (eq 1).[17]

$$Cp_2Fe_2(CO)_4 \xrightarrow{PPh_3} \underset{\mathbf{1}}{Cp_4Fe_4(CO)_4} + \underset{\mathbf{2Ph}}{(PhC_5H_4)Cp_3Fe_4(CO)_4} + Cp_3Fe_3(CO)_3(PPh_2) \quad (1)$$

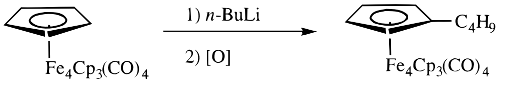
Chromatographic purification afforded **1** in 27% yield, together with two minor products. Since **1** is quite robust both thermally and photochemically, the minor products could not result from its decomposition but are of interest in terms of the mechanism of its formation.

One of the two minor products from the synthesis of **1** is $(PhC_5H_4)Cp_3Fe_4(CO)_4$ (**2Ph**). This compound was identified by its ^1H NMR spectrum, which confirmed the presence of two kinds of cyclopentadienyl groups, one of which is substituted by a phenyl group. Otherwise, in terms of its IR, mass, and UV−vis spectra, this species is quite similar to **1**. Compound **2Ph** was independently synthesized as described below.

The second minor component from the synthesis of **1** is the trinuclear cluster, $Cp_3Fe_3(CO)_3(PPh_2)$. This new compound was obtained as olive green crystals which are slightly air-sensitive in solution but stable in the solid state. Its $^{31}P\{^1H\}$ NMR spectrum consists of a single peak at δ 231.9, the low field position characteristic of a μ-PR_2 moiety.[18] The ^1H NMR spectrum shows two sets of C_6H_5 resonances as well as two C_5H_5 resonances, the latter in a 2:1 ratio. FDMS shows a molecular ion peak at 624. The IR spectrum of this trinuclear complex has bands at 1769 and 1760 cm^{-1}, assigned to μ_2-CO, and at 1633 cm^{-1}, which is at the low end of the range for μ_3-CO. Collectively these data point to a trinuclear cluster of C_s symmetry, as shown below.



Reactions of $Cp_4Fe_4(CO)_4$ with Alkyl- and Aryllithium Reagents. The reactivity of **1** toward organolithium reagents was explored in an effort to effect deprotonation,[19] although this was not achieved in this series of experiments. The addition of *n*-butyllithium (*n*-BuLi) to THF solutions of **1** at −40 °C gave olive green solutions which became bright green upon treatment with Ph_2S_2. A conventional aerobic workup afforded **2Bu** together with unreacted **1** (eq 2). We routinely added Ph_2S_2 to the reactions after the addition of the organolithium reagent to test for the presence of organolithium species. No PhS-substituted clusters were generated in this way although such C_5H_4SPh derivatives were prepared by alternative methods (see below). The nonobservation of C_5H_4SPh derivatives shows that alkyl and aryllithium reagents do not deprotonate **1**. When the alkylation of **1** was conducted on toluene solutions, the supernatant became colorless upon the addition of the *n*-BuLi



(2)

2Bu

---

(12) Representative reactions of ferrocene functionalization: Metalations: Hedberg, F. C.; Rosenberg, H. *Tetrahedron Lett.* **1969**, *46*, 4011. Rausch, M. D.; Ciappenelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127. Rebiere, F.; Samuel, O.; Kagan, H. B. *Tetrahedron Lett.* **1990**, *31*, 3121. Acylation of ferrocene: Kott, K. L.; McMahon, R. J. *J. Org. Chem.* **1992**, *57*, 3097. Cunningham, A. F., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 4864. Cunningham, A. F., Jr. *Organometallics* **1997**, *16*, 1114.

(13) Shriver, D. F.; Kristoff, J. S. *Inorg. Chem.* **1974**, *13*, 499. Shriver, D. F.; Woodcock, C. *Inorg. Chem.* **1986**, *25*, 2137. Allan, G. R.; Rychnovsky, S. J.; Venzke, C. H.; Boggess, T. F.; Tutt, L. *J. Phys. Chem.* **1994**, *98*, 216. Pittman, C. U., Jr.; Ryan, R. C.; McGee, J.; O'Conner, J. P. *J. Organomet. Chem.* **1979**, *178*, C43.

(14) King, R. B. *Inorg. Chem.* **1966**, *5*, 2227. Neuman, M. A.; Trinh-Toan; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 3383.

(15) Trinh-Toan; Fehlhammer, W. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 3389. Ferguson, J. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 3409.

(16) Massa, M. A.; Rauchfuss, T. B. *Chem. Mater.* **1991**, *3*, 788.

(17) Landon, S. J.; Rheingold, A. L. *Inorg. Chim. Acta* **1981**, *47*, 187. White, A. J. *J. Organomet. Chem.* **1979**, *168*, 197. White, A. J.; Cunningham, A. J. *J. Chem. Edu.* **1980**, *57*, 317.

(18) For example, the $^{31}P\{1H\}$ NMR spectrum of $FeCo_2(\mu-CO)(CO)7(\mu-PPh_{2)2}$ shows doublets at δ 206 and 235 vs 85% H_3PO_4: Young, D. A. *Inorg. Chem.* **1981**, *20*, 2049.

(19) Guillaneux, D.; Kagan, H. B. *J. Org. Chem.* **1995**, *60*, 2502. Sanders, R.; Mueller-Westerhoff, U. T. *J. Organomet. Chem.* **1996**, *512*, 219.

Table 1. Effects of Reaction Parameters on the Reaction RLi + **1**[a]

equiv RLi	substrate	products
0.5 *n*-BuLi	**1**	20% **2Bu**, 80% **1**
1.1 *n*-BuLi	**1**	44% **2Bu**, 47% **1**
2.0 *n*-BuLi	**1**	44% **2Bu**, 47% **1**
1.1 *n*-BuLi	**1** + 1 equiv of TMEDA	44% **2Bu**, 47% **1**
1.1 *t*-BuLi	**1**	21% **2(*t*-Bu)**, 22% **1**
1.1 PhLi	**1**	9% **2Ph**, 83% **1**
1.1 *n*-BuLi	**1** + 1 equiv of Cp_2Fe	46% **2Bu**, 40% **1**, 100% Cp_2Fe
1.1 *n*-BuLi	**2Bu**	45% **3(Bu)$_2$**, 45% **2Bu**

[a] See Experimental Section for conditions.

concomitant with the appearance of an olive precipitate. The precipitate redissolved upon exposure to air, and standard workup gave **2Bu** together with unreacted **1**, both in ca. 42% yield.

A series of experiments were conducted to investigate the influence of reaction conditions on the alkylation of **1** (Table 1). The yields were good when one considers that we recover substantial amounts of unreacted **1** after workup of the reaction mixture. The fact that increased amounts of *n*-BuLi do not increase the yields of **2Bu** shows that **1** is completely consumed in the reaction with 1 equiv of the BuLi, the moderate yields of **2Bu** notwithstanding. It appears that alkylation is competitive with reduction since **1** is recovered upon aerobic workup. Strong support for this redox pathway comes from the isolation of biphenyl in the reaction of **1** and PhLi. We propose that biphenyl is formed according to eq 3.

$$Cp_4Fe_4(CO)_4 + PhLi \rightarrow {}^{+}[Cp_4Fe_4(CO)_4]^{-} + 0.5Ph_2 \qquad (3)$$

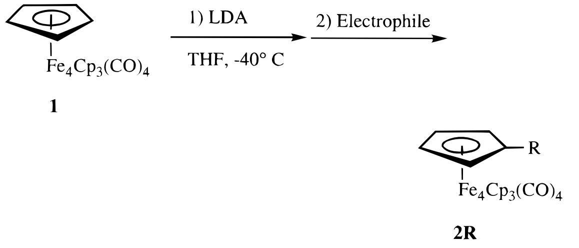
We examined the competition between **1** and ferrocene for BuLi. An equimolar solution of **1** and ferrocene was treated with 1 equiv of *n*-BuLi in the presence of TMEDA under conditions utilized for the lithiation of ferrocene.[19] The reaction mixture was quenched with DMF and the products were isolated by chromatography on silica gel.[20] This reaction produced **2Bu** together with unreacted **1** and ferrocene. Neither $Fe(C_5H_4CHO)Cp$ nor **2CHO** was formed. We observed similar results using *t*-BuLi and PhLi (Table 1). In all cases ferrocene was recovered unchanged from these reactions.

Dialkyl clusters were never obtained from the reaction of **1** and *n*-BuLi, even when an excess of *n*-BuLi was employed. This shows that the initial reaction of **1** with *n*-BuLi deactivates the cluster toward further alkylation. Dialkylated clusters could however be prepared by the reaction of **2Bu** with *n*-BuLi. The resulting dibutyl cluster $(n\text{-BuC}_5H_4)_2Cp_2Fe_4(CO)_4$ (**3(Bu)$_2$**) was obtained in 45% yield, comparable to that observed for the formation of **2Bu** from **1** + BuLi (eq 4). ^{1}H NMR analysis

$$\underset{\textbf{2Bu}}{(n\text{-BuC}_5H_4)Cp_3Fe_4(CO)_4} \xrightarrow{n\text{-BuLi}} \underset{\textbf{3(Bu)}_2}{(n\text{-BuC}_5H_4)_2Cp_2Fe_4(CO)_4} \qquad (4)$$

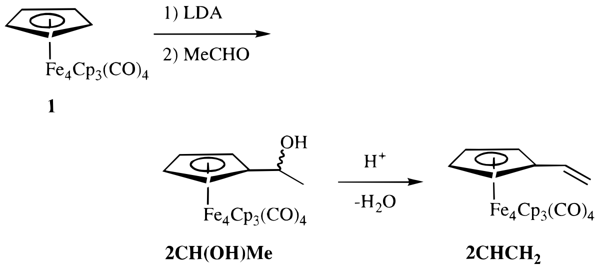
revealed that **3(Bu)$_2$** consists of >95% of the isomer with butyl groups on different cyclopentadienyl ligands. Similarly, treatment of the phenyl-substituted cluster **2Ph** with *n*-BuLi gave $(n\text{BuC}_5H_4)(PhC_5H_4)Cp_2Fe_4(CO)_4$ (**3BuPh**) as the exclusive product in 30% yield. ^{1}H NMR analysis clearly showed that the butyl and phenyl substituents are located on different cyclopentadienyl groups and that two Cp groups remain unsubstituted.

