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Mechanistic Aspects of the Reaction of Anionic Iron(0)–Olefin Complexes with Organic Halides. Detection and Characterization of Paramagnetic Organometallic Intermediates

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Abstract: The scope and the mechanism of the reactions of [CpFe(COD)][Li(TMEDA) (Cp = $C_5H_5^-$; COD = 1,5-cyclooctadiene; TMEDA = $Me_2NCH_2CH_2NMe_2$), **1**, with a number of organic monohalides and geminal dihalides were investigated. With monohalides organic coupling products were observed, and, in particular, the coupling and cross-coupling of benzyl and allyl halides were studied in detail. The addition of 1 equiv of benzyl halide to **1** in benzene resulted in the initial formation of $[CpFe(COD)(CH_2Ph)]$, **7**. The predominant pathway involved an initial one-electron transfer from $[CpFe(COD)]^-$ to $PhCH_2X$ to form $PhCH_2X^{\bullet-}$ and $[CpFe(COD)]^\bullet$. $PhCH_2X^{\bullet-}$ quickly disproportionated to form $PhCH_2^\bullet$ and X^-. The benzyl radical then added to $[CpFe(COD)]^\bullet$. Once formed $[CpFe(COD)(CH_2Ph)]$ reacted with TMEDA in a disproportionation reaction to form 0.5 equiv of the paramagnetic compound, $[(TMEDA)Fe(CH_2Ph)_2]$, **3**, and 0.5 equiv of $FeCp_2$. When additional benzyl (or allyl) halide was added, it reacted with $[(TMEDA)Fe(CH_2Ph)_2]$ to form the coupled (or cross-coupled) product. This coupling reaction involved the intermediacy of benzyl (and allyl) radicals, and the experimental results were consistent with the product being formed by the coupling of two radicals in solution.

The formation and decomposition of metal–hydrocarbyl species are ubiquitous steps in a multitude of organic transformations that are mediated by transition metals. As a result, the chemistry of transition-metal–hydrocarbyls has been the subject of intense scrutiny in recent years. One of the most important synthetic routes to such compounds involves the reaction of anionic transition-metal complexes with organic halides.[1] Two major thrusts have dominated research in this area. The first encompasses the use of transition-metal anions in synthesis. The following anionic metal species are representative of complexes which have significant synthetic utility: $Fe(CO)_4^{2-}$,[2] $CpFe(CO)_2^-$,[3] and $Co(CO)_4^-$.[4] The second major thrust has involved mechanistic studies, both of the metal–carbon bond formation process and also of the decomposition pathways. Among the anionic metal species investigated are $CpFe(CO)_2^-$,[5] $Fe(CO)_4^{2-}$,[6] $Mn(CO)_5^-$,[7] $CpMo(CO)_3^-$,[8] $Co(dmgH)(py)^-$,[9] and $[CpCo(CO)]_2^-$.[10] Thus far, almost all the work in this area has focused on metal carbonylates as the anionic species. In contrast, the reactivity of the analogous anionic olefin–metal complexes has received scant attention. The reactivity of the olefin complexes is expected to differ from that of the corresponding carbonylates in at least three respects. First, the metal center in the anionic olefin species is expected to be more nucleophilic due to the coordination of a weaker π-acid. Second, olefins bind less strongly than carbon monoxide to metals, especially in higher oxidation states. As a result, reactive coordinatively unsaturated species may be accessible upon oxidation of anionic olefin complexes. Finally, the use of carbonylate anions to generate metal–hydrocarbyls sometimes lead to the formation of metal–acyl species through a subsequent CO insertion into the M–C bond.[11] This step is not possible for anionic–olefin complexes.

In this paper the results of our studies on the reaction of $[CpFe(ol)_2]^-$ [12] with selected organic monohalides and geminal dihalides is discussed. In the case of monohalides, $[CpFe(ol)_2]^-$ acted as a coupling reagent. With geminal dihalides two general types of reaction were observed: (a) carbene type addition of the organic group to the olefinic ligand and (b) coupling reaction to form olefins. Mechanistic studies on the coupling of monohalides led to the identification and characterization of a novel paramagnetic intermediate of the type, L_2FeR_2 (e.g., L = Me_2NCH_2-

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[•] Abstract published in *Advance ACS Abstracts*, February 15, 1994.

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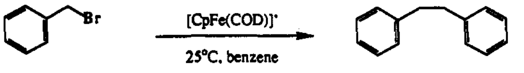
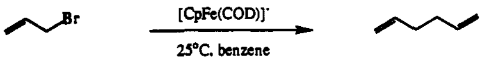
CH_2NMe_2; R = CH_2Ph).[13] This is a rare example of a well-characterized paramagnetic metal–hydrocarbyl species that is an intermediate in an organometallic reaction sequence. Finally, the studies also allowed us to distinguish between one- and two-electron pathways in the formation and decomposition of this paramagnetic intermediate.

Results and Discussions

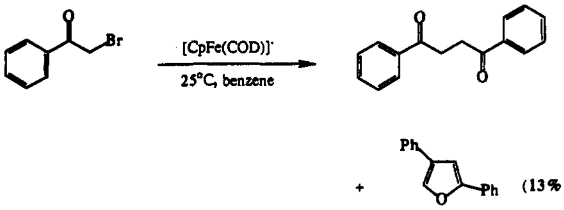
A. Coupling of Organic Monohalides Mediated by [CpFe(COD)]⁻. The addition of 3 equiv of benzyl bromide to [CpFe(COD)][Li(TMEDA)] (Cp = $C_5H_5^-$; COD = 1,5-cyclooctadiene; TMEDA = $Me_2NCH_2CH_2NMe_2$), **1**, in benzene at 25 °C resulted in the formation of $PhCH_2CH_2Ph$ (84% yield relative to **1**) in a few minutes. Similarly, the coupled product, 1,5-hexadiene was formed (83% yield relative to **1**) when 3 equiv of allyl bromide was added to a solution of **1** at 25 °C. An analogous reaction with bromoacetophenone resulted in the formation of the coupled product $PhCOCH_2CH_2COPh$ together with 1,3-diphenylfuran (23% and 13% yield, respectively, relative to **1**). Finally, the coupled product biphenyl was formed (22% yield) when bromobenzene was added to a solution of **1** in benzene at 25 °C. These coupling reactions are summarized in eqs 1–4.



(84%) (1)

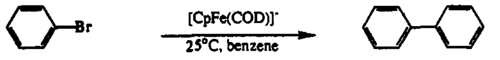


(83%) (2)



(23%)

(13%) (3)



(22%) (4)

Furthermore, the addition of 1 equiv of benzyl chloride to a solution of **1** in benzene followed by the addition of 1 equiv allyl bromide resulted in the formation of the cross-coupled product $PhCH_2CH_2CH{=}CH_2$ (44% yield relative to **1**) as the major product. Bibenzyl (10%), 1,5-hexadiene (26%), and benzyl bromide (1%) were also formed, eq 5 (vide infra). The only soluble iron containing product characterized at the end of these reactions was Cp_2Fe.

$$\underset{\mathbf{1}}{[CpFe(COD)][Li(TMEDA)]} \xrightarrow[\text{2. } CH_2{=}CH_2CHBr]{\text{1. } PhCH_2Cl \text{ (1 equiv.)}} \underset{(44\%)}{PhCH_2CH_2CH{=}CH_2} + \underset{(11\%)}{PhCH_2CH_2Ph} + \underset{(26\%)}{CH_2{=}CHCH_2CH_2CH{=}CH_2} + \underset{(1\%)}{PhCH_2Br} \quad (5)$$

B. Reactions of [CpFe(COD)]⁻ with Geminal Dihalides. The reaction of **1** with diiodomethane resulted in the formation of 1-methyl-1,5-cyclooctadiene in 44% yield (eq 6). The reaction of benzal bromide with **1** resulted in the formation of bicyclo[6,1,0]nonane-4-enyl-9-phenyl in 26% yield and a trace amount of stilbene <1% (eq 7). The reaction of Ph_2CCl_2 with **1** resulted in the formation of the coupled product $Ph_2C{=}CPh_2$ in 49% yield (eq 8).

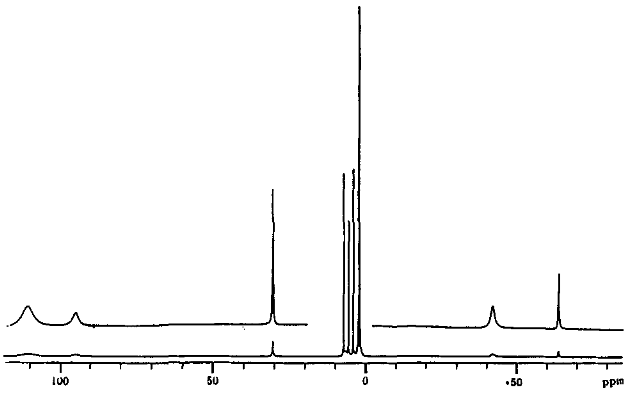
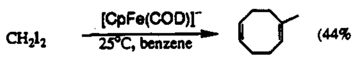
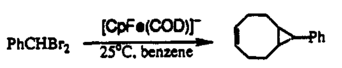


Figure 1. Typical ^1H NMR spectrum (200.1 MHz) of the reaction: [CpFe(COD)][Li(TMEDA)] + $PhCH_2Br$ (1:1 ratio) in benzene-d_6; sweep width: 120 to –120 ppm.



(44%) (6)



(26%) (7)

$$Ph_2CCl_2 \xrightarrow[25°C,\ \text{benzene}]{[CpFe(COD)]^-} Ph_2C{=}CPh_2 \quad (49\%) \qquad (8)$$

C. Mechanistic Studies. After obtaining information concerning the general reactivity of $CpFe(olefin)_2^-$ complexes, attention was focused on the mechanism of the coupling reactions. Coupling reactions are an important method of forming carbon–carbon bonds in organic synthesis. Despite their widespread use, however, there is much that is not yet known pertaining to their mechanisms. Hence, we endeavored to elucidate mechanistic details of the coupling reactions which we encountered.

Identification of the Paramagnetic Intermediate. Mechanistic studies on the reaction of $CpFe(olefin)_2^-$ were initiated by examining the stoichiometric reaction of benzyl halide with **1** and $[CpFe(CH_2{:}CH_2)_2]^-$–$[Li(TMEDA)]^+$, **2**. The addition of 1 equiv of $PhCH_2X$ to **1** in benzene or toluene at 25 °C resulted in the change in solution color from yellow to red. At 20 °C, the ^1H NMR (200 MHz) spectrum of this solution exhibited broad singlets at +947, +30.5, –42.3, and –64.5 ppm in the intensity ratio of 2:2:2:1 and two very broad resonances at +111.7 and +95.6 ppm in the intensity ratio of 3:1 (Figure 1). A delay time of 4.3 s was used between scans, and this was deemed sufficient for obtaining accurate integrations since nuclei relax rapidly in a paramagnetic environment. In any event, an average error of 3.3% was found for the intensity ratios reported above. By using ^2H NMR spectroscopy (Figure 2) and selectively labeled compounds as outlined in Table 1, the first four resonances were assigned to the benzylic, meta, ortho, and para hydrogens, respectively, of a paramagnetically shifted benzyl group. The two broad resonances at +111.7 and +95.6 ppm were assigned to the methyl and methylene groups, respectively, of coordinated TMEDA, based on the following observations. The coordination of COD was ruled out because the position of the vinylic resonance (5.5 ppm) corresponded to that of free COD. Furthermore, the removal of volatiles from the reaction mixture resulted in the quantitative removal of COD. When the residue was redissolved, the paramagnetically shifted NMR resonances were found to be unaffected. There was no coordination of the solvent (arene) since the above resonances were also observed when the reaction was carried out in THF, COD, and pentane (Table 2). Finally,

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[13] Some results have already been reported, see: Hill, D. H.; Sen, A. *J. Am. Chem. Soc.* **1988**, *110*, 1650.

Table 1. ^{2}H NMR Resonances[a] (Integrals[b]) in the Following Reaction: **1** + RX → **3** + $\mathrm{Cp_2Fe}$ in Benzene at 20 °C

reactants	benzyl	*m*-phenyl	*o*-phenyl	*p*-phenyl	Cp
1-Cp-h_5 + benzyl-d_7 chloride	947 (2D)	30.5 (2D)	−42.3 (2D)	−64.5 (1D)	
1-Cp-h_5 + benzyl-α,α-d_2 bromide	947				
1-Cp-h_5 + benzyl-α-d_1 bromide	947				
1-Cp-h_5 + benzyl-*2,3,4,5,6*-d_5 chloride		30.5 (2D)	−42.3 (2D)	−64.5 (1D)	
1-Cp-h_5 + benzyl-*3*-d_1 chloride		30.5			
1-Cp-d_5 + benzyl-d_7 chloride	947 (2D)	30.5 (2D)	−42.3 (2D)	−64.5 (1D)	4.0 (5D)

[a] Chemical shifts in ppm. [b] Average error, 3.3%.

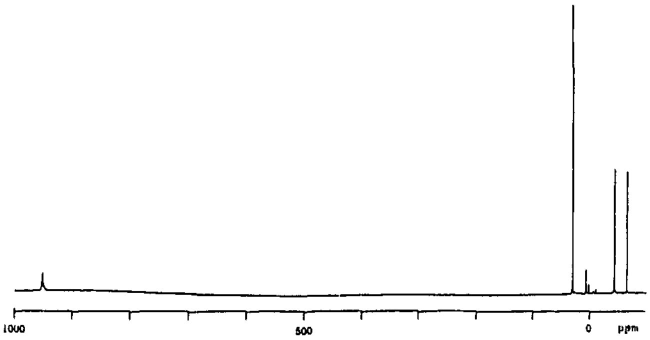

Figure 2. Typical ^{2}H NMR spectrum (30.2 MHz) of the reaction: [CpFe(COD)][Li(TMEDA)] + $\mathrm{C_6D_5CD_2Cl}$ (1:1 ratio) in benzene; sweep width: 1000 to −100 ppm.

Table 2. ^{2}H NMR Isotropic Shifts for $\mathrm{(TMEDA)Fe(CD_2C_6D_5)_2}$ in Selected Solvents

solvent	benzyl	*m*-phenyl	*o*-phenyl	*p*-phenyl
benzene	947	30.5	−42.3	−64.5
THF	932	29.6	−42.5	−64.8
COD	958	29.8	−43.1	−65.4
pentane	970	29.9	−42.8	−65.4

NMR spectroscopy revealed that the Cp ligand was present in the form of $\mathrm{Cp_2Fe}$. In addition to the NMR resonances described thus far, there were broad overlapping resonances between 2.3 and 1.8 ppm as a result of allylic COD hydrogens and 0.5 equiv of uncoordinated TMEDA (relative to **1**).

In summary, the NMR spectroscopic data indicated that a paramagnetic complex **3** was formed through the reaction of **1** with $\mathrm{PhCH_2X}$ and that **3** contained 0.5 equiv of TMEDA and 1 equiv of $\mathrm{CH_2Ph}$ relative to **1**. Furthermore, the simultaneous formation of 0.5 equiv of $\mathrm{Cp_2Fe}$ indicated that 0.5 equiv of Fe (relative to **1**) was present in **3**. Thus, **3** contained Fe, TMEDA, and $\mathrm{CH_2Ph}$ fragments in the ratio of 1:1:2, i.e., its formula was $\mathrm{(TMEDA)Fe(CH_2Ph)_2}$, (eq 9). The equivalence of the hydrogens on the two benzyl groups necessitated a structure with an S_n axis, and this can be accommodated by postulating a (distorted) tetrahedral structure for **3**. In this context, a similar paramagnetic, tetrahedral, Fe(II) complex, $\mathrm{(dippe)FeR_2}$ (dippe = 1,2-bis(diisopropylphosphino)ethane), has been reported recently.[14] Although this compound has a different type of ligand (bisphosphine versus bisamine for **3**) the ^{1}H NMR chemical shifts and line widths follow similar trends [^{1}H NMR (δ, ppm; $W_{1/2}$, Hz) $\mathrm{(dippe)Fe(CH_2Ph)_2}$, 35.3, 85 (*m*-phenyl), −57.5, 500 (*o*-phenyl), −74.7, 100 (*p*-phenyl); $\mathrm{(TMEDA)Fe(CH_2Ph)_2}$, 30.5, 110 (*m*-phenyl), −42.3, 350 (*o*-phenyl), −64.5, 110 (*p*-phenyl)].

$$\underset{\mathbf{1}}{[\mathrm{CpFe(COD)}][\mathrm{Li(TMEDA)}]} + \mathrm{PhCH_2X} \xrightarrow[\text{benzene}]{} 0.5\underset{\mathbf{3}}{[\mathrm{(TMEDA)Fe(CH_2Ph)_2}]} + 0.5\mathrm{Cp_2Fe} + \mathrm{LiX} + \mathrm{COD} + 0.5\mathrm{TMEDA} \quad (9)$$

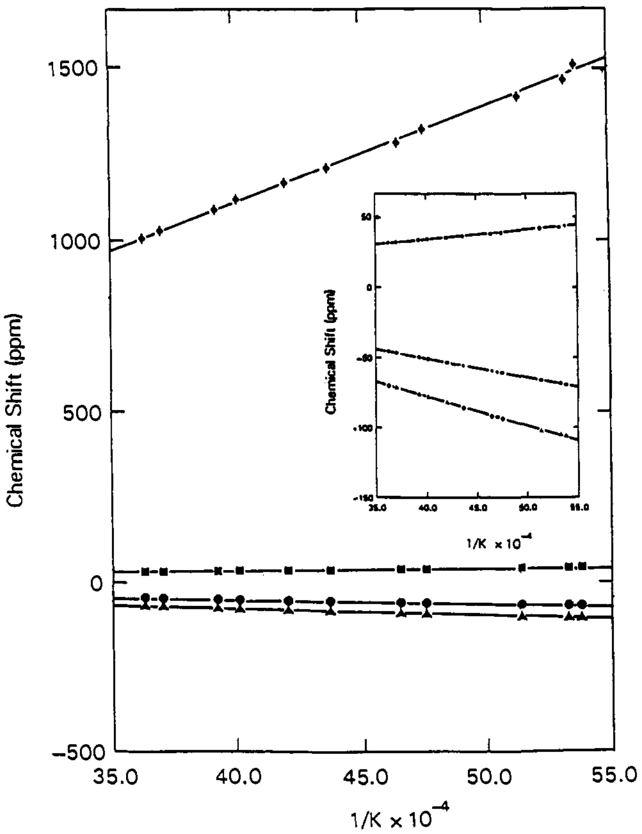

Figure 3. Plot of chemical shift (30.2 MHz) vs 1/K for $\mathrm{(TMEDA)Fe(CH_2Ph)_2}$ in toluene.

As would be expected, **3** was also produced by the reaction of 1 equiv of benzyl halide with $\mathrm{[CpFe(CH_2{:}CH_2)_2][Li(TMEDA)]}$, **2** (see eq 10). The ^{1}H NMR spectra of the two reaction solutions (cf. eqs 9 and 10) were identical except for the presence of COD in the reaction of **1** and $\mathrm{CH_2{:}CH_2}$ in the reaction of **2**. The structure of **3** was further confirmed by its independent synthesis by the dropwise addition of solution of $\mathrm{(TMEDA)_{\it x}FeCl_2}$ in benzene-d_6 to a solution of benzyllithium[15] in benzene-d_6 (eq 11).

$$\underset{\mathbf{2}}{[\mathrm{CpFe(CH_2{:}CH_2)_2}][\mathrm{Li(TMEDA)}]} + \mathrm{PhCH_2X} \xrightarrow[\text{benzene}]{} 0.5\underset{\mathbf{3}}{[\mathrm{(TMEDA)Fe(CH_2Ph)_2}]} + 0.5\mathrm{FeCp_2} + \mathrm{LiX} + 2\mathrm{CH_2{:}CH_2} + 0.5\mathrm{TMEDA} \quad (10)$$

$$\mathrm{(TMEDA)_{\it x}FeCl_2} + 2\mathrm{LiCH_2Ph} \xrightarrow[\substack{\text{benzene}\\ -2\mathrm{LiCl},\ -(x-1)\,\mathrm{TMEDA}}]{} \underset{\mathbf{3}}{\mathrm{(TMEDA)Fe(CH_2Ph)_2}} \quad (11)$$

Isotropic NMR Shift of $\mathrm{(TMEDA)Fe(CH_2Ph)_2}$ versus Temperature. A linear relationship between the isotropic shift and the reciprocal of the absolute temperature was observed for the hydrogens of the benzyl group of **3**, as was expected of a paramagnetic compound[16] (Figure 3). The absence of any breaks indicated that there was no transition to a different spin state