Metalation of $Cp_4Fe_4(CO)_4$. Several bases were examined for their ability to deprotonate **1**. No reactions could be detected when we used $KN(SiMe_3)_2$, NaH, and KH, although these bases do hasten the decomposition of **1**. Lithium diisopropylamide (LDA) proved, however, to be a versatile reagent for ring metalation.[21] THF solutions of the lithiated species, while unstable at room temperature, are stable at low temperature. The addition of electrophiles to these solutions afforded the functionalized clusters, **2R** (eq 5). Generally both mono- and disubstituted clusters were obtained, with greater yields for the former when 1.3−1.5 equiv of LDA was used. Representative is the synthesis of the formyl-substituted clusters. Treatment of a THF solution of **1**/LDA with DMF followed by acidification gave $(C_5H_4CHO)Cp_3Fe_4(CO)_4$ (**2CHO**) in 56% yield. Analysis of the crude product prior to acidification revealed the formation of an intermediate containing a Me_2N group; we assume that this is the hemiaminal $(C_5H_4CH(NMe_2)OH)Cp_3Fe_4(CO)_4$.[22] Treatment of this species with aqueous HCl gave **2CHO**. Addition of acetaldehyde to the lithiated cluster followed by acid-catalyzed dehydration gave the vinyl derivative $(C_5H_4CHCH_2)Cp_3Fe_4(CO)_4$ (**2CHCH$_2$**) (eq 6). This compound had previously been prepared in a three-step sequence beginning with the inefficient acetylation of **1**.[16]



(5)

R = CHO, CH=CH$_2$, CO$_2$H



(6)

While most of the functionalized clusters were purified by chromatography, the carboxylic acid $(C_5H_4CO_2H)Cp_3Fe_4(CO)_4$ (**2CO$_2$H**) was isolated by extraction into aqueous base followed by reacidification. The optical spectra of an aqueous **2CO$_2$$^-Na^+$** and CH_2Cl_2 solution of **1** are almost identical (Figure 1). Both are intensely green-colored solutions. Titration methods indicate that the pK_a of **2CO$_2$H** is 6.4 ± 0.1 in 66% ethanolic water.[23]

The scope of the cluster functionalization chemistry was explored through the synthesis of a trisubstituted derivative. Treatment of **3BuPh** with LDA followed by DMF gave the

---

[20] Mueller-Westerhoff, U. T.; Yang, Z.; Ingram, G. *J. Organomet. Chem.* **1993**, *463*, 163.

[21] Sun, X.; Kenkre, S. L.; Remenar, J. F.; Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* **1997**, *119*, 4765 and references therein.

[22] Brandsma, L. *Preparative Polar Organometallic Chemistry*; Springer-Verlag: New York, 1990; Vol. 2, pp 7 and 8. March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; pp 488−490 and 896−898.

[23] $FeCp(C_5H_4CO_2H)$: p*K*a = 7.26 (34% H2O/EtOH); 7.3 (34% H_2O/DMF). Rinehart, K. L., Jr.; Motz, K. L.; Moon, S. J. *J. Am. Chem. Soc.* **1957**, *79*, 2749.

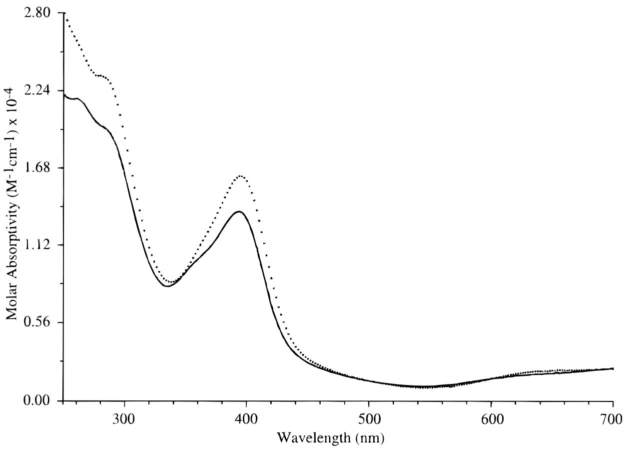
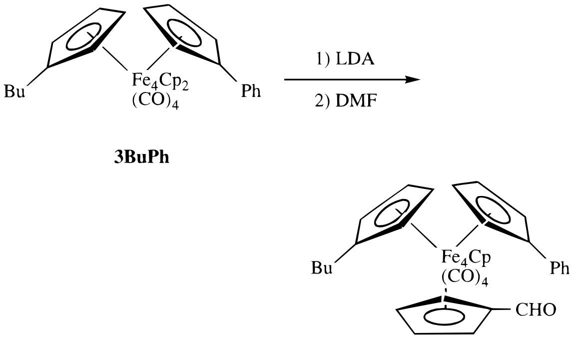


Figure 1. UV−vis spectra of a 0.066 mM solution of **$2CO_2^-Na^+$** in 0.1 M NaOH and a 0.64 mM solution of **1** in CH_2Cl_2.

formyl (**4Bu(CHO)Ph**) in 16% yield with unreacted **3BuPh** (eq 7). The low yields indicate that the phenyl and butyl groups deactivate the attached C_5H_4 ligands as has been observed in substituted ferrocenes.[24] ^1H NMR analysis indicates that **4Bu(CHO)Ph** consists of a 9:1 mixture of isomers. The more abundant isomer is assigned as $(C_5H_4CHO)(n\text{-}BuC_5H_4)(PhC_5H_4)CpFe_4(CO)_4$ based on the observation of a resonance for one unsubstituted Cp ligand. The minor species has the same formula but has two unsubstituted Cp groups. The minor species is probably $(n\text{-}BuC_5H_3CHO)(PhC_5H_4)Cp_2Fe_4(CO)_4$. This assignment, which is tentative, is based on the fact that the butyl resonances are shifted vs the major isomer suggesting that this group is now on the formyl-substituted ring.



3BuPh

(7)

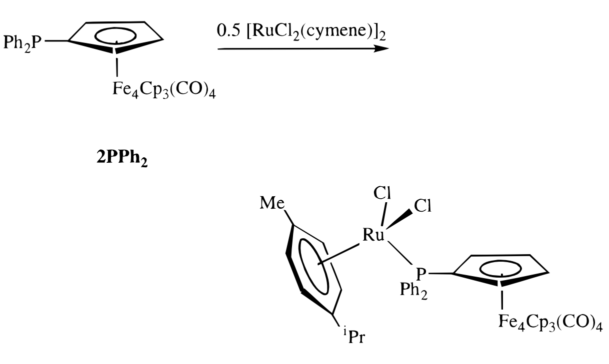
4Bu(CHO)Ph

Electrochemical Studies. Solutions of **1** in CH_2Cl_2 undergo irreversible oxidation at 1113 mV, a reversible oxidation at 458 mV, and a reversible reduction at −1339 mV (vs Ag/AgCl).[15] The behavior of the alkyl- and aryl-substituted clusters is similar except that both oxidative processes become reversible. Significant effects of the substituents on the redox potentials were observed for the formyl-substituted clusters. For example in **2CHO**, all of the redox potentials are shifted anodically by 100−200 mV. The addition of a second formyl substituent in the case of **$3(CHO)_2$** results in a further 70 mV change (vs **2CHO**).[25]

PPh_2-Substituted Clusters and Transition Metal Derivatives. Solutions of **1**/LDA are reactive toward main group electrophiles. Using Ph_2S_2 as the electrophile, we obtained $(C_5H_4SPh)Cp_3Fe_4(CO)_4$ (**2SPh**) and $(C_5H_4SPh)_2Cp_2Fe_4(CO)_4$ (**$3(SPh)_2$**), which were easily separated from **1** by chromatography. Preliminary studies showed that analogous Me_3Si-substituted derivatives could also be obtained in this manner.[26]

The reactivity of the lithiated clusters toward main group electrophiles encouraged us to prepare tertiary phosphine derivatives. The use of PPh_2Cl provided $(C_5H_4PPh_2)Cp_3Fe_4(CO)_4$ (**$2PPh_2$**) in 55% yield. Using 4 equiv of LDA, we obtained $(C_5H_4PPh_2)_2Cp_2Fe_4(CO)_4$ (**$3(PPh_2)_2$**) in 60% yield. Preliminary studies showed that treatment of **$2PPh_2$** with 3.3 equiv of LDA followed by PPh_2Cl gave, in addition to **$3(PPh_2)_2$**, the trisubstituted cluster **$4(PPh_2)_3$**, identified on the basis of microanalytical and spectroscopic data. $^{31}P\{^1H\}$ NMR spectra of dichloromethane-d_2 solutions of each of these three compounds showed single resonances near δ −20.0. These phosphine-substituted clusters are air stable although solutions do oxygenate to give the corresponding phosphine oxides. Oxidation of the **$2PPh_2$** with H_2O_2 gave the phosphine oxide **$2P(O)Ph_2$**, with $\delta^{31}P = 22.4$.[27]

The coordinating ability of **$2PPh_2$** was demonstrated through its reaction with $[RuCl_2(cymene)]_2$, a source of the 16 e^- fragment $RuCl_2(cymene)$ (cymene is *p*-isopropyltoluene) (eq 8).



$2PPh_2$

(8)

$RuCl_2(cymene)$(**$2PPh_2$**)

The product, $RuCl_2(cymene)$(**$2PPh_2$**), was obtained in high yield. This dark green adduct, which is highly soluble in organic solvents, was identified on the basis of microanalytical and spectroscopic data. The $^{31}P\{^1H\}$ NMR spectrum consisted of a single resonance at δ 19.5, 39 ppm downfield of the free ligand. The ^1H NMR data are consistent with a molecule of idealized C_s symmetry.

Single-crystal X-ray diffraction analysis of $RuCl_2(cymene)$(**$2PPh_2$**) revealed that the cluster is not strongly affected by the ruthenium center (Figure 2, Table 3). The Ru−P and Ru−Cl bond lengths are 2.377, 2.394, and 2.409 Å, respectively. These distances are comparable to the Ru−P and Ru−Cl bond distances in analogous compounds, i.e., $(cymene)RuCl_2(PPh_2Me)$ and $(C_6H_6)RuCl_2(PPh_2Me)$, where average bonds lengths are in the range of 2.407−2.423 Å for Ru−Cl and 2.341−2.372 Å for Ru−P.[28] The Cl−Ru−Cl bond angle of 88.03° is comparable to the above arene−ruthenium phosphine complexes. The H···H distances in **1**, and we assume in **$2PPh_2$**,

---

[24] Beukesev, R. A.; Bach, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 890.

[25] Sabbatini, M. M.; Cesarotti, E. *Inorg. Chim. Acta* **1977**, *24*, L9. Connelly, N. G.; Geiger, W. E. *Chem. Rev. (Washington, D.C.)* **1996**, *96*, 877.

[26] Massa, M. A. M.S. Thesis, University of Illinois at Urbana−Champaign, 1992.

[27] The corresponding phosphine-sulfides were prepared: $\delta^{31}P$ 34.382 and 35.196 for **$2P(S)Ph_2$** and **$3(P(S)Ph_2)_2$**, respectively.

[28] Representative $RuCl_2(cymene)(PR_3)$ complexes: Browning, J.; Bushnell, G. W.; Dixon, L. R.; Hilts, R. W. *J. Organomet. Chem.* **1993**, *452*, 205. Pertici, P.; Pitzalis, E.; Marchetti, F.; Rosini, C.; Salvador, P.; Bennett, M. A. *J. Organomet. Chem.* **1994**, *466*, 221. Bennett, M. A.; Robertson, G. B.; Smith, A. K. *J. Organomet. Chem.* **1972**, *43*, C41. Coleman, A. W.; Zhang, H.; Bolt, S. G.; Atwood, J. L.; Dixneuf, P. H. *J. Coord. Chem.* **1987**, *16*, 9.

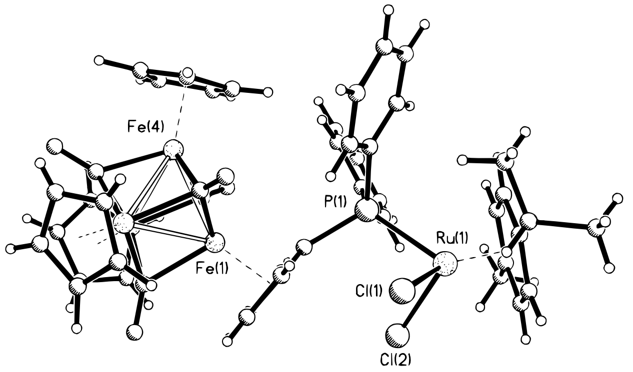


Figure 2. ORTEP drawing of $RuCl_2$(cymene)(**$2PPh_2$**) with thermal ellipsoids set at 50%.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $RuCl_2$(cymene)(**$2PPh_2$**)

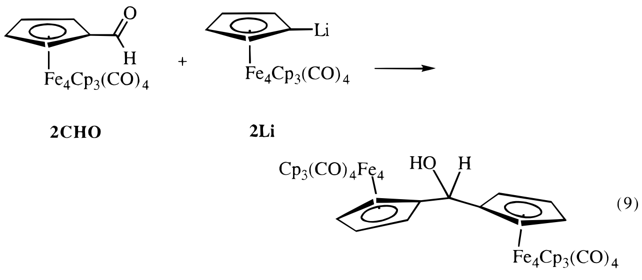
Ru−cymene^{a}	2.216 (11)	C(8)−P(1)−Ru(1)	112.3 (2)
Ru(1)−P(1)	2.377 (2)	P(1)−C(8)−Fe(1)	146.2 (4)
Ru(1)−Cl^{a}	2.402 (8)	Cl(1)−Ru(1)−Cl(2)	88.03 (7)
P(1)−C(8)	1.824 (8)		

[a] Average values for bond lengths (Å) and bond angles (deg).

are near the sum of the van der Waals radii. This crowded environment pushes the phosphorus atom in $RuCl_2$(cymene)(**$2PPh_2$**) out of the C_5 plane of its attached cyclopentadienyl group by ~20.1°. The substituted cyclopentadienyl group itself is not significantly distorted from planarity.

Compound **$2PPh_2$** forms complexes with a variety of other metal ions.[29] For example, **$2PPh_2$** and the cyclooctadiene (COD) complex $[IrCl(COD)]_2$ react to give the green adduct IrCl(COD)(**$2PPh_2$**). The assignment of this species was confirmed by FABMS, microanalytical, and spectroscopic data. The $^{31}P\{^1H\}$ NMR spectrum consisted of a single resonance at δ 5.255, 25 ppm downfield of the free ligand. Addition of 1 equiv of PPh_3 to a CD_2Cl_2 solution of IrCl(COD)(**$2PPh_2$**) resulted in displacement of **$2PPh_2$**.

Double Cubane Clusters. The reactivity of the lithiated clusters toward organic electrophiles led us to investigate routes to double cubane clusters. Treatment of THF solutions of **1**/LDA with **2CHO** afforded one principal product, which we formulated as the secondary alcohol $[(C_5H_4)Cp_3Fe_4(CO)_4]_2$CHOH (**$(2)_2$CHOH**) (eq 9).[30] The high polarity of this species was indicated by its chromatographic properties. Its ^1H NMR spectrum is consistent with idealized C_s symmetry: in addition to one C_5H_5 resonance for six equivalent Cp groups, we observe four sets of multiplets corresponding to the two C_5H_4 groups that are related by a mirror plane through CH(OH). These assignments are fully supported by the $^1H-^1H$ COSY data which reveal strong coupling between C*H*OH and the D_2O-exchangeable CHO*H*. Electrochemical measurements show that **$(2)_2$CHOH** undergoes oxidation at two closely spaced couples, 523 and 410 mV (vs Ag/AgCl, Figure 3).[31]



(9)

$(2)_2$CHOH

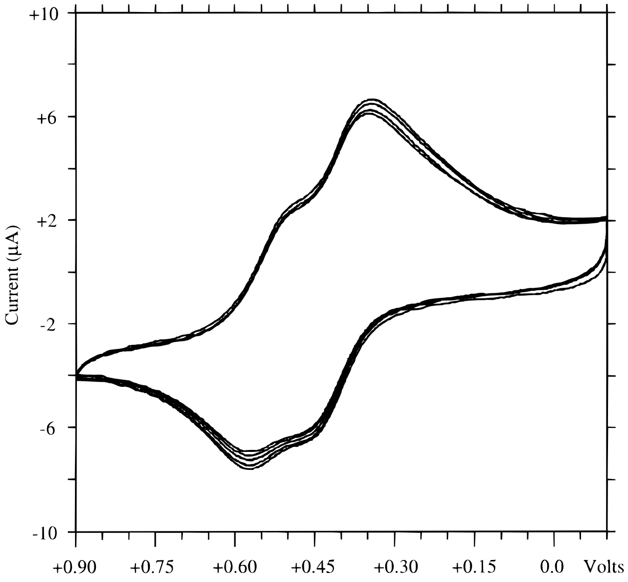


Figure 3. Cyclic voltammagram of a CH_2Cl_2 solution of **$(2)_2$CHOH** (0.1 mM Bu_4NPF_6, scan rate = 100 mV/s, reference electrode = Ag/AgCl, working electrode = Pt).

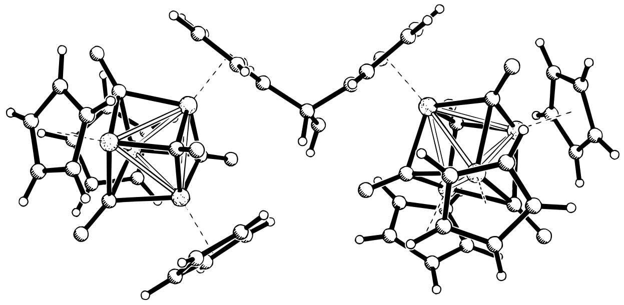


Figure 4. ORTEP drawing of **$(2)_2$CHOH** with thermal ellipsoids set at 50%.

The structure of **$(2)_2$CHOH** was confirmed by single crystal X-ray diffraction. Due in part to crystal quality and a twinning problem, the structure refined only sufficiently to discern the molecular structure. These results are consistent with an idealized C_s symmetry in solution (Figure 4). In the solid state, however, one $Cp_3Fe_4(CO)_4$ subunit is rotated ~180° relative to the other. The C−C−C angle at C25 in **$(2)_2$CHOH** is 116° and this same carbon lies 5.2 and 8.8° out of the planes defined by the attached cyclopentadienyl rings. For neither $RuCl_2$(cymene)(**$2PPh_2$**) nor **$(2)_2$CHOH** do we observe any significant distortion of the central $C_{20}Fe_4(CO)_4$ cores relative to **1**.[14] The average Fe−Fe bond length of 2.52 Å for the two new structures is identical with that in **1**, as are other structural parameters associated with the cluster cores.

---

(29) We also prepared $Rh(COD)Cl_2$(**$2PPh_2$**) ($\delta^{31}P$ 12.754: d, J = 152 Hz) and Rh(CO)Cl(**$2PPh_2$**)$_2$ ($\delta^{31}P$ 37.112: d, J = 169 Hz).

(30) We detected small amounts of the "triple" cubane cluster by the reaction of **$3(CHO)_2$** with 2 equiv of **1**/LDA to give the triple cluster **$3[CHOH)_2]_2$** as verified by mass spectral analysis.

(31) Bis(ferrocenyl)methanol, Fc_2CHOH: Pauson, P. L.; Watts, W. E. *J. Chem. Soc.* **1962**, 3880. Tirouflet, J.; Laviron, E.; Mugnier, Y. *J. Organomet. Chem.* **1973**, *50*, 241. Lupan, S.; Kapon, M.; Cais, M.; Herbstein, F. H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1025 (*Angew. Chem.* **1972**, *84*, 1104). Brown, G. M.; Meyer, T. J.; Cowan, D. O.; LeVanda, C.; Kaufman, F.; Roling, P. V.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 506. Linked metallocenes: Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637. Electrochemistry of $[FcSiR_2]_n$: Rulkens, R.; Lough, A. J.; Manners, I.; Lovelace, S. R.; Grant, C.; Geiger, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 12683.