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Table 3. Bond Distances (Å) from the Crystal Structure of **4**

Fe–P1	2.168(1)	C11–C12	1.386(5)	C42–C43	1.376(6)
Fe–P2	2.162(1)	C11–C16	1.380(5)	C43–C44	1.374(6)
Fe–C1	2.094(4)	C12–C13	1.383(6)	C44–C45	1.368(7)
Fe–C2	2.106(4)	C13–C14	1.367(6)	C45–C46	1.380(6)
Fe–C3	2.099(4)	C14–C15	1.364(7)	C50–C51	1.479(6)
Fe–C4	2.084(4)	C15–C16	1.383(6)	C51–C52	1.394(5)
Fe–C5	2.080(4)	C21–C22	1.385(6)	C51–C56	1.389(6)
Fe–C50	2.154(4)	C21–C26	1.380(5)	C52–C53	1.372(6)
P1–C6	1.857(4)	C22–C23	1.383(6)	C53–C54	1.349(8)
P1–C11	1.837(4)	C23–C24	1.366(7)	C54–C55	1.376(7)
P1–C21	1.837(4)	C24–C25	1.371(7)	C55–C56	1.391(7)
P2–C7	1.848(4)	C25–C26	1.378(5)		
P2–C31	1.837(4)	C31–C32	1.389(5)		
P2–C41	1.831(4)	C31–C36	1.377(6)		
C1–C2	1.400(6)	C32–C33	1.379(6)		
C1–C5	1.396(5)	C33–C34	1.372(6)		
C2–C3	1.407(5)	C34–C35	1.368(5)		
C3–C4	1.397(5)	C35–C36	1.377(6)		
C4–C5	1.412(6)	C41–C42	1.387(5)		
C6–C7	1.516(5)	C41–C46	1.383(6)		

within the temperature range studied. At 186 K, in toluene, the resonances due to the benzylic, meta, ortho, and para hydrogens of the benzyl group of **3** were at +1508(!), +43.8, –69.2, and –106.4 ppm, respectively (46.1 MHz, ^{2}H NMR). Note that the observation of only one resonance each for the four positions of the benzyl group, even at low temperatures, supported η^1- rather than η^3-coordination of the benzyl group to Fe.

Reactions of (TMEDA)Fe(CH$_2$PH)$_2$ with Benzyl and Allyl Halides. The coupling product, PhCH$_2$CH$_2$Ph, was formed in minutes upon the addition of excess PhCH$_2$X to a solution of (TMEDA)Fe(CH$_2$Ph)$_2$ at 25 °C (eq 12). Similarly, the compound, PhCH$_2$CH$_2$CH=CH$_2$, was the predominant product (44% yield, balance PhCH$_2$CH$_2$Ph 11% and 1,5-hexadiene 26%) formed when CH$_2$=CHCH$_2$Br was added to **3** at 25 °C (eq 13). Clearly, these reactions establish the intermediacy of **3** in the coupling of benzyl halides and the cross-coupling of benzyl and allyl halides by **1**.

$$\mathbf{3} + \mathrm{PhCH_2X} \xrightarrow[\text{benzene}]{} \mathrm{PhCH_2CH_2Ph} \qquad (12)$$

$$\mathbf{3} + 2\mathrm{CH_2{=}CHCH_2Br} \xrightarrow[\text{benzene}]{} \mathrm{PhCH_2CH_2CH{=}CH_2}\ (44\%) + \mathrm{PhCH_2CH_2Ph}\ (11\%) + \mathrm{CH_2{=}CHCH_2CH_2CH{=}CH_2}\ (26\%) \qquad (13)$$

Identification of the Intermediate Species CpFe(COD)(CH$_2$Ph). In order to probe for intermediates in the conversion of **1** to **3**, the reaction of **1** with PhCH$_2$X was examined in the presence of DIPHOS (=Ph$_2$P(CH$_2$)$_2$PPh$_2$). By itself, **1** did not react with DIPHOS presumably because the replacement of COD by the stronger donor, DIPHOS, would result in further increase in electron density at the already electron-rich Fe(0) center. The addition of 1 equiv of PhCH$_2$X to an equimolar solution of **1** and DIPHOS in benzene at 25 °C led to the virtually quantitative formation of the diamagnetic compound, CpFe(DIPHOS)(CH$_2$Ph), **4**, together with a small amount of CpFe(DIPHOS)X (see eqs 14 and 15). The structure of **4** was established by ^{1}H NMR[17] and ^{31}P NMR spectroscopy in solution and by an X-ray crystal structure determination in the solid state (Figure 4). **4** has an unexceptional three-legged piano-stool structure with normal bond lengths and bond angles (Tables 3 and 4). The small amount of CpFe(DIPHOS)X observed (eqs 14 and 15) was apparently formed through a metal–halogen exchange process with benzyl halide to form CpFe(COD)X and benzyllithium or benzyl radical (vide infra). Metal–halogen exchange reactions of this type are well-known with anionic metal complexes. As expected, less halogen exchange took place in the reaction of **1** with benzyl chloride compared to benzyl bromide, as evidenced by the smaller amount of CpFe(DIPHOS)Cl, **5** (1.8% relative to **1**), formed compared to CpFe(DIPHOS)Br, **6** (2.8%), in the reaction of benzyl halide with **1** in the presence of DIPHOS.

$$\mathbf{1} + \mathrm{PhCH_2Cl} \xrightarrow[\text{benzene}]{\text{DIPHOS}} \underset{\mathbf{4}\ (98.2\%)}{\mathrm{CpFe(DIPHOS)(CH_2Ph)}} + \underset{\mathbf{5}\ (1.8\%)}{\mathrm{CpFe(DIPHOS)Cl}} \qquad (14)$$

$$\mathbf{1} + \mathrm{PhCH_2Br} \xrightarrow[\text{benzene}]{\text{DIPHOS}} \underset{\mathbf{4}\ (93.9\%)}{\mathrm{CpFe(DIPHOS)(CH_2Ph)}} + \underset{\mathbf{6}\ (2.8\%)}{\mathrm{CpFe(DIPHOS)Br}} \qquad (15)$$

$$\begin{tikzcd}
\underset{\mathbf{1}}{[\mathrm{CpFe(COD)}][\mathrm{Li(TMEDA)}]} + \mathrm{PhCH_2X} \arrow[rr, "\text{-TMEDA, -LiX}", "\text{benzene}"'] & & \underset{\mathbf{7}}{\mathrm{CpFe(COD)(CH_2Ph)}} \arrow[dl, "\begin{array}{l}0.5\ \text{TMEDA}\\ \text{-}0.5\ \mathrm{Cp_2Fe}\end{array}"'] \arrow[d, "\text{DIPHOS}"] \\
& \underset{\mathbf{3}}{0.5\ \mathrm{(TMEDA)Fe(CH_2Ph)_2}} & \underset{\mathbf{4}}{\mathrm{CpFe(DIPHOS)(CH_2Ph)}} \quad (16)
\end{tikzcd}$$

As shown in eq 16, the formation of **4** appears to indicate that the initial species formed in the reaction of **1** with PhCH$_2$X in benzene was [CpFe(COD)(CH$_2$Ph)], **7**. In the presence of DIPHOS, **4** was formed from **7** by ligand replacement. However, in the absence of a strongly coordinating ligand, **7** underwent disproportionation and reacted with TMEDA to form **3** and Cp$_2$Fe (see eq 9).

In summary, the evidence discussed thus far indicates that the coupling of benzyl halides mediated by **1** in benzene involved three basic steps: (a) the formation of **7** by the reaction of **1** with PhCH$_2$X, (b) the disproportionation of **7** to **3** and Cp$_2$Fe, and (c) the reductive coupling of RX (R = PhCH$_2$, CH$_2$=CHCH$_2$) by **3**.

Mechanism of Oxidative Addition of Benzyl Halide. In general, the reduction of RX by a low-valent metal complex, such as **1**, may occur by one of three different mechanistic pathways: (a) inner-sphere electron transfer (halide ion transfer) (eq 17), (b) outer-sphere electron transfer (eq 18), or (c) bimolecular nucleophilic substitution, i.e., S$_N$2 (eq 19).[18]

Inner-Sphere Electron Transfer

$$[\mathrm{Fe^0}]^- + \mathrm{RX} \longrightarrow [\mathrm{Fe^1{\cdot}X}]^- + \mathrm{R}{\bullet} \xrightarrow{[\mathrm{Fe^0}]^-} [\mathrm{Fe^1{\cdot}X}]^- + [\mathrm{Fe^1{\cdot}R}]^- \qquad (17)$$

Outer-Sphere Electron Transfer

$$\begin{tikzcd}
{[\mathrm{Fe^0}]^-} + \mathrm{RX} \arrow[r] & {[\mathrm{Fe^1}]} + \mathrm{RX}^{\overset{\bullet}{-}} \arrow[dr] & \\
& & \mathrm{R}{\bullet} + \mathrm{X}^-
\end{tikzcd}$$

$$[\mathrm{Fe^1}] + \mathrm{R}{\bullet} + \mathrm{X}^- \longrightarrow [\mathrm{Fe^{II}{\cdot}R}] + \mathrm{X}^- \qquad (18)$$

Nucleophilic Substitution

$$[\mathrm{Fe^0}]^- + \mathrm{RX} \longrightarrow [\mathrm{Fe^{II}{\cdot}R}] + \mathrm{X}^- \qquad (19)$$

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(15) Seyferth, D.; Suzuki, R.; Murphy, C. J.; Sabet, C. R. *J. Organomet. Chem.* **1964**, *2*, 431.

(16) La Mar, G. N.; Horrocks, W. DeW.; Holm, R. H. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

(17) Felkin, H.; Knowles, P. J.; Meunier, B. *J. Organomet. Chem.* **1978**, *146*, 151.

(18) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; Chapters 2 and 7.