Table 3. Comparison of Reactivity of Ferrocene and $Cp_4Fe_4(CO)_4$

reagent or process	ferrocene	$Cp_4Fe_4(CO)_4$
BuLi	mono- and dideprotonation	addition and reduction
$LiNR_2$	NR	mono- and dideprotonation
Ac_2O/H_3PO_3	mono- and diacetylation (60 °C)	slow acetylation (100 °C)
oxidation	$E_{1/2} = 469$ mV	$E_{1/2} = 448$ mV
reduction	NR	$E_{1/2} = -1339$ mV
acidity of RCO_2H	$pK_a = 7.26^{a,23}$	$pK_a = 6.4^{a}$
effect of CHO on $E_{1/2}$	$\Delta E_{1/2} = 300$ mV	$\Delta E_{1/2} = 150$ mV

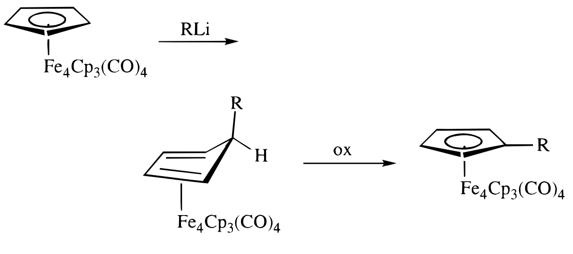
[a] 34% H_2O/EtOH (v/v).

Preliminary experiments show that oligomeric derivatives of **1** could be prepared. Treatment of the formyl cluster **2CHO** with LDA was expected to result in lithiation of one cyclopentadienyl group, which in turn could alkylate a formyl group intermolecularly. Size exclusion chromatographic analysis of the crude reaction showed a broad peak whose retention time was less than that of **(2)$_2$(CHOH)(CHO)**, indicating greater molecular volume. FABMS analysis confirmed the formation of dimers.

Discussion

The tetranuclear species **1**, one of the first examples of a cyclopentadienyl metal cluster,[14] has been the subject of several studies aimed at improving its synthesis. King originally prepared **1** in 14% yield by thermolysis of $Cp_2Fe_2(CO)_4$ followed by a lengthy workup. Since then several variations on this procedure have been reported, including the use of UV irradiation,[32] the use of triphenylphosphine as a coreactant, and the combination of both, leading to reported yields up to 80%.[17] Our method reliably produces **1** in ~27% yield. It is interesting that the synthesis cogenerates small but comparable amounts of **2Ph** and the new cluster $Cp_3Fe_3(CO)_3(PPh_2)$. These products obviously result from fragmentation of PPh_3, a process that has been previously observed in high-temperature reactions involving PPh_3 and organometallic complexes.[33]

The major finding in this work is that **1** can indeed be functionalized via a variety of methods.[26] First, alkyl- and aryllithium species add to the cubane to give the alkylated and arylated derivatives. Addition of electrophiles to the RLi/**1** solutions failed to show any evidence for deprotonation; furthermore, multiple additions were not observed. To explain these findings, we propose that the organolithium reagent adds to **1**, giving an anionic adduct that undergoes dehydrogenation upon oxidative work up (eq 10). This pattern has been observed previously for mono- and binuclear Cp compounds.[34] The occurrence of addition vs deprotonation contrasts with the situation for ferrocene where *n*-BuLi cleanly leads to double deprotonation.[35] An obvious explanation for the differing reactivity of ferrocene and **1** is that, as electrochemical studies have shown, the carbonyl cluster is easily reduced. The reducibility of **1** is undesirable in that electron-transfer reactions limit the utility of the nucleophilic addition of organolithium reagents. For example, the reaction of **1** and PhLi produces mainly biphenyl but only small amounts of **2Ph.** The reduction of the cluster by the organolithium reagent to give $[Li(THF)_n^+][Cp_4Fe_4(CO)_4^-]$ is consistent with the relatively mild potential for the $Cp_4Fe_4(CO)_4^{0/-}$ couple (−1.3 V vs Ag/AgCl).



(10)

Functionalization of **1** is most usefully conducted via metalation with use of lithium diisopropylamide (LDA). The facility of this process highlights the enhanced acidity of the Cp ligands in **1** relative to those in ferrocene, which is unreactive toward LDA. By using this methodology, the cluster can be functionalized with a wide variety of groups, e.g. CHO, SPh, COOH, $CH(OH)CH_3$, and PPh_2. Via two- and three-step reactions, it was possible to obtain reasonable yields of both doubly and triply substituted clusters. A number of the functionalized species have interesting properties, i.e., water solubility for the **2CO$_2$H** species and metal-complexing ability for the **2PPh$_2$**. It is possible to adjust the redox properties of the cluster as demonstrated by our study on the formylated cluster $(C_5H_4CHO)_xCp_{4-x}Fe_4(CO)_4$ ($x = 1, 2$). Finally, the versatility of these methods was demonstrated by the finding that the formylated cluster serves as a precursor to a double cluster.

Comparison of $Cp_4Fe_4(CO)_4$ and Ferrocene. In closing, it is instructive to compare the properties of **1** and ferrocene. Both are thermally robust CpFe species which, to some extent, can be viewed as sandwich compounds. The disparate reactivity of these two species (Table 3) indicates that **1** is more electron-deficient than ferrocene. By virtue of the multinuclear character of **1**, its chemistry is subject to some complications arising from multifunctionalization, e.g. dilithiation with LDA. On the other hand the addition of carbanions, which we think has further potential, is more selective. The structure of the core in **1** is hardly affected by the derivatization, reminiscent of the behavior of ferrocene, although the redox properties do vary in the expected way. Overall there is every prospect to expect a rich chemistry to evolve for $Cp_4Fe_4(CO)_4$.

Experimental Section

General. All reactions were carried out under a nitrogen atmosphere involving standard Schlenk techniques. $Cp_2Fe_2(CO)_4$,[36] $[RuCl_2(cymene)]_2$,[37] $[IrCl(COD)]_2$,[38] acetaldehyde (Aldrich), *n*-BuLi (1.6 M in hexanes, Aldrich), *t*-BuLi (2.0 M in hexanes, Aldrich), *N*,*N*-dimethylformamide (DMF, Aldrich), ethyl acetate (Fisher Chemical),

---

[32] Symon, D. A.; Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1973**, 1879.

[33] Garrou, P. E.; Dubois, R. A.; Jung, C. W. *CHEMTECH* **1985**, *15*, 123. Garrou, P. E. *Chem. Rev. (Washington, D.C.)* **1985**, *85*, 171.

[34] Lui, L.-K.; Luh, L.-S. *Organometallics* **1996**, *15*, 5263. Pasynkiewicz, S.; Buchowicz, W.; Poplawska, J.; Pietrylowski, A.; Zathara, J. *J. Organomet. Chem.* **1995**, *490*, 189.

[35] Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merril, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241.

[36] King, R. B.; *Organometallic Synthesis*; Academic Press: New York, 1965; Vol. 1, pp 114 and 115.

[37] Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74.

[38] Herdé, J. L.; Lambert, J. C.; Senoff, G. V. *Inorg. Synth.* **1974**, *15*, 18.

glacial acetic acid (Fisher Chemical), lithium diisopropylamide (LDA, 1.5 M in cyclohexanes, Aldrich), phenyl disulfide (Aldrich), PhLi (1.8 M 70/30 cyclohexane/diethyl ether), *p*-toluenesulfonic acid (Aldrich), triphenylphosphine (Kodak and ACROS), and *m*-xylene (Aldrich) were used without any special purification. PPh_2Cl (Aldrich) was distilled prior to use. Solvents were purified by distillation: CH_2Cl_2 (from CaH_2 under N_2), toluene (from K/Ph_2CO), and THF (K/Ph_2CO).

Reactions were monitored by HPLC: detector wavelength = 400 nm, Varian 2510 HPLC pump, 2550 UV detector, and Rainin Microsorb-MV, C18 Column Product 86-200-D5, elution rates = 1 mL/min with 15% H_2O in MeOH. Gas chromatographic analysis were performed on a Hewlett-Packard 5890A gas chromatograph: HP-1 methyl silicone gum capillary column (10 m × 0.53 mm × 2.65 μm), FID detector, He flow = 29 mL/min, oven temperature: initial = 60 °C (4 min), final = 200 °C (15 min), rate = 10 °C/min, injector temperature = 150 °C, detector temperature = 210 °C. Infrared spectra were obtained with a Mattson Galaxy Series FT-IR 3000 with a NaCl plate or KBr pellets. Optical spectra were obtained with a Hewlett-Packard 8452A diode array spectrophotometer. ^1H NMR spectra were recorded on a U400 or U500 Varian FT-NMR spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded on a U400 Varian FT-NMR spectrometer with chemical shifts referenced to 85% H_3PO_4. Chemical shifts are reported in δ units. Mass spectra were obtained by the University of Illinois Mass Spectroscopy Laboratory. Microanalyses were performed by the School of Chemical Sciences Microanalytical Laboratory.

Cyclic voltammograms were recorded on a Bioanalytical System BAS-CV 50W electrochemical analyzer with a platinum working electrode. All measurements were performed at ambient temperatures under a nitrogen atmosphere in 0.1 mM CH_2Cl_2 solutions of $(n\text{-Bu})_4NPF_6$ vs Ag/AgCl as the reference electrode. Concentrations ranged from 1.5 to 2.0 mM. IR compensation was employed with each measurement. The ferrocene$^{+/0}$ couple was 469 mV under these conditions. $E_{1/2}$ values are reported (vs Ag/AgCl); the couples are described as irreversible (i) and reversible (r) depending on the ratio of the anodic to cathodic currents, i_a/i_c. Couples were considered reversible when this ratio was within 10% of unity.