Table 4. Bond Angles (deg) from the Crystal Structure of 4

P1–Fe–P2	85.29(4)	C2–Fe–C5	65.6(1)	Fe–C1–C2	71.0(2)
P1–Fe–C1	124.1(1)	C2–Fe–C50	120.4(1)	Fe–C1–C5	69.9(2)
P1–Fe–C2	94.6(1)	C3–Fe–C4	39.0(1)	C2–C1–C5	108.4(3)
P1–Fe–C3	98.9(1)	C3–Fe–C5	66.0(2)	Fe–C2–C1	70.0(2)
P1–Fe–C4	133.4(1)	C3–Fe–C50	157.2(1)	Fe–C2–C3	70.2(2)
P1–Fe–C5	160.2(1)	C4–Fe–C5	39.6(2)	C1–C2–C3	108.0(3)
P1–Fe–C50	91.8(1)	C4–Fe–C50	134.8(2)	Fe–C3–C2	70.7(2)
P2–Fe–C1	150.5(1)	C5–Fe–C50	98.3(2)	Fe–C3–C4	69.9(2)
P2–Fe–C2	155.1(1)	Fe–P1–C6	110.8(1)	C2–C3–C4	107.8(4)
P2–Fe–C3	116.2(1)	Fe–P1–C11	114.8(1)	Fe–C4–C3	71.1(2)
P2–Fe–C4	96.7(1)	Fe–P1–C21	122.3(1)	Fe–C4–C5	70.1(2)
P2–Fe–C5	112.5(1)	C6–P1–C11	104.6(2)	C3–C4–C5	108.2(3)
P2–Fe–C50	84.5(1)	C6–P1–C21	102.7(2)	Fe–C5–C1	71.0(2)
C1–Fe–C2	38.9(2)	C11–P1–C21	99.6(2)	Fe–C5–C4	70.3(2)
C1–Fe–C3	65.6(2)	Fe–P2–C7	107.1(1)	C1–C5–C4	107.7(4)
C1–Fe–C4	65.7(1)	Fe–P2–C31	122.3(1)	P1–C6–C7	110.2(3)
C1–Fe–C5	39.1(1)	Fe–P2–C41	120.2(1)	P2–C7–C6	107.4(3)
C1–Fe–C50	91.8(2)	C7–P2–C31	100.5(2)	P1–C11–C12	119.8(3)
C2–Fe–C3	39.1(1)	C7–P2–41	104.6(2)	P1–C11–C16	121.9(3)
C2–Fe–C4	65.5(1)	C31–P2–C41	99.5(2)	C12–C11–C16	117.7(4)
C11–C12–C13	121.1(4)	P2–C41–C42	118.2(3)		
C12–C13–C14	120.0(4)	P2–C41–C46	124.0(3)		
C13–C14–C15	119.8(4)	C42–C41–C46	117.7(4)		
C14–C15–C16	120.3(4)	C41–C42–C43	121.1(4)		
C11–C16–C15	121.0(4)	C42–C43–C44	120.1(4)		
P1–C21–C22	120.1(3)	C43–C44–C45	119.8(4)		
P1–C21–C26	121.6(3)	C44–C45–C46	120.0(4)		
C22–C21–C26	118.3(3)	C41–C46–C45	121.2(4)		
C21–C22–C23	120.8(4)	Fe–C50–C51	116.2(3)		
C22–C23–C24	119.7(4)	C50–C51–C52	121.6(3)		
C23–C24–C25	120.7(4)	C50–C51–C56	121.4(3)		
C24–C25–C26	119.4(4)	C52–C51–C56	117.0(4)		
C21–C26–C25	121.2(4)	C51–C52–C53	121.7(4)		
P2–C31–C32	120.0(3)	C52–C53–C54	120.8(4)		
P2–C31–C36	122.1(3)	C53–C54–C55	119.5(4)		
C32–C31–C36	117.7(4)	C54–C55–C56	120.5(4)		
C31–C32–C33	120.9(4)	C51–C56–C55	120.5(4)		
C32–C33–C34	120.2(3)				
C33–C34–C35	119.5(4)				
C34–C35–C36	120.2(4)				
C31–C36–C35	121.4(3)				

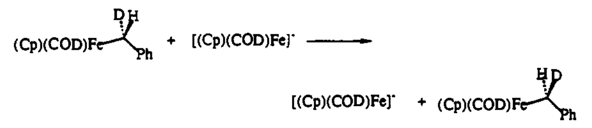
Since the benzyl radical, $PhCH_2^{\bullet}$, was formed in pathways involving one-electron processes (i.e., eqs 17 and 18), racemization at the benzylic carbon would occur in the formation of **7** from chiral PhCHDX. On the other hand, a two-electron nucleophilic substitution process would result in the inversion of configuration at the benzylic carbon.[19] One- and two-electron processes may thus be distinguished by determining the stereochemistry of the addition product of **1** and chiral PhCHDX.

Determination of Stereochemistry at the Benzylic Carbon: Evidence Supporting the Involvement of Benzyl Radicals. Experiments were undertaken to distinguish one- and two-electron processes by observing the stereochemical course of reaction. Since the initial addition product, **7**, was too unstable for direct stereochemical analysis, it was necessary to convert **7** in a stereospecific manner to a more stable compound in which the stereochemistry of the benzylic carbon could be determined. This was done by intercepting **7** with the chiral chelating ligand *S*,*S*-chiraphos(2*S*,3*S*-bis(diphenylphosphino)butane), in a reaction analogous to eq 14. In the resultant compound, CpFe(*S*,*S*-chiraphos)(CH_2Ph), **8**, the benzylic protons H_A and H_B are now diastereotopic. Thus, the stereochemical change at the benzylic carbon (racemization vs inversion) could be determined from the relative ^1H NMR intensities of H_A and H_B when chiral PhCHDX was used.

The dropwise addition of (*R*)-benzyl-α-d_1 chloride[20] to a benzene solution of **1** in the presence of *S*,*S*-chiraphos led to the formation of **8**-d_1 which was 80% racemized[21] at the benzylic carbon. Similarly, the use of (*S*)-benzyl-α-d_1 bromide[20] led to the formation of **8**-d_1 which was >95% racemized[21] at the benzylic carbon. However, it was important to determine whether the racemization occurred *during* the formation of the Fe–C bond or because of some *subsequent* rearrangement process which occurred prior to (or after) the coordination of *S*,*S*-chiraphos. For example, rearrangement processes involving the exchange of groups between metals have been previously established to be responsible for the racemization of chiral carbon centers in some oxidative addition reactions[9] (see eq 20).

$$(CO)_5Mn{\cdot}R + (CO)_5Mn^- \longrightarrow (CO)_5Mn^- + (CO)_5Mn{\cdot}R \quad (20)$$

$$(R = MeCH(CO_2Et))$$



(21)

The possibility of exchange of the benzyl group between CpFe(COD)(CHDPh) and $CpFe(COD)^-$ (eq 21) in the presence of *S*,*S*-chiraphos was, however, ruled out as a viable mechanistic pathway. A solution containing (*R*)-benzyl-α-d_1 chloride in benzene-d_6 was added dropwise to a solution containing **1** and 5 equiv of *S*,*S*-chiraphos in benzene. The relative integrals of the benzylic protons (H_A and H_B) obtained in this reaction were identical to the relative integrals when 1 equiv of *S*,*S*-chiraphos

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(19) (a) Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 838. (b) Lau, K. S. Y.; Wong, P. K.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5832.

(20) (a) Streitweiser, A.; Wolfe, J. R. *J. Am. Chem. Soc.* **1957**, *79*, 903. (b) Stille, J. K.; Lau, K. S. Y. *J. Am. Chem. Soc.* **1976**, *98*, 5841.

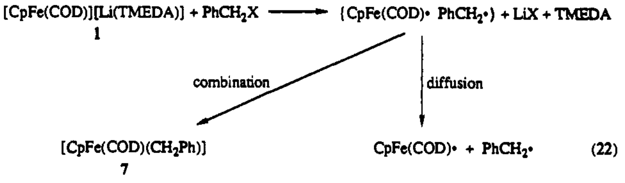
(21) Corrected value. The benzyl chloride used was 98ee. The benzyl bromide was 47.8ee. See Experimental Section.

was present. Furthermore, when using 1 equiv of *S*,*S*-chiraphos, less than 1.6% of ferrocene (vs **8**) was formed in the reaction, indicating that the coordination of *S*,*S*-chiraphos to **7** to generate **8** was much faster than the disproportionation of **7** to **3** and ferrocene. Also, only 1.2% CpFe(*S*,*S*-chiraphos)Cl, **9**, was formed (vs **8**) in the reaction of (*R*)-benzyl-α-d_1 chloride. Similarly, only 2.1% CpFe(*S*,*S*-chiraphos)Br, **10**, was formed when (*S*)-benzyl-α-d_1 bromide was reacted. Finally, there are no other reasonable stereochemical rearrangement pathways available to the iron–benzyl species prior to the coordination of *S*,*S*-chiraphos. For example, although there was no direct evidence for the formation of an η^3-benzyl species, if this species was momentarily present before phosphine coordination, neither a suprafacial nor antarafacial shift would result in the inversion of configuration.[22] Thus, it may be concluded that the racemization at the benzylic carbon was due to the intermediacy of a benzyl radical formed by a one-electron-transfer process (cf. eqs 17 and 18).

In general, reactions which involve the formation of an intermediate radical species at a chiral carbon atom result in the racemization of that chiral carbon center. However, radical reactions sometimes take place with retention of configuration.[23] A few electron-transfer reactions of anionic metal complexes with alkyl halides also take place with retention of configuration. For example, the addition products resulting from the reaction of $[Co(dmgH)(py)]^-$ with the following electrophiles are formed with retention of configuration: dibenzoannelated *exo*-7-bromonorcarrane,[24] 1-adamantyl bromide,[25] 1-norbornyl bromide,[27] and chiral 1-methyl-2,2-diphenylcyclopropyl bromide.[26] However, these reactions seem to be special cases. In these reactions, pathways which would produce other stereochemical results are either greatly inhibited or entirely precluded because of the structure of the reactants. Most reactions of anionic metal complexes with alkyl halides that involve alkyl–radical intermediates take place with racemization.[27] In contrast to radical reactions, S_N2 type oxidative addition reactions of carbon electrophiles with anionic transition-metal complexes usually proceed stereospecifically with inversion of configuration.[27]

In general, the mechanistic pathway followed varies as a function of the nucleophilicity of the anionic metal complex, the structure of the alkyl group, and the particular halide leaving group.[28] Simultaneous competing one- and two-electron processes sometimes occur. In one such case, when cyclopropylcarbinyl halides were reacted with $[CpFe(CO)_2]^-$ or $[(CH_3)_3Sn]^-$, the one-eletron pathway was favored when X = I. The two-electron pathway was favored when X = Cl.[29] In reactions where both pathways simultaneously operate, the proportion of product formed through the one-electron pathway decreases in the order I > Br > Cl. The rate of one-electron transfer from metal complexes to benzyl halides has been determined to be much faster for the bromide compared to the chloride. For example, the rate of electron transfer of $[Co(CN)_5]^{3-}$ to benzyl halides has been determined.[30] The rate decreases in the order I > Br > Cl (X = I, $k = 3.8 \times 10^3$ M^{-1} s^{-1}; X = Br, $k = 2.3$ M^{-1} s^{-1}; X = Cl, $k = 4.9 \times 10^{-4}$ M^{-1} s^{-1}). Furthermore, a competitive one-electron transfer pathway was suggested as being responsible for increased racemization observed in the reaction of chiral benzyl bromide (vs benzyl chloride) with $Pd(PEt_3)_4$.[19a] Consequently, if one- and two-electron pathways were competing in the reactions of $[CpFe(COD)]^-$ with chiral benzyl halides, the one-electron transfer pathway would be more significant when using benzyl bromide (compared to benzyl chloride). As a result, more racemization would be expected with benzyl bromide. The increased amount of racemization observed in the reaction of chiral benzyl bromide with **1** (>95% vs 80% for benzyl chloride) was consistent with this hypothesis. The nonracemized product formed in the reaction of chiral benzyl chloride with **1** and *S*,*S*-chiraphos was presumably the result of a competing two-electron transfer (S_N2) pathway.

Evidence for Inner-Sphere Electron-Transfer Pathway. Although inner- and outer-sphere electron transfers are often difficult to distinguish, there is evidence that both may be involved in varying extents in the present case. The small amount of CpFe(DIPHOS)Br and CpFe(DIPHOS)Cl detected may be produced as the result of an inner-sphere electron-transfer mechanism. In addition, there is evidence that an outer-sphere pathway was involved in the reactions to a significant extent. The initial formation of $[CpFe(COD)]^\bullet$, **11**, would be indicative of an outer-sphere electron-transfer pathway (eq 22). This species has been reported to be formed by the reaction of $CpFe(COD)^-$ with trityl chloride (eq 23).[12]



(22)

$$\underset{\mathbf{1}}{[CpFe(COD)][Li(TMEDA)]} + Ph_3CCl \longrightarrow \underset{\mathbf{11}}{[CpFe(COD)]^\bullet} + Ph_3C^\bullet + LiCl + TMEDA \quad (23)$$

When this latter reaction was monitored by ^1H NMR (200 MHz) spectroscopy in benzene-d_6, a significant broadening of the resonances in the "normal" region (0–10 ppm) was observed, and, in addition, there was a broad resonance at +45 ppm due to the Cp ligand in **11**. The assignment of this resonance was confirmed by the detection by ^2H NMR (30 MHz) of a resonance at 45 ppm when **1-Cp-d_5** was allowed to react with trityl chloride in benzene. In order to determine if **11** was also formed in the reaction of **1** with $PhCH_2X$, 1.1 equiv of $PhCH_2Cl$ was added to **1-Cp-d_5** in benzene, and the ^2H NMR spectrum of the resultant solution was recorded immediately. The spectrum showed resonances at +44.8 and 4.0 ppm in the ratio of 0.7:1.0. The second resonance was due to Cp_2Fe and, with time, grew in intensity (note that the resonances due to **3** would not be visible by ^2H NMR spectroscopy). After 1 h, the resonance at 44.8 ppm had disappeared entirely. The detection of the resonance at 44.8 ppm indicated the participation of **11** in the reaction. The reaction of **1-d_5** with $C_6D_5CD_2Cl$ was also monitored (as a function of time) with similar results. The direct observation of **11** by NMR spectroscopy supported the participation of an outer-sphere electron-transfer pathway in the reaction of **1** with $PhCH_2X$ (eq 22).

Identification of a Second Paramagnetic Intermediate Species in the Reaction of $CpFe(ol)_2^-$ with $PhCH_2X$ in THF. As mentioned previously, the reaction of **1** with 1 equiv of $PhCH_2X$ in THF resulted in the formation of **3**. The formation of **3** was indicated (^2H NMR, 46.1 MHz) by resonances at 931, 29.6, −42.5, and −64.8 ppm. When exactly 1 equiv of $PhCH_2X$ was added, an *additional* minor paramagnetic species, **12**, was detected having resonances at 954.3, 30.7, −50.1, and −77.8 ppm in a 4:4:4:2 ratio,

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[22] Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 845.

[23] For specific examples, see: (a) Walborsky, H. M.; Allen, L. E. *J. Am. Chem. Soc.* **1971**, *93*, 5465. (b) Engstrom, J. P.; Greene, F. D. *J. Org. Chem.* **1972**, *37*, 968. (c) Johnson, R. A.; Seltzer, S. *J. Am. Chem. Soc.* **1973**, *95*, 938. (d) Lee, K.-W.; Horowitz, N.; Ware, J.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 2622.

[24] Schaffler, J.; Retey, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 845.

[25] Eckert, H.; Lenoir, D.; Ugi, I. *J. Organomet. Chem.* **1977**, *141*, C23.

[26] Jensen, F. R.; Buchanan, D. H. *J. Chem. Soc., Chem. Commun.* **1973**, 153.

[27] Flood, T. C. In *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Geoffroy, G. L., Eds.; Wiley: New York, 1981; Vol. 12, p 37.

[28] For a general discussion, see: (a) Stille, J. K.; Lau, K. S. Y. *Acc. of Chem. Res.* **1977**, *10*, 434. (b) Reference 30.

[29] (a) Krusic, P. J.; Fagan, P. J.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 250. (b) San Filippo, J., Jr.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.

[30] Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 582.

respectively. This minor species was typically present in approximately a 1:5 ratio to **3**. The addition of excess TMEDA to this solution resulted in the conversion of **12** to **3** as determined by ^{2}H NMR spectroscopy. If the reaction was performed in a mixed solvent system consisting of THF and benzene, the relative amount of **12** present, compared to **3**, decreased as the relative amount of THF in the solvent decreased. Several conclusions concerning the structure of **12** could be made from the above observations. First, the similarity of the NMR spectra of **3** and **12** indicated that **12** probably had a structure analogous to **5**, i.e., a distorted tetrahedron, containing two benzyl ligands and two other ligands (coordinated in lieu of TMEDA). Second, these other ligands could be displaced by added TMEDA. Finally, in reactions performed in mixed solvent systems, the coordination of these other ligands was favored by increasing amounts of THF (vs benzene) in the solvent.

The only two additional compounds present which could act as ligands in **12** were COD and THF. There was a substantial amount of evidence against the coordination of COD. First, the olefinic resonance and integral (^{1}H NMR 5.5 ppm, 4 H, corresponding to free COD) indicated that COD was not coordinated to the paramagnetic species. Second, **12** was not detected at all when benzene was used as the reaction solvent. Third, and most importantly, **12** was not detected (^{2}H NMR) when COD was used as the reaction solvent. In contrast there was evidence that THF was coordinated. First, **12** was detected only when THF was used as the solvent. Second, the relative amount of **12** formed vs **3** increased upon increasing the relative amount of THF (vs benzene) in mixed solvent systems (thus, in effect, increasing the concentration of THF vs TMEDA). In conclusion, based on the preceding observations, compound **12** was assigned as $(THF)_2Fe(CH_2Ph)_2$, see eqs 24 and 25.

$$\underset{\mathbf{1}}{[CpFe(COD)][Li(TMEDA)]} + PhCH_2X \xrightarrow[\cdot\,0.5\,Cp_2Fe,\ \cdot\,0.6\,TMEDA,\ \cdot\,LiX,\ \cdot\,COD]{THF} 0.4\,[\underset{\mathbf{3}}{(TMEDA)Fe(CH_2Ph)_2}] + 0.1\,[\underset{\mathbf{12}}{(THF)_2Fe(CH_2Ph)_2}] \quad (24)$$

$$\underset{\mathbf{12}}{(THF)_2Fe(CH_2Ph)_2} + TMEDA \longrightarrow \underset{\mathbf{3}}{(TMEDA)Fe(CH_2Ph)_2} \quad (25)$$

Mechanism of Coupling of (TMEDA)Fe(CH₂Ph)₂ with RX. The reduction of RX (R = $PhCH_2$, $CH_2{=}CHCH_2$) by **3** to give the final coupling product may also take place by either a one-electron (eq 26) or a two-electron process (eq 27). The latter oxidative addition pathway would lead to a Fe(IV) organometallic intermediate—a seemingly unlikely prospect. Several approaches were taken to distinguish between these two pathways.

$$Fe^{II}(CH_2Ph)_2 + RX \longrightarrow [Fe^{III}(CH_2Ph)_2]^+ + RX^{\pm}$$
$$RX^{\pm} \longrightarrow R\cdot + X^-$$
$$R\cdot \xrightarrow[\text{or } Fe^{III}(CH_2Ph)_2^+]{Fe^{II}(CH_2Ph)_2} RCH_2Ph \quad (26)$$

$$Fe^{II}(CH_2Ph)_2 + R\text{-}X \longrightarrow Fe^{IV}(CH_2Ph)_2(R)(X) \longrightarrow RCH_2Ph \quad (27)$$

One method of distinguishing between the two pathways is to take advantage of the equivalence of the hydrogens at the 1 and 3 positions of the allyl radical.

$$CH_2{=}CHCH_2^{\bullet} \leftrightarrow {}^{\bullet}CH_2CH{=}CH_2$$

Thus, if the mechanism shown in eq 26 was followed, the addition of either $CH_2{=}CHCD_2Br$ or $CD_2{=}CHCH_2Br$ to **3** would result in the formation of a cross-coupled product in which deuterium was present at both 1 and 3 positions of the allyl fragment.

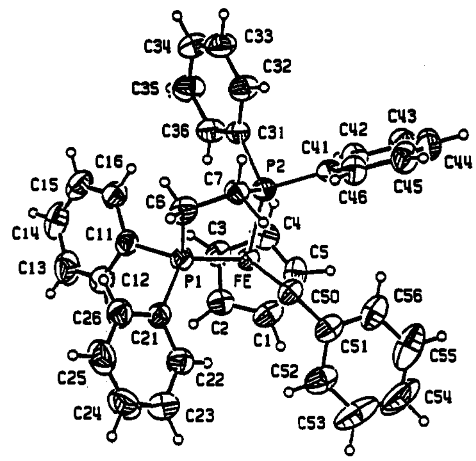


Figure 4. ORTEP of [CpFe(DIPHOS)(CH₂Ph)].