Reaction of $Cp_2Fe_2(CO)_4$ and PPh_3. A 250-mL Schlenk flask was charged with 5.17 g (0.0146 mol) of $Cp_2Fe_2(CO)_4$, 4.31 g (0.0164 mol) of PPh_3, and 150 mL of *m*-xylene. The dark red mixture was heated at reflux with the oil bath set at 185 °C. After 10 h, the dark green-brown solution was cooled to room temperature. This solution was then passed through a plug of 125 g of silica gel. Eluting with 800 mL of CH_2Cl_2 gave unreacted $Cp_2Fe_2(CO)_4$, leaving a dark green band. The green band was then eluted with 500 mL of 1:1 acetone and CH_2Cl_2 (v/v). The solvent was removed and the dark green residue was extracted into 25 mL of 4% acetone in CH_2Cl_2 (v/v) and passed through a 4 × 40 cm silica gel column to give 3 bands. The first band was brown-green $Cp_3Fe_3(CO)_3(PPh_2)$, the second band was dark green **2Ph**, and **1** eluted last as a bright green band. Solutions of **1** in *m*-xylene remain unchanged after heating at 139 °C for 24 h in the presence of PPh_3. Solutions of **1** are also photochemically stable, even in refluxing *m*-xylene solutions (12 h).

$Cp_4Fe_4(CO)_4$ (1). Yield: 1.162 g (27% yield). Anal. Calcd for $C_{25}H_{20}Fe_4O_4$: C, 48.13; H, 3.38; Fe, 37.49. Found: C, 48.10; H, 3.34, N, 0.0; Fe, 36.97. FDMS: 596 (M$^+$). UV−vis (CH_2Cl_2): 396 nm. IR (KBr): ν_{CO} 1621 cm^{-1}. ^1H NMR (C_6D_6): δ 4.596 (s, 20 H). HPLC: 4.0 min. $E_{1/2}$: 1113 (i), 458 (r), −1339 (r) mV.

$(PhC_5H_4)Cp_3Fe_4(CO)_4$ (2Ph). Yield: 97 mg (3% yield). Anal. Calcd for $C_{30}H_{24}Fe_4O_4$: C, 53.63; H, 3.60; Fe, 33.24. Found: C, 52.59; H, 3.89, N, 0.0; Fe, 30.83. FDMS: 672 (M$^+$). UV−vis (CH_2Cl_2): 400 nm. IR (KBr): ν_{CO} 1621 cm^{-1}. ^1H NMR (C_6D_6): δ 7.816 (d, *J* = 8 Hz, 2 H), 7.147 (t, *J* = 8 Hz, 2 H), 7.025 (t, *J* = 8 Hz, 1 H), 4.859 (t, *J* = 1 Hz, 2 H), 4.650 (t, *J* = 1 Hz, 2 H), 4.450 (s, 15 H). HPLC: 8.5 min. $E_{1/2}$: 1160 (r), 447 (r), −1354 (r) mV.

$Cp_3Fe_3(CO)_3(PPh_2)$. Yield: 75 mg (1% yield). Anal. Calcd for $C_{30}H_{25}Fe_3O_3P$: C, 57.01; H, 4.11; Fe, 26.51; P, 4.90. Found: C, 57.01; H, 3.99, N, 0.0; Fe, 25.85; P, 3.50. FDMS: 624 (M$^+$). UV−vis (CH_2Cl_2): 390 nm. IR (KBr): ν_{CO} 1760, 1769, 1632 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.603 (t, *J* = 7 Hz, 2 H), 7.483−7.418 (m, 3 H), 7.244 (d, *J* = 7 Hz, 1 H), 7.174 (t, *J* = 7 Hz, 2 H), 6.556 (t, *J* = 9 Hz, 2 H), 4.707 (s, 5 H), 4.619 (s, 10 H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 231.85. HPLC: 5.1 min. $E_{1/2}$: 188 (r), −1380 (r) mV.

General Procedure for the Reaction of RLi with $Cp_4Fe_4(CO)_4$. In a typical reaction, a 0.015 M THF solution of **1** at −40 °C (MeCN/CO_2) was treated with 1.1 equiv of a solution of RLi. After 30 min, the resulting green to green-brown solution was charged with 1.1 equiv of Ph_2S_2. The solution was allowed to warm to room temperature and then opened to the atmosphere. After evaporation of the solvents, the green-brown residue was extracted into a minimum volume of 4% acetone in CH_2Cl_2 and this solution was passed through a 4 × 30 cm column of silica gel eluting with the same solvent. Typically, the first band was the desired product and the second band was unreacted **1**. While we routinely used Ph_2S_2 as a quenching agent, its use did not affect these conversions.

$(PhC_5H_4)Cp_3Fe_4(CO)_4$ (2Ph). Following the standard procedure, a solution of 0.135 g (0.226 mmol) of **1** in 20 mL of THF at −40 °C was treated with 0.014 mL (0.25 mmol) of a 1.8 M cyclohexane/diethyl ether solution (70:30 v/v) of PhLi to give **2Ph**, identified by ^1H NMR spectroscopy, and unreacted **1** (133 mg). Yield: 8 mg (5%). Gas chromatographic analysis of the crude reaction mixture (after 30 min at room temperature) for Ph_2 and Ph_2S gave Ph_2S/Ph_2 = 0.095. In a control experiment, a solution of 50 mg (0.229 mmol) of Ph_2S_2 in 20 mL of THF at −40 °C was treated with 0.014 mL (0.25 mmol) of the same PhLi solution and worked up as above. Analysis of the crude reaction mixture by gas chromatography gave Ph_2S/Ph_2 = 1.7.

$(n\text{-}BuC_5H_4)Cp_3Fe_4(CO)_4$ (2Bu). A solution of 0.546 g (0.916 mmol) of **1** in 50 mL of THF at −40 °C was treated with 0.68 mL (1.1 mmol) of a 1.6 M hexane solution of *n*-BuLi to give **2Bu** and unreacted **1** (246 mg). Yield: 262 mg (44%). Anal. Calcd for $C_{28}H_{28}Fe_4O_4$: C, 51.59; H, 4.33; Fe, 34.27. Found: C, 51.48; H, 4.43; N, 0.0; Fe, 34.12. FDMS: 641 (M$^+$). UV−vis (CH_2Cl_2): 398 nm. IR (KBr): ν_{CO} 1620 cm^{-1}. ^1H NMR (C_6D_6): δ 4.623 (s, 15 H), 4.554 (t, *J* = 2 Hz, 2 H), 4.366 (t, *J* = 2 Hz, 2 H), 2.473 (t, *J* = 7 Hz, 2 H), 1.404 (quintet, *J* = 7 Hz, 2 H), 1.2 (sextet, *J* = 7 Hz, 2 H), 0.816 (t, *J* = 7 Hz, 3 H). HPLC: 10.5 min. $E_{1/2}$: 1148 (r), 406 (r), −1406 (r) mV.

$(n\text{-}BuC_5H_4)_2Cp_2Fe_4(CO)_4$ (3(Bu)$_2$). A solution of 0.109 g (0.167 mmol) of **2Bu** in 20 mL of THF at −40 °C was treated with 0.12 mL (0.20 mmol) of a 1.6 M hexane solution of *n*-BuLi to give **3(Bu)$_2$** and unreacted **2Bu** (43 mg). Yield: 53 mg (45%). Anal. Calcd for $C_{32}H_{36}Fe_4O_4$: C, 54.28; H, 5.12; Fe, 31.55. Found: C, 54.53; H, 5.02; Fe, 31.84. FDMS: 708 (M$^+$). UV−vis (CH_2Cl_2): 398 nm. IR (KBr): ν_{CO} 1621 cm^{-1}. ^1H NMR (C_6D_6): δ 4.650 (s, 10 H), 4.584 (t, *J* = 2 Hz, 4 H), 4.392 (t, *J* = 2 Hz, 4 H), 2.504 (t, *J* = 7 Hz, 4 H), 1.422 (quintet, *J* = 8 Hz, 4 H), 1.224 (sextet, *J* = 7 Hz, 4 H), 0.824 (t, *J* = 7 Hz, 6 H). HPLC: 38.1 min.

$(t\text{-}BuC_5H_4)Cp_3Fe_4(CO)_4$ (2(*t*-Bu)). A solution of 0.262 g (0.439 mmol) of **1** in 100 mL of toluene at −40 °C was treated with 0.30 mL (0.51 mmol) of a 2.0 M hexanes solution of *t*-BuLi resulting in a brown-green precipitate forming immediately. After 30 min, 0.200 g (0.788 mmol) of I_2 was added and the resulting mixture was allowed to warm to room temperature. After 24 h, the solvent was removed and the green residue was purified by column chromatography to give **2(*t*-Bu)** together with unreacted **1** (57 mg). Yield: 61 mg (21%). Anal. Calcd for $C_{28}H_{28}Fe_4O_4$: C, 51.59; H, 4.33; Fe, 34.27. Found: C, 51.74; H, 4.57; N, 0.0; Fe, 34.32. FABMS: 641 (M$^+$). UV−vis (CH_2Cl_2): 398 nm. IR (KBr): ν_{CO} 1625 cm^{-1}. ^1H NMR (C_6D_6): δ 4.642 (s, 15 H), 4.521 (t, *J* = 2 Hz, 2 H), 4.361 (t, *J* = 2 Hz, 2 H), and 1.310 (s, 9 H). HPLC: 9.5 min. $E_{1/2}$: 1094 (r), 400 (r), −1400 (r) mV.