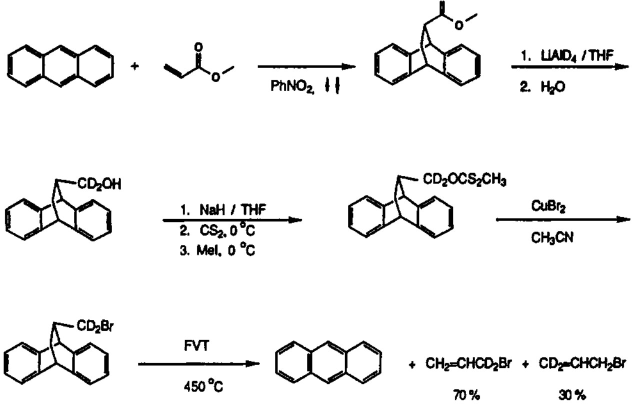


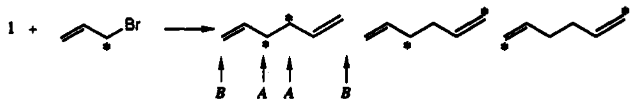
Figure 5. Synthesis of allyl-*1,1*-d_2 bromide.

The synthesis of allyl-1,1-d_2 bromide is outlined in Figure 5. In the synthesis, routes which involved allyl-d_2 alcohol were avoided. This was because allyl alcohol has a high propensity to polymerize. Thus, it would have been necessary to add radical inhibitors to stabilize the compound. Following flash vacuum pyrolysis (FVP) in the final step, a mixture of allyl-1,1-d_2 and allyl-3,3-d_2 bromide (**13a** and **13b**, respectively) in the ratio of 70:30 was obtained.

The addition of allyl-d_2 bromide, **13** (= **13a** (70%) + **13b** (30%)), to a benzene solution of **3** resulted in the formation of the cross-coupled product in which the deuterium was *completely* scrambled between 1 and 3 positions of the allyl fragment (eq 28).

$$\mathbf{3} + \mathbf{13} \rightarrow PhCH_2CH_2CH{=}CD_2 + PhCH_2CD_2CH{=}CH_2 \quad (28)$$

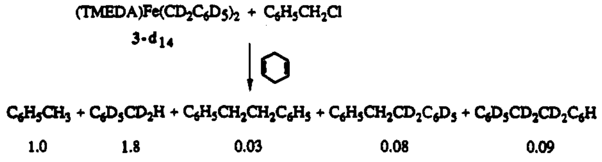
An analogous labeling studies was also performed in order to probe the mechanism of the formation of 1,5-hexadiene by the reaction of $CH_2{=}CHCH_2Br$ with **1**. This reaction presumably also involved two basic steps. The first was the formation of an iron–allyl species, by the reaction of **1** with allyl bromide. This species then reacted with a second equiv of allyl bromide to form 1,5-hexadiene. In each step, the use of allyl halide labeled at either 1 or 3 position would result in the formation of an allyl fragment with the label retained in one position or scrambled between two positions (1 and 3). As a result, three possible isotopomers of 1,5-hexadiene may form in the reaction of excess labeled allyl bromide with **1** (eq 29). The ratio of isotopomers obtained can be determined from the integrations (^{2}H NMR) of the allylic (position A) and the terminal vinylic (position B) resonances.



(29)

The predicted and experimentally determined isotopomer ratios obtained by using allyl-d_2 bromide, **13** (=**13a** (70%) + **13b** (30%)) are summarized in Table 5. The experimental results clearly indicated that complete deuterium scrambling occurred in both steps in the formation of 1,5-hexadiene.

The observation of deuterium scrambling between 1 and 3 positions of the allyl fragments in the coupling and cross-coupling of allyl halides was consistent with the intermediacy of allyl radicals and, hence, with mechanistic steps involving one-electron transfers. Unfortunately, however, these results do not necessarily rule out two-electron oxidative addition or nucleophilic displacement steps since the involvement of a symmetrical iron–η^3-allyl species at any stage would also lead to scrambling. As described below, there is some additional evidence that organic radicals were involved in the second step of the coupling reaction. A sample of (TMEDA)Fe($CD_2C_6D_5$)$_2$, **3-*d*$_{14}$**, was dissolved in 1,4-cyclohexadiene. Then a solution containing 4 equiv of C_6H_5-CH_2Cl in 1,4-cyclohexadiene was added to it at 22 °C. The products formed along with their respective ratios are shown in eq 30.



$$\underset{\textbf{3-d}_{14}}{(\mathrm{TMEDA})\mathrm{Fe}(CD_2C_6D_5)_2} + C_6H_5CH_2Cl \longrightarrow \underset{1.0}{C_6H_5CH_3} + \underset{1.8}{C_6D_5CD_2H} + \underset{0.03}{C_6H_5CH_2CH_2C_6H_5} + \underset{0.08}{C_6H_5CH_2CD_2C_6D_5} + \underset{0.09}{C_6D_5CD_2CD_2C_6H} \quad (30)$$

The most obvious trend was that in the presence of 1,4-cyclohexadiene, a good H-atom donor, the yield of the coupling product, bibenzyl, is suppressed in favor of toluene formation. This clearly indicated the participation of benzyl radicals in the formation of bibenzyl from 3 and $PhCH_2X$, (cf. eq 26). A more intriguing observation was the formation of $C_6D_6CD_2H$. This must arise from $C_6D_5CD_2^{\bullet}$ formed by the homolysis of a Fe–$CD_2C_6D_5$ bond. According to eq 26, an iron(III)–benzyl species was formed by the one-electron oxidation of 3. The homolysis of the iron–benzyl bond in this species with the concomitant reduction of the iron to the divalent state and the formation of a benzyl radical would not be unusual. The above observation, together with the product ratios obtained for eq 30, therefore, indicated that the major pathway for the formation of the final coupling products may involve the coupling of *two* free-radicals in solution. This conclusion was further supported by an analysis of the products formed by the reaction of 3 with varying amounts of CH_2=$CHCH_2Br$ (eqs 31 and 32). The ratio of the cross-coupling product, $PhCH_2CH_2CH$=CH_2, to the homocoupling product, CH_2=$CHCH_2CH_2CH$=CH_2, obtained was found to decrease with increasing CH_2=$CHCH_2Br$ concentration. This was expected if the cross-coupling product was formed via free benzyl radicals that were derived from 3.[31] In the presence of excess CH_2=$CHCH_2Br$, halogen abstraction as shown in eq 33 will occur. The resulting abundance of allyl radicals would then lead to an enhanced yield of 1,5-hexadiene. Note that the observation of $C_6D_5CD_2Br$ in the reaction shown in eq 32 was consistent with this mechanistic scenario.

$$\underset{\mathbf{3}}{(\mathrm{TMEDA})\mathrm{Fe}(CH_2Ph)_2} + 2.0CH_2{=}CHCH_2Br \xrightarrow[\text{benzene}]{} \underset{1.0}{PhCH_2CH_2CH{=}CH_2} + \underset{0.6}{CH_2{=}CHCH_2CH_2CH{=}CH_2} + \underset{0.3}{PhCH_2CH_2Ph} + \underset{0.02}{PhCH_2Br} \quad (31)$$

$$\underset{\mathbf{3}\text{-}\boldsymbol{d}_{14}}{(\mathrm{TMEDA})\mathrm{Fe}(CD_2C_6D_5)_2} + 20.0CH_2{=}CHCH_2Br \xrightarrow[\text{benzene}]{} \underset{1.00}{C_6D_6CD_2CH_2CH{=}CH_2} + \underset{0.96}{CH_2{=}CHCH_2CH_2CH{=}CH_2} + \underset{0.15}{C_6D_6CD_2CD_2C_6D_6} + \underset{0.32}{C_6D_6CD_2Br} \quad (32)$$

$$PhCH_2^{\bullet} + CH_2{=}CHCH_2Br \rightarrow PhCH_2Br + CH_2{=}CHCH_2^{\bullet} \quad (33)$$

In summary, the formation of coupled (or cross coupled) products by the reaction of (TMEDA)Fe(CH_2Ph)$_2$ with RX (R = CH_2Ph or CH_2CH=CH_2) proceeded via a pathway which involved free radicals. There was evidence that the radicals may actually couple in solution. There are other transition-metal mediated coupling reactions which proceed by the coupling of free organic radicals in solution.[31] In review, the following evidence supports these conclusions: (a) the scrambling of the label when using allyl-*1,1*-d_2 bromide, (b) the suppression of the coupling reaction when 1,4-cyclohexadiene was used as the reaction solvent, and (c) the increased yield of 1,5-hexadiene and the increased amount of benzyl bromide formed when the ratio of allyl bromide vs (TMEDA)Fe(CH_2Ph)$_2$ was increased.

Summary of Reaction Mechanisms. The addition of 1 equiv of benzyl halide to [CpFe(COD)][Li(TMEDA)], **1**, in benzene resulted in the initial formation of [CpFe(COD)(CH_2Ph)], **7**. The predominant pathway involved an initial one-electron transfer from [CpFe(COD)]$^-$ to $PhCH_2X$ to form $PhCH_2X^{\bullet}$ and [CpFe(COD)]$^{\bullet}$. $PhCH_2X^{\bullet-}$ quickly disproportionated to form $PhCH_2^{\bullet}$ and X^-. The benzyl radical then added to [CpFe(COD)]$^{\bullet}$. Once formed [CpFe(COD)(CH_2Ph)] reacted with TMEDA in a disproportionation reaction to form 0.5 equiv of [(TMEDA)Fe(CH_2Ph)$_2$], **3**, and 0.5 equiv of $FeCp_2$. When additional benzyl (or allyl) halide was added, it reacted with [(TMEDA)Fe(CH_2Ph)$_2$] to form the coupled (or cross-coupled) product. This coupling reaction involved the intermediacy of benzyl (and allyl) radicals, and the experimental results were consistent with the product being formed by the coupling of two radicals in solution.

It is important to reiterate that several lines of evidence that point to (TMEDA)Fe(CH_2Ph)$_2$, **3**, being the key intermediate in the coupling reactions mediated by **1**. First, if **3** was an intermediate it must be capable of reacting with added benzyl halide to produce bibenzyl. This was established in numerous experiments involving the careful generation of **3** followed by the addition of benzyl halides to give bibenzyl. The virtually quantitative generation of **3** was confirmed by NMR analysis in those cases prior to the addition of the second equivalent of benzyl halide. Second, the intermediacy of **3** implies that the primary reaction pathway must involve its formation, i.e., eq 34 must be the primary pathway for the formation of bibenzyl. However, there are two other pathways which could also result in the coupled product but which would not involve **3** as the key intermediate.

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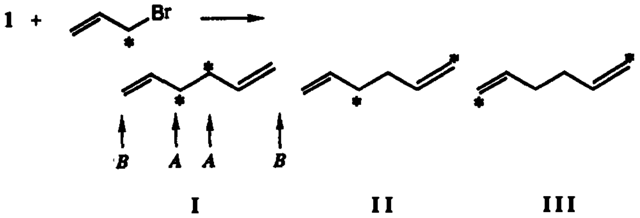
[31] For a specific example of benzyl radicals derived from metal–benzyl species coupling in solution, see: Fukuzumi, S.; Ishikawwa, K.; Tanaka, T. *Organometallics* **1987**, *6*, 358.

Table 5. Predicted and Experimental Isotopomer Ratios Obtained in the Reaction of **1** with **13** in Benzene



mechanism	isotopomer ratio I	isotopomer ratio II	isotopomer ratio III	^{2}H NMR integral ratio A	^{2}H NMR integral ratio B
no scrambling	7.00	0.00	3.00	7.00	3.00
scrambling in first step only	4.75	2.50	2.75	6.00	4.00
scrambling in second step only	4.75	2.50	2.75	6.00	4.00
scrambling in both steps	2.50	5.00	2.50	5.00	5.00
experimental result				5.02	4.98

These are shown below in eqs 35 and 36.

$$\mathrm{PhCH_2X} \underset{\mathrm{CpFe(COD)^-}}{\overset{k_1}{\longrightarrow}} \underset{\mathbf{7}}{\mathrm{CpFe(COD)CH_2Ph}} \underset{\substack{\mathrm{TMEDA,}\\ -\mathrm{COD}\\ -0.5\mathrm{FeCp_2}}}{\overset{k_2}{\longrightarrow}}$$

$$\underset{\mathbf{3}}{0.5\mathrm{(TMEDA)Fe(CH_2Ph)_2}} \underset{\mathrm{PhCH_2X}}{\overset{k_3}{\longrightarrow}} \mathrm{PhCH_2CH_2Ph} \quad (34)$$

$$\mathrm{PhCH_2X} \underset{\mathrm{CpFe(COD)CH_2Ph,\ 7}}{\overset{k_4}{\longrightarrow}} \mathrm{PhCH_2CH_2Ph} \quad (35)$$

$$\mathrm{PhCH_2X} \underset{\mathrm{[CpFe(COD)^\bullet PhCH_2^\bullet]}}{\overset{k_5}{\longrightarrow}} \mathrm{PhCH_2CH_2Ph} \quad (36)$$

The pathway shown in eq 35 involves the direct reaction of **7** with benzyl halide to form bibenzyl. Although **7** was not directly detected, its presence was implicated in the formation of **3**. The pathway shown in eq 36 involves the direct reaction of CpFe(COD)$^\bullet$ and PhCH$_2^\bullet$ with benzyl halide to form bibenzyl. CpFe(COD)$^\bullet$, **11**, was directly detected in the reaction leading to the formation of **3**.

If either of the pathways shown in eqs 35 or 36 was the primary pathway for dibenzyl formation, then the addition of 1 equiv of benzyl halide to CpFe(COD)$^-$ would be expected to produce significant amounts of bibenzyl and very little **3**. This would be the necessary result if $k_4 > k_2$ or if $k_5 > k_2$. Significant amounts of bibenzyl would also be formed relative to **3** if $k_4 = k_2$ or if $k_5 = k_2$. These predictions need to be compared with the experimental data. The careful dropwise addition of a solution containing benzyl-d_7 halide to an efficiently mixed solution of **1** resulted in the generation of a solution in which **3**-d_{14} was the major (>98%) benzyl containing species as detected by ^{2}H NMR spectroscopy. The virtual quantitative formation of **3** necessitated that $k_2 \gg k_4$ (if k_4 occurred at all) and that $k_2 \gg k_5$ (if k_5 occurred at all). Thus, **3** was a key intermediate in the formation of the coupling product.

Experimental Section

General Methods. Unless noted otherwise, all manipulations were performed in a N$_2$-filled glovebox, where all solvents and reagents were stored. Standard techniques were used for all Schlenk line and vacuum line manipulations.

Table 6. Crystal Data and Data Collection Summary for Compound **4**

formula	$C_{38}H_{36}P_2Fe$	M_r	610.50
space group	$P2_1/c$	crystal system	monoclinic
cell dimensions			
a, Å	11.913		
b, Å	14.438(1)	β, deg	98.36(1)
c, Å	18.181(1)	Z	4
V, Å	3093.9(4)		
D_{cal}, mg m^{-3}	1.31	F(000)	1280
radiation	Mo Kα	λ, Å	0.71069
μ, mm^{-1}	0.616	T, K	293
θ, range, deg	2–20	scan method	$\omega/2\theta$
ω-scan width, deg	$(0.80 \pm 0.35 \tan\theta)$	crystal decay	none
total data measd	3490		
data used [$I > 3\sigma(I)$]	2277	no. of variables	370
data:parameter	6.1		
R, R_w = $(\Sigma\Delta^2/\Sigma wF_o^2)^{1/2}$	0.082, 0.084		
$(\Delta/\sigma)_{max}$ in last cycle	<0.1		

Solvents and Reagents. The solvents used were treated as follows. Benzene, diethyl ether, tetrahydrofuran (THF), and toluene were distilled from sodium benzophenone ketyl under an N$_2$ atmosphere. Hexane, heptane, methylene chloride, and pentane were distilled from CaH$_2$ under a N$_2$ atmosphere. THF-d_8 was dried by stirring with lithium aluminum hydride followed by vacuum transfer. Benzene-d_6, and chloroform-d_1 were dried over CaH$_2$ and then vacuum transferred. Once dry and deoxygenated, benzene-d_6 and THF-d_8 were stored in glass bulbs sealed by a Kontes valve. All other solvents were stored in bottles and Teflon-lined caps.

The reagents used were treated as follows. Allyl bromide (Aldrich), benzaldehyde (Aldrich), benzyl bromide (Aldrich), benzyl chloride (Aldrich), benzal bromide (Aldrich), and diiodomethane (Aldrich) were vacuum distilled from CaH$_2$. 2-Bromoacetophenone (Aldrich) was recrystallized first from ethanol followed by recrystallization from petroleum ether. Benzyl-d_7 chloride (Aldrich), 1,2-bis(diphenylphosphino)ethane (DIPHOS) (Strem), *m*-bromotoluene (Aldrich), *S,S*-chiraphos (Aldrich), lithium aluminum deuteride (Aldrich), lithium dispersion in mineral oil (Alfa), phosphorous tribromide (Aldrich), phosphorous oxychloride (Aldrich), and sulfuryl chloride were used as received. 1,4-Cyclohexadiene was dried over molecular sieves and vacuum transferred. It was tested for dryness prior to use by adding it to a vial of **1**, and checking for decomposition. 1,5-Cyclooctadiene (Aldrich) was first refluxed over CaH$_2$, then refluxed over LiAlH$_4$, and vacuum distilled. Dichloroacetophenone (Aldrich) was degassed by three freeze–thaw cycles and then dried over molecular sieves. Ferrocene (Aldrich) was sublimed (dynamic vacuum). *N,N,N',N'*-Tetraethylenediamine (Aldrich) was purified by literature methods with the final drying step being vacuum distillation from sodium benzophenone ketyl.

Spectroscopy. Routine ^{1}H NMR (200.1- or 300.1-MHz), ^{2}H NMR (30.2- or 46.1-MHz), ^{13}C NMR (50.3- or 75.5-MHz), and ^{31}P NMR (81.0- or 121.5-MHz) spectra were recorded on a Bruker WP-200 or AM-300 spectrometer. The chemical shifts for ^{1}H NMR spectra are reported in units of parts per million relative to tetramethylsilane at 0.00 ppm by using, where possible, the residual protons in the solvent as an internal standard (benzene-d_6, 7.15; THF-d_8, 3.58; chloroform-d_1, 7.24 ppm), or TMS. Routine ^{2}H NMR spectra were recorded unlocked. Confirmatory ^{2}H NMR spectra were sometimes recorded with a JEOL PS-100 spectrometer (15.3-MHz) equipped with ^{19}F lock. The chemical shifts for ^{2}H NMR spectra are reported relative to TMS-d_{12} at 0.00 ppm and are referenced by using the ^{2}H NMR resonance of the solvent as an internal standard (benzene, 7.15; THF, 3.58) or an external reference. The chemical shifts of ^{13}C NMR spectra are reported relative to TMS at 0.00 ppm and are referenced by using the ^{13}C resonance of the solvent as an internal standard (benzene-d_6, 128.0; THF-d_8, 67.4; chloroform-d_1, 77.0 ppm). All ^{31}P NMR spectra were proton decoupled and are reported in units of parts per million downfield of 85% phosphoric acid (H$_3$PO$_4$) and are referenced externally.

Variable temperature spectra were run using a coaxial tube system with the sample in the internal 4-mm tube and a methanol/HCl solution in the outer 5-mm tube.[32] The probe temperature was first lowered to

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[32] Van Gleet, A. L. *Anal. Chem.* **1970**, *42*, 6789.

173 K. All subsequent readings were taken as the temperature of the probe was warmed to room temperature. The temperature of the sample was determined to be at equilibrium when the difference in chemical shift (^1H NMR) between the two methanol resonances was constant over a 5-min period. Once both the temperature of the probe and that of the sample were at equilibrium, an additional 10 min were allowed to pass before acquiring an NMR spectrum. The temperature of the sample was determined by observing the position of the methanol resonances by ^1H NMR immediately (within 1 min) before and after acquiring each ^2H NMR spectrum.

Gas chromatography analysis were carried out with a Varian 3700 gas chromatograph, which was equipped with a flame ionization detector. A 10 ft × $^1/_8$ in. stainless steel column having a 10% SP-2100 packing on 80/100 Supelcoport was employed. Peak areas were determined by either cut and weigh or by computer interface. In a few cases GC analysis was also performed with a Hewlett-Packard Model 5880A which was equipped with a capillary column (cross-linked methyl silicate).

Gas chromatography–mass spectrometry was performed on a system composed of a Finnigan 9500 gas chromatograph, a Finnigan 3200 mass spectrometer, and a Finnigan 6000 mass spectral data system. Impact energy was imparted at 70 eV. In the case of chemical ionization, methane was used as reagent gas. Minimum detection limits were 35 and 60 amu for electron impact and chemical ionization, respectively.