$(n\text{-}BuC_5H_4)(PhC_5H_4)Cp_2Fe_4(CO)_4$ (3BuPh). A solution of 1.151 g (1.713 mmol) of **2Ph** in 150 mL of THF at −40 °C was treated with 1.40 mL (2.24 mmol) of a 1.6 M hexanes solution of *n*-BuLi to give **3BuPh** and unreacted **2Ph** (0.647 g). Yield: 0.375 g (30%). Anal. Calcd for $C_{34}H_{32}Fe_4O_4$: C, 56.09; H, 4.43; Fe, 30.68. Found: C, 56.05; H, 4.20; N, 0.0; Fe, 30.42. FDMS: 728 (M$^+$). UV−vis (CH_2Cl_2): 402 nm. IR (KBr): ν_{CO} 1622 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.770 (d, *J* = 8 Hz, 2 H), 7.425 (t, *J* = 8 Hz, 2 H), 7.342 (t, *J* = 8 Hz, 1 H), 4.996 (t, *J* = 2 Hz, 2 H), 4.822 (t, *J* = 2 Hz, 2 H), 4.507 (s, 10 H), 4.441 (t, *J* = 2 Hz, 2 H), 4.285 (t, *J* = 2 Hz, 2 H), 2.433 (t, *J* = 8 Hz, 2 H), 1.514 (sextet, *J* = 8 Hz, 2 H), 1.360 (quintet, *J* = 8 Hz, 2 H), 0.921 (t, *J* = 8 Hz, 3 H). HPLC: 28.2 min. $E_{1/2}$: 1126 (r), 500 (r), −1414 (r) mV.

General Procedure for Lithiation of $Cp_4Fe_4(CO)_4$. In a typical reaction, a 0.015 M THF solution of **1** at −40 °C ($MeCN/CO_2$) was treated with 1.3 equiv of a 1.5 M solution of LDA in cyclohexane. After 30 min, the resulting green to green-brown solution was charged with 1.3 equiv of the electrophile (RX) and the solution was allowed to warm to room temperature. The solvent was removed. The resulting green-brown residue was extracted into a minimum volume of 4% acetone and CH_2Cl_2 (v/v) and passed through a 4 × 30 cm column of silica gel eluting with the same solution. Three bands were typically isolated: $(C_5H_4R)_xCp_{4-x}Fe_4(CO)_4$, where $x = 1$, 2, and unreacted **1**.

Formylation of 1. A solution of 1.022 g (1.715 mmol) of **1** in 150 mL of THF at −40 °C was treated with 1.8 mL (2.6 mmol) of a 1.5 M cyclohexane solution of LDA followed by the addition of 1.0 mL (13 mmol) of DMF. After 2 h, the reaction mixture was treated with the following: 5 mL of 3 M HCl, 100 mL of H_2O, and 100 mL of EtOAc. The two layers were separated and the aqueous layer was washed with 50 mL of EtOAc. The organic layers were combined, dried with $MgSO_4$, and filtered. Evaporation of the solvent left a green residue that was purified by column chromatography to give unreacted **1** (256 mg), **2CHO**, and **3(CHO)$_2$**.

$(C_5H_4CHO)Cp_3Fe_4(CO)_4$ (2CHO). Recovered: 596 mg (56% yield). Anal. Calcd for $C_{25}H_{20}Fe_4O_5$: C, 48.13; H, 3.23; Fe, 35.81. Found: C, 47.71; H, 3.32, N, 0.0; Fe, 35.46. FDMS: 624 (M^+). UV−vis (CH_2Cl_2): 396 nm. IR (KBr): ν_{CO} 1644, 1620 cm^{-1}. ^1H NMR (C_6D_6): δ 9.962 (s, 1 H), 4.911 (t, $J = 2.4$ Hz, 2 H), 4.566 (t, $J = 2.4$ Hz, 2 H), 4.537 (s, 15 H). HPLC: 3.3 min. $E_{1/2}$: 1308 (i), 572 (r), −1110 (r) mV.

$(C_5H_4CHO)_2Cp_2Fe_4(CO)_4$ (3(CHO)$_2$). Recovered: 85 mg (8% yield). Anal. Calcd for $C_{26}H_{20}Fe_4O_6$: C, 47.91; H, 3.09; Fe, 34.27. Found: C, 47.93; H, 3.34, N, 0.0; Fe, 34.23. FDMS: 652 (M^+). UV−vis (CH_2Cl_2): 400 nm. IR (KBr): ν_{CO} 1690, 1629 cm^{-1}. ^1H NMR (C_6D_6): δ 9.857 (s, 2 H), 4.855 (t, $J = 2$ Hz, 4 H), 4.529 (t, $J = 2$ Hz, 4 H), 4.493 (s, 10 H). HPLC: 2.6 min. $E_{1/2}$: 1289 (i), 617 (r), −1110 (r) mV.

Reaction of 1 with Acetaldehyde. A solution of 0.625 g (1.05 mmol) of **1** in 100 mL of THF at −40 °C was treated with 1.53 mL (2.29 mmol) of a 1.5 M cyclohexane solution of LDA followed by the addition of 2.0 mL (35 mmol) of acetaldehyde. The resulting green solution was warmed to room temperature and the solvent removed. The dark green residue was extracted into 100 mL of toluene followed by the addition of 0.235 g (1.24 mmol) of *p*-toluenesulfonic acid and the solution was warmed to reflux with a Dean−Stark trap attached. After 1 h, HPLC indicated complete conversion of the alcohol to the vinyl derivative. The solution was cooled to room temperature and the solvent was removed. The resulting green residue was purified by column chromatography to give **3(CHCH$_2$)$_2$**, **2CHCH$_2$**, and unreacted **1** (134 mg).

$(C_5H_4CHCH_2)Cp_3Fe_4(CO)_4$ (2CHCH$_2$). Recovered: 402 mg (62% yield). FDMS: 622 (M^+). UV−vis (CH_2Cl_2): 398 nm. IR (KBr): ν_{CO} 1626 cm^{-1}. ^1H NMR (C_6D_6): δ 6.456 (dd, $J = 9$, 11 Hz, 1 H), 5.566 (dd, $J = 18$, 1 Hz, 1 H), 5.085 (dd, $J = 11$, 1 Hz, 1 H), 4.590 (s, 15 H), 4.556 (t, $J = 2$ Hz, 2 H), 4.488 (t, $J = 2$ Hz, 1 H). HPLC: 5.6 min.

$(C_5H_4CHCH_2)_2Cp_2Fe_4(CO)_4$ (3(CHCH$_2$)$_2$). Recovered: 63 mg (9% yield). Anal. Calcd for $C_{28}H_{24}Fe_4O_4$: C, 51.91; H, 3.73; Fe, 34.48. Found: C, 51.89; H, 3.99; N, 0.0; Fe, 34.24. FDMS: 648 (M^+). UV−vis (CH_2Cl_2): 398 nm. IR (KBr): ν_{CO} 1625 cm^{-1}. ^1H NMR (C_6D_6): δ 6.460 (dd, $J = 18$, 1 1 Hz, 1 H), 5.574 (dd, $J = 18$, 1 Hz, 1 H), 5.086 (dd, $J = 11$, 1 Hz, 1 H), 4.588 (s, 15H), 4.557 (t, $J = 2$ Hz, 2 H), 4.484 (t, $J = 2$ Hz, 1 H). HPLC: 8.4 min. $E_{1/2}$: 1185 (r), 434 (r), −1380 (r) mV.

$(C_5H_4CO_2H)Cp_3Fe_4(CO)_4$ (2CO$_2$H). A solution of 0.306 g (0.514 mmol) of **1** in 75 mL of THF at −40 °C was treated with 0.5 mL (0.75 mmol) of a 1.5 M cyclohexane solution of LDA. After 30 min, the green-brown solution was purged with 30 g of CO_2. The resulting green solution was allowed to warm to room temperature. After 2 h, the solvent was removed. The resulting dark green residue was extracted into 50 mL of 0.1 M NaOH solution. The resulting dark green solution was filtered, washing the green solid with 20 mL of deionized H_2O to recover unreacted **1** (92 mg). The filtrate was acidified with 0.5 mL of 12 M HCl to give a green precipitate, **2CO$_2$H**. Yield: 149 mg (45%). Anal. Calcd for $C_{25}H_{20}Fe_4O_6{\cdot}H_2O$: C, 45.65; H, 3.37; Fe, 33.96. Found: C, 45.60; H, 3.10; N, 0.0; Fe, 31.89. FABMS: 641 ($M^+ + 1$). UV−vis: (CH_2Cl_2) 396 nm; (0.1 M NaOH) 394 nm. IR (KBr): ν_{CO} 1676, 1632 and ν_{OH} 3432 cm^{-1}. ^1H NMR (C_6C_6): δ 11.063 (s, 1 H), 5.001 (t, $J = 2$ Hz, 2 H), 4.839 (t, $J = 2$ Hz, 2 H), 4.789 (s, 15 H). HPLC: 1.8 min.

$(C_5H_4CHO)(n\text{-}BuC_5H_4)(PhC_5H_4)CpFe_4(CO)_4$ (4Bu(CHO)Ph). A solution of 0.670 g (0.920 mmol) of **3BuPh** in 150 mL of THF at −40 °C was treated with 1.4 mL (2.1 mmol) of a 1.5 M cyclohexane solution of LDA followed by the addition of 1.0 mL (13 mmol) of DMF. After 2 h, 2 mL of a 3 M HCl solution was added. After 15 min, the solvent was concentrated and the green-brown residue was extracted into 100 mL of $CHCl_3$ and washed with 2 × 50 mL portions of H_2O. The organic layer was dried with $MgSO_4$ and filtered and the solvent was removed. The resulting green residue was purified by column chromatography to give unreacted **3BuPh** (297 mg) and **4Bu(CHO)Ph**. Yield: 112 mg (16%). Anal. Calcd for $C_{35}H_{32}Fe_4O_5$: C, 56.60; H, 4.27; Fe, 29.55. Found: C, 56.40; H, 4.04; N, 0.0; Fe, 30.01. FDMS: 756 (M^+). UV−vis (CH_2Cl_2): 406 nm. IR (KBr): ν_{CO} 1689, 1626 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.973 (s, 1 H), 7.750 (d, $J = 7$ Hz, 2 H), 7.128 (t, $J = 7$ Hz, 2 H), 7.022 (t, $J = 7$ Hz, 1 H), 4.860−4.820 (m, 3 H), 4.680−4.630 (m, 2 H), 4.430−4.410 (m, 2 H), 4.398 (s, 5 H), 4.390−4.370 (m, 2 H), 4.310−4.290 (m, 1 H), 4.250−4.230 (m, 1H), 4.230−4.210 (m, 1 H), 2.366 (t, $J = 7$ Hz, 2 H), 1.339 (quintet, $J = 8$ Hz, 2 H), 1.171 (sextet, $J = 8$ Hz, 2 H), 0.801 (t, $J = 8$ Hz, 3 H). $E_{1/2}$: 1266 (r), 536 (r), −1197 (r) mV.

PhS Derivatives of 1. A solution of 0.426 g (0.715 mmol) of **1** in 100 mL of THF at −40 °C was treated with 1.30 mL (1.95 mmol) of a 1.5 M cyclohexane solution of LDA followed by the addition of 0.714 g (3.27 mmol) of Ph_2S_2. The resulting green residue was purified by column chromatography to give **3(SPh)$_2$**, **2SPh**, and unreacted **1** (81 mg).

$(C_5H_4SPh)Cp_3Fe_4(CO)_4$ (**2SPh**). Recovered: 170 mg (34% yield). Anal. Calcd for $C_{30}H_{24}Fe_4O_4S$: C, 51.18; H, 3.43; Fe, 31.73; S, 4.55. Found: C, 51.29; H, 3.61; N, 0.0; Fe, 31.73; S, 4.48. FDMS: 704 (M^+). UV−vis (CH_2Cl_2): 398 nm. IR (KBr): ν_{CO} 1628 cm^{-1}. ^1H NMR (C_6D_6): δ 7.295 (d, $J = 7$ Hz, 2 H), 6.926 (t, $J = 7$ Hz, 2 H), 6.849 (t, $J = 7$ Hz, 1 H), 4.675 (s, 15 H), 4.652 (t, $J = 2$ Hz, 2 H), 4.567 (t, $J = 2$ Hz, 2 H). HPLC: 8.1 min. $E_{1/2}$: 1136 (i), 432 (r), −1318 (r) mV.

$(C_5H_4SPh)_2Cp_2Fe_4(CO)_4$ (3(SPh)$_2$). Recovered: 97 mg (14% yield). Anal. Calcd for $C_{36}H_{28}Fe_4O_4S_2$: C, 53.24; H, 3.47; Fe, 27.50; S, 7.90. Found: C, 53.38; H, 3.68; N, 0.0; Fe, 27.56; S, 7.84. FDMS: 812 (M^+). UV−vis (CH_2Cl_2): 404 nm. IR (KBr): ν_{CO} 1628 cm^{-1}. ^1H NMR (C_6D_6): δ 7.304 (d, $J = 7$ Hz, 4 H), 6.930 (t, $J = 7$ Hz, 4 H), 6.856 (t, $J = 7$ Hz, 2 H), 4.781 (s, 10 H), 4.722 (t, $J = 2$ Hz, 4 H), 4.668 (t, $J = 2$ Hz, 4 H). HPLC: 20.0 min. $E_{1/2}$: 1160 (i), 474 (r), −1263 (r) mV.

PPh$_2$ Derivatives of 1. A solution of 0.401 g (0.673 mmol) of **1** in 100 mL of THF at −40 °C was treated with 1.0 mL (1.5 mmol) of a 1.5 M cyclohexane solution of LDA followed by the addition of 0.32 mL (1.6 mmol) of PPh_2Cl. The resulting green residue was purified by column chromatography to give **3(PPh$_2$)$_2$**, **2PPh$_2$**, and unreacted **1** (75 mg).

$(C_5H_4PPh_2)(Cp)_3Fe_4(CO)_4$ (2PPh$_2$). Recovered: 289 mg (55% yield). Anal. Calcd for $C_{36}H_{29}Fe_4O_4P$: C, 55.44; H, 3.75; Fe, 28.64; P, 3.97. Found: C, 55.59; H, 4.00; N, 0.0; Fe, 28.24; P, 4.05. FDMS: 780 (M^+). UV−vis (CH_2Cl_2): 400 nm. IR (KBr): ν_{CO} 1623 cm^{-1}. ^1H NMR (C_6D_6): δ 7.644 (dt, $J = 7$, 1 Hz, 4 H), 7.088 (dd, $J = 7$, 2 Hz, 4 H), 7.020 (dt, $J = 7$, 1 Hz, 2 H), 4.697 (s, 15 H), 4.642 (t, $J = 2$ Hz, 2 H), 4.551 (dt, $J = 2$, 1 Hz, 2 H). $^{31}P\{^1H\}$ NMR: (C_6D_6) δ −18.84; (CD_2Cl_2) δ −20.00. HPLC: 4.1 min. $E_{1/2}$: 448 (r), −1338 (r) mV.

$(C_5H_4PPh_2)_2(Cp)_2Fe_4(CO)_4$ (3(PPh$_2$)$_2$). Recovered: 68 mg (9% yield). Anal. Calcd for $C_{48}H_{38}Fe_4O_4P_2$: C, 59.80; H, 3.97; Fe, 23.14; P, 6.42. Found: C, 59.46; H, 4.03; N, 0.0; Fe, 21.97; P, 6.26. FDMS: 964 ($M^+ - 1$). UV−vis (CH_2Cl_2): 406 nm. IR (KBr): ν_{CO} 1617 cm^{-1}. ^1H NMR (C_6D_6): δ 7.625 (t, $J = 7$ Hz, 8 H), 7.075 (d, $J = 7$ Hz, 8 H), 7.018 (t, $J = 7$ Hz, 4 H), 4.836 (s, 10 H), 4.750 (t, $J = 2$ Hz, 4 H), 4.613 (brs 4 H). $^{31}P\{^1H\}$ NMR: (C_6D_6) δ −19.01; (CD_2Cl_2) δ −20.21. HPLC: 14.4 min. $E_{1/2}$: 449 (r), −1338 (r) mV.

Table 4. Crystal Data and Structural Refinement Details for $RuCl_2$(cymene)(**$2PPh_2$**) and **$(2)_2CHOH$**

empirical formula	$C_{46}H_{43}Cl_2Fe_4O_4PRu$	$C_{49}H_{40}Fe_8O_9$
formula wt	1086.14	1219.61
temp, K	198(2)	198(2)
wavelength, Å	0.710 73	0.710 73
crystal system	orthorhombic	monoclinic
space group	$Pna2_1$	Cc
unit cell dimens		
a, Å	28.1184(5)	30.471(3)
b, Å	9.5734(2)	9.5138(8)
c, Å	14.8812(11)	15.0487(13)
β, deg	90	110.752
V, Å^3	4005.85(11)	4079.5(6)
Z	4	4
d(calcd), mg/m^3	1.801	1.986
abs coeff, mm^{-1}	2.002	2.824
crystal size, mm	0.52 × 0.22 × 0.03	0.008 × 0.07 × 0.28
θ range for data collection, deg	1.45−28.26	2.54−19.99
index ranges:	$-37 \leq h \leq 36, -12 \leq k \leq 12, -12 \leq l \leq 19$	$-33 \leq h \leq 36, -11 \leq k \leq 6, -17 \leq l \leq 16$
collect method:	$\omega-\theta$ scan profiles	$\omega-\theta$ scan profiles
no. of reflcns	25113 [R(int) = 0.0667]^a	4075 [R(int) = 0.0878]^a
no. of indep reflcns	7540 [6092 obs, $I > 4\sigma(I)$]	2487 [2089 obs, $I > 4\sigma(I)$]
refinement method (shift/err = −0.610)	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/parameters	7540/1/564	2461/14/191
goodness-of-fit on F^2	1.042	1.303
final R indices (obs data):	$R_1 = 0.046$, $wR_2 = 0.0994^b$	$R_1 = 0.0880$, $wR_2 = 0.1657^b$
R indices (all data)	$R_1 = 0.0704$, $wR_2 = 0.117$	$R_1 = 0.1133$, $wR_2 = 0.1850$
absolute structural parameter	0.43(3)	−0.01(8)
largest diff; peak and hole, e Å^{-3}	0.637; −0.527	0.660; −0.736

[a] $R(\text{int}) = \sum|F_o^2 - F_o^2(\text{mean})|/\sum[F_o^2]$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma 2(F_o^2) + (0.0109P)^2 + 7.5500P]$ and $P = (F_o^2 - 2F_c^2)/3$.

$(C_5H_4PPh_2)_3(Cp)Fe_4(CO)_4$ ($4(PPh_2)_3$). A solution of 0.354 g (0.454 mmol) of **$2PPh_2$** in 130 mL of THF at −40 °C was treated with 1.0 mL (1.5 mmol) of a 1.5 M cyclohexane solution of LDA followed by the addition of 0.40 mL (2.0 mmol) of PPh_2Cl. The resulting green residue was purified by column chromatography to give **$2PPh_2$** (60 mg), **$3(PPh_2)_2$** (259 mg). Yield of **$4(PPh_2)_2$**: 110 mg (21%). Anal. Calcd for $C_{60}H_{48}Fe_4O_4P_3$: C, 62.70; H, 4.21; Fe, 19.46; P, 8.08. Found: C, 62.58; H, 4.27; N, 0.0; P, 7.94. FDMS: 1148 (M^+). UV−vis (CH_2Cl_2): 410 nm. IR (KBr): ν_{CO} 16 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.622−7.530 (m, 12 H), 7.093−6.989 (m, 18 H), 5.015 (s, 5 H), 4.953−4.933 (m, 6 H), 4.737−4.712 (m, 6 H). ^{31}P{^{1}H} NMR: (C_6D_6) δ −18.93; (CD_2Cl_2) δ −20.03.

$[C_5H_4PPh_2(RuCl_2(\text{cymene}))]Cp_3Fe_4(CO)_4$ ($RuCl_2$(cymene)($2PPh_2$)). A solution of 0.050 g (0.082 mmol) of $[RuCl_2(\text{cymene})]_2$ and 20 mL of THF at 4 °C (ice bath) was treated with 0.132 g (0.169 mmol) of **$2PPh_2$**. The dark green solution was allowed to warm to room temperature. After 14 h, the solvent was removed. The dark green residue was extracted into 20 mL of CH_2Cl_2 diluted with 80 mL of MeOH and the solvent was reduced. The resulting dark green precipitate was filtered and air-dried. Yield: 0.137 g (78%). Anal. Calcd for $C_{46}H_{43}Cl_2Fe_4O_4PRu$: C, 50.87; H, 3.99; Fe, 20.64; P, 2.85; Ru, 9.34. Found: C, 49.50; H, 4.04; N, 0.0; Fe, 18.99; P, 2.35; Ru, 8.09. FABMS: 1886 (M^+ + 1), 1051 ($MH^+ - Cl^-$). UV−vis (CH_2Cl_2): 404 nm. IR (KBr): ν_{CO} 1629 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.202−8.162 (m, 4 H), 7.548 (brs, 6 H), 5.345−5.333 (m, 2 H), 5.047 (brs, 2 H), 5.010−4.996 (m, 2 H), 4.767−4.763 (m, 2 H), 4.585 (s, 15 H), 2.420 (s, J = 7 Hz, 1 H), 1.727 (s, 3 H), 0.942 (d, J = 7 Hz, 6 H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 19.48. $E_{1/2}$: 462 (r), −1176 (r) mV.

$[C_5H_4PPh_2(Ir(COD)Cl)]Cp_3Fe_4(CO)_4$ (IrCl(COD)($2PPh_2$)). A solution of 0.030 g (0.045 mmol) of $[Ir(COD)Cl]_2$ and 15 mL of degassed MeOH at 4 °C (ice bath) was treated with 0.066 g (0.085 mmol) of **$2PPh_2$**. The solution was allowed to warm to room temperature. After 16 h, the solvent was removed and the green residue was extracted into 5 mL of CH_2Cl_2 and diluted with 60 mL of Et_2O. The resulting green precipitate was filtered and dried. Yield: 0.080 g (80%). Anal. Calcd for $C_{44}H_{41}ClFe_4IrO_4P$: C, 47.36; H, 3.70; Cl, 3.18; Fe, 20.02; Ir, 17.23; P, 2.78. Found: C, 47.00; H, 4.00; N, 0.0; Fe, 19.82; P, 2.38. FABMS: 1081 ($M^+ - Cl^-$). UV−vis (CH_2Cl_2): 402 nm. IR (KBr): ν_{CO} 1634 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.762−7.737 (m, 4 H), 7.038 (t, J = 7 Hz, 4 H), 6.957 (t, J = 7 Hz, 2 H), 5.280−5.275 (m, 2 H), 4.861 (s, 17 H), 4.564 (brs, 2 H), 3.224−3.207 (m, 2 H), 2.197−2.150 (m, 4 H), 1.588−1.548 (m, 2 H), 1.417−1.404 (m, 2 H). ^{31}P{^{1}H} NMR: (C_6D_6) δ 5.768; (CD_2Cl_2) δ 5.255. $E_{1/2}$: 464 (r), −1600 (r) mV.

$[(C_5H_4)Cp_3Fe_4(CO)_4]_2CHOH$ ($(2)_2CHOH$). A solution of 0.209 g (0.351 mmol) of **1** in 50 mL of THF at −40 °C was treated with 0.35 mL (0.52 mmol) of a 1.5 M cyclohexane solution of LDA. After 30 min, 0.200 g (0.321 mmol) of **2CHO** dissolved in 25 mL of THF was added by cannula transfer. The resulting dark green solution was allowed to stir, warming to room temperature. After 6 h, 1 mL of H_2O was added. After 15 min, the solvent was removed. The resulting green residue was purified by column chromatography to give unreacted **1** (123 mg), unreacted **2CHO** (66 mg), and **$(2)_2CHOH$**. Yield: 151 mg (38%). Anal. Calcd for $C_{49}H_{40}Fe_8O_9$: C, 48.25; H, 3.30; Fe, 36.65. Found: C, 48.60; H, 3.49; N, 0.0; Fe, 34.20. FABMS: 1219 (M^+). UV−vis (CH_2Cl_2): 396 nm. IR (KBr): ν_{OH} 3398, ν_{CO} 1628 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.638 (brs, 1H), 4.845 (s, 32 H), 4.767 (q, J = 2 Hz, 2 H), 4.646 (d, J = 2 Hz, 1 H), 4.605 (q, J = 2 Hz, 2 H), 4.468−4.462 (m, 2 H). HPLC: t_R = 16.1 min. $E_{1/2}$: 1078 (i), 523 (r), 410 (r), −1246 (r), −1399 (r) mV.

$(C_5H_4((C_5H_4CHOH)Cp_3Fe_4(CO)_4))(C_5H_4CHO)Cp_2Fe_4(CO)_4$ ($(2)_2$(CHOH)(CHO)). A solution of 0.214 g (0.343 mmol) of **2CHO** in 50 mL of THF at −40 °C was treated with 0.34 mL (0.51 mmol) of LDA. After 5 h the reaction was quenched with 1 mL of H_2O and the solvent was evaporated. The resulting dark green residue was extracted into 10 mL of THF and passed through a 3 × 30 cm column of Bio-beads SX-3 in 2-mL portions eluting with THF to give two bands. The first band was green-brown (n = 1) and the second was unreacted **2CHO** (72 mg). Yield: 40 mg (9%). FABMS: 1250 (M^+ + 1).

Crystallographic Analysis of $RuCl_2$(cymene)($2PPh_2$). Green platelike crystals of $RuCl_2$(cymene)(**$2PPh_2$**) were grown by vapor diffusion of Et_2O into CH_2Cl_2 solutions. The data crystal was attached to a thin glass fiber with Paratone-N oil (Exxon). The data crystal was bound by the (1 0 0), (−1 0 0), (0 1 0), (0 −1 0), (0 0 1), and (0 0 −1) faces. Distances from the crystal center to these facial boundaries were 0.015, 0.015, 0.260, 0.260, 0.110, and 0.110 mm, respectively. Data were measured at 198 K on a Siemens P4 diffractometer. Crystal and refinement details are give in Table 4. Systematic conditions suggested the ambiguous space group *Pna*2_1; refinement confirmed the absence of a symmetry center. Three standard intensities monitored every 90 min showed no decay. Step-scanned intensity data were reduced by profile analysis[39] and corrected for Lorentz−polarization effects and for absorption (SHELXTL version 5.03). Scattering factors and anomalous dispersion terms were taken from standard tables.[40]

The structure was solved by Direct Methods;[41] correct positions for Ru, Fe, and Cl were deduced from a vector-map. Subsequent cycles of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis revealed positions for all non-H atoms. Methyl H atom positions were optimized by rotation about the R−C bonds with idealized contributors. H atom *U*'s were assigned as 1.2 times U_{eq} of adjacent non-H atoms. Non-H atoms were refined with anisotropic thermal coefficients. Successful convergence of the full-matrix least-squares refinement on F^2 [42] was indicated by the maximum shift/error for the last cycle. The highest peak in the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

Crystallographic Analysis of (2)$_2$CHOH. Green platelike crystals of **(2)$_2$CHOH** were grown by vapor diffusion of Et_2O into CH_2Cl_2 solutions. The data crystal was attached to a thin glass fiber with Paratone-N oil (Exxon). The data crystal was bound by the (−1 0 0), (1 0 0), (1 1 0), (−1 0 0), (0 0 1), and (0 0 −1) faces. Distances from the crystal center to these facial boundaries were 0.004, 0.004, 0.035, 0.035, 0.140, and 0.140 mm, respectively. Data were measured at 198 K on a Siemens P4 diffractometer. Crystal and refinement details are given in Table 4. Systematic conditions suggested the ambiguous space group *Cc*; refinement confirmed the absence of a symmetry center. Three standard intensities monitored every 90 min showed no decay. Step-scanned intensity data were reduced by profile analysis[39] and corrected or Lorentz and polarization effects and for absorption (SHELXTL version 5.03). Scattering factors and anomalous dispersion terms were taken from standard tables.[40]

The best available data crystal was twinned. Two distinct orientations related by rotation about the α-axis were identified and integrated. Reflections with overlapping 3-dimensional integration boxes were omitted prior to filtering each nonoverlapping data set to remove statistical outliers. A global scale factor was refined against intensities observed in both filtered nonoverlapping sets to determine the percent contribution from each intergrowth. The primary orientation represented 67.5% of the total crystal volume. All further calculations were performed with use of data only from the major component.

The structure was solved by Direct Methods;[41] correct positions for all non-hydrogen atoms were deduced from a vector map. Data with $5.0 \leq 2\theta \leq 40$ were used for refinement. H atom *U*'s were assigned as 1.2 times U_{eq} of the adjacent non-H atoms. The Fe atoms were refined anisotropically. C atoms of the nonfunctionalized Cp rings were constrained to the same isotropic displacement parameter. The C and O atoms of the carbonyl moieties were also constrained separately to equivalent isotropic displacement parameters. The isotropic displacement parameter of the C atoms of the functionalized cyclopentadienyl groups and the C and O of the alcohol were allowed to freely refine. Successful convergence of the full-matrix least-squares refinement on F^2 [42] was indicated by the maximum shift/error for the last cycle. The highest peak in the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

Acknowledgment. Funding was provided by the National Science Foundation (CHE 95-28409) and the Department of Energy (DEFG02-96ER45439). NMR spectra were obtained in the Varian-Oxford Instrument Center for Excellence in NMR. Funding for this instrumentation was provided in part from the W. M. Keck Foundation, the National Institutes of Health (PHS 1 S10 RR10444-01), and the National Science Foundation (NSF CHE 96-10502).

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for $C_{46}H_{43}Fe_4O_4PRu$ and $C_{49}H_{40}Fe_8O_9$ (21 pages). See any current masthead page for ordering and Internet access instructions.

JA972557T

---

[39] Coppens, P.; Blessing, R. H.; Becker, P. *J. Appl. Crystallogr.* **1972**, *7* 488.

[40] Wilson, A. J. C., Ed. *International Tables for X-ray Crystallography* Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, (a) scattering factors, pp 500−502, and (b) anomalous dispersion corrections, pp 219−222.

[41] Sheldrick, G. M. SHELXS-86 *Acta Crystallogr.* **1990**, *A46*, 467. Egert, E.; Sheldrick, G. M. *Acta Crystallogr.* **1985**, *A41*, 262.

[42] Sheldrick, G. M. SHELXS-94.