Preparative gas chromatography was performed on a Varian Aerograph Model 920 gas chromatograph, which was equipped with a thermal conductivity detector. A 10 ft × $^1/_2$ in. stainless steel column having 10% SP-2100 packing on 80/100 Supelcoport was employed. Samples were collected in glass U-tubes immersed in liquid N_2.

Synthesis of Deuterium Labeled Organic Compounds. Synthesis of Benzyl-d_5 Chloride. Benzyl-d_5 chloride was synthesized by the chloromethylation of benzene. Literature procedures were followed throughout with the substitution of benzene-d_6 for benzene-d_0.[33] The product was found to be pure by GC and MS: ^1H NMR (CCl_4) (ppm) 4.40(s); MS (*m*/*z*) 131 (M), 96 (M – 35).

Synthesis of Benzyl-α-d_1 Bromide. Benzyl-α-d_1 alcohol was synthesized by the reduction of benzaldehyde with lithium aluminum deuteride.[34] Benzyl-α-d_1 alcohol was brominated with PBr_3 to give benzyl-α-d_1 bromide.[35] Literature procedures were followed throughout with the substitution of lithium aluminum deuteride for lithium aluminum hydride. The product was found to be pure by GC and MS: ^1H NMR ($CDCl_3$) (ppm) 4.38 (s, 1H), 7.24–7.31 (m, 5H); MS (*m*/*z*) 171 (M), 92 (M – 79).

Synthesis of Benzyl-α-,α-d_2 Bromide. Benzyl-α-d_2 alcohol was synthesized by the reduction of benzoic acid with lithium aluminum deteride.[36] Benzyl-α-d_2 alcohol was brominated with PBr_3 to give benzyl-α-d_2 bromide.[35] Literature procedures were followed throughout with the substitution of lithium aluminum deuteride for lithium aluminum hydride. The product was found to be pure by GC and MS: MS (*m*/*z*) 172 (M), 93 (M – 79).

Synthesis of Benzyl-3-d_1 Chloride. *m*-Bromotoluene was reduced to toluene-m-d_1 with lithium aluminum deuteride.[37] Toluene-m-d_1 was chlorinated with sulfuryl chloride and benzoyl peroxide.[38] Literature procedures were followed throughout with the substitution of lithium aluminum deuteride for lithium aluminum hydride. The product was found to be pure by GC and MS.

Synthesis of Allyl-*1,1*-d_2 Bromide. 9,10-Ethanoanthracene-11-methanol-*13*-d_2 was synthesized according to literature procedures.[39] This alcohol was then converted to the xanthate, 9,10-ethanoanthracene-11-meth-*13*-d_2-xanthatemethyl in a procedure exactly analogous to the literature procedure for the d_0-alcohol. The xanthate was brominated by a procedure analogous to the literature method for the bromination of the d_0-xanthate.[40]

In a 25-mL, round-bottom flask attached to a flash-vacuum pyrolysis (FVP) unit, a saturated sample (5 mL) of 9,10-ethanoanthracene-11-bromomethane in benzene was frozen with liquid N_2. The FVP apparatus was evacuated, and the pyrolysis was carried out at 450 °C. The volatile components were collected in a U-tube immersed in liquid N_2. Analysis by GC of the contents of the U-tube indicated that allyl bromide was formed, and only trace amounts of starting material was present. The solution of allyl bromide in benzene was dried by using type 4Å molecular sieves and then stored in the glovebox in a dark bottle. The position of the deuterium atoms in allyl-d_2 bromide in the solution was determined by ^2H NMR. The solution was found to contain 70.6% allyl-*1,1*-d_2 bromide and 29.4% allyl-*3,3*-d_2 bromide. The concentration of allyl bromide in the solution was determined to be 0.168 M (GC analysis using an added internal standard).

Synthesis of Organometallic Complexes. [CpFe(COD)][Li(TMEDA)], 1. The compound was prepared by the literature method[12] with the modifications being that the reaction was done at room temperature, and the reaction time was (typically) 24 h.

[CpFe(CH_2:CH_2][Li(TMEDA)], 2. This compound was prepared by the literature method.[12]

[(Cp-d_5)Fe(COD)][Li(TMEDA)], 1-d_5. In a 100-mL, round-bottom flask freshly sublimed ferrocene-d_{10} (2.56 g, 1.31 mmol), Li sand (0.28 g, 40.4 mmol), COD (5.20 mL, 42.4 mmol), and 17 mL of THF were placed. The solution was stirred rapidly for 24 h. The red solution was then filtered to remove excess Li sand, and then 7.7 mL of TMEDA was added to the solution. The solvent was then removed on a high vacuum line. The yellow residue was rinsed with diethyl ether (3 × 15 mL). The yellow solid was dissolved in a minimum amount of THF (ca. 5 mL). This solution was added dropwise to rapidly stirring diethyl ether (400 mL). The resulting yellow precipitate was collected on a frit and dried in vacuo (10^{-3} mmHg). This resulted in the isolation of 3.53 g (0.998 mmol) of **1**-d_5 (75.6% yield): $^{13}C\{^1H\}$ NMR (THF-d_8) 35.1 (CH_2, COD), 46.3 (CH_3, TMEDA), 48.6 (*C*H, COD), 58.5 (s, CH_2, TMEDA), 74.8 (t, *J* = 26 Hz, C_5D_5) ppm; ^2H NMR (benzene) 3.85 ppm.

Reactions of [CpFe(COD)]$^-$ with Excess Organic Halides. The identity of reaction products were determined by gas chromatographic analysis (GC and GC/MS) and further confirmed by one of the following methods. When authentic samples were readily available, the identity of products were confirmed by coinjection of authentic samples. In all other cases, products were isolated by either gas or liquid chromatography and characterized by NMR spectroscopy. Yields were determined by comparing the integral peak areas to that of an added internal standard (*p*-xylene). Correction factors were determined by established methods.[41]

Reaction of 1 with Excess Benzyl Bromide. In a 25-mL, round-bottom flask equipped with a magnetic stir bar were placed **1** (0.033 g, 0.093 mmol) and benzene (5 mL). As this solution was rapidly stirred, benzyl bromide (33.5 μL, 0.282 mmol) was added with a pipettor. The color of the solution immediately became very dark red. The solution was stirred for 10 min during which precipitate formed, and the solution regained a yellow appearance. The solution was exposed to air and centrifuged resulting in a clear yellow solution and a dark precipitate. Gas chromatographic analysis of the reaction solution indicated that the following products were present (yields): COD (99%), TMEDA, ferrocene (48%), benzyl bromide, and bibenzyl (84%); GC–MS (*m*/*z*) COD 109 (M + 1), 108 (M), 80 (M – 28), 79 (M – 29), 67 (M – 41), 54 (M – 54); ferrocene 187 (M + 1), 186 (M), 121 (M – 65), 56 (M – 130); bibenzyl 183 (M + 1), 182 (M), 105 (M – 77), 91 (M – 91).

The reaction of **1** with excess benzyl chloride was done in an analogous manner.

Reaction of 1 with Allyl Bromide. In a 2-dram vial were placed **1** (0.044 g, 0.13 mmol) and benzene (2 mL). As the solution gently swirled, allyl bromide (32.4 μL, 0.37 mmol) was added with a pipettor. The color of the solution immediately turned very dark red. After 10 min a small amount of precipitate had formed, and the solution had a yellow appearance. The solution was exposed to air and centrifuged resulting in brown precipitate and a clear yellow solution. Gas chromatographic analysis of the reaction solution indicated that the following products were present (yields): COD (99%), TMEDA, ferrocene (45%), 1,5-hexadiene (83%), and allyl bromide GC–MS (*m*/*z*) 1,5-hexadiene 82 (M), 67 (M – 15), 54 (M – 28).

Reaction of 1 with Bromoacetophenone. In a 2-dram vial were placed **1** (0.044 g, 0.13 mmol) and benzene (2 mL). As this solution was gently swirled, a solution containing bromoacetophenone (0.084 g, 0.42 mmol)

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(34) (a) Nystrom, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1947**, *69*, 1197. (b) Fieser, L. F.; Fieser, M. *Fieser & Fieser's Reagents for Organic Synthesis*; Wiley-Interscience: New York, 1967; Vol. 1, p 581.

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in benzene (1 mL) was added. The solution turned red. The solution was swirled for 10 min and then exposed to air resulting in the formation of a precipitate. The solution was centrifuged resulting in the separation of a yellow solution and brown precipitate. Gas chromatographic analysis of the reaction solution indicated that the following products were present (yields): COD (100%), TMEDA, ferrocene (49.5%), bromoacetophenone, 1,3-diphenylfuran (13%), and 1,4-diphenylbutane-1,4-dione (23%); GC–MS (*m/z*) 1,4-diphenylbutane-1,4-dione 267 (M + 29), 239 (M + 1), 238 (M), 161 (M – 77); 1,3-diphenylfuran 224 (M + 2), 223 (M + 1), 222 (M). In another reaction, 1,4-diphenylbutane-1,4-dione and 1,3-diphenylfuran were isolated by the following procedure. The solvent was removed in vacuo from the reaction solution. The solid residue was dissolved in CH_2Cl_2 (1 mL). The products, 1,4-diphenylbutane-1,4-dione and 1,3-diphenylfuran, were eluted from a silica gel column by gradually changing the elutant solvent from 100% hexane to 100% CH_2Cl_2: 1,4-diphenylbutane-1,4-dione ^{1}H NMR (ppm) 3.34 (s, 4 H), 7.31–7.45 (m, 6 H), 7.92 (d, *J* = 7 Hz, 4 H); $^{13}C\{^1H\}$ NMR (ppm) 32.4, 128.0, 128.5, 133.0, 136.6, 198.5; 1,3-diphenylfuran ^{1}H NMR (ppm) 6.90 (s, 1 H), 7.18–7.69 (m, 11 H); $^{13}C\{^1H\}$ NMR (ppm) 104.0, 123.8, 125.8, 127.1, 127.6, 128.4, 128.7, 128.8, 130.6, 132.4, 137.9, 154.8.

Reaction of 1 with Bromobenzene. In a 100-mL, round-bottom flask equipped with a magnetic stir bar were placed **1** (0.109 g, 0.31 mmol) and benzene (17.2 mL). As this solution was stirred, bromobenzene (130 μL, 1.24 mmol) was added with a pipettor. The solution turned red and then yellow-brown. The solution was stirred 12 h and then exposed to air. Centrifugation of the solution resulted in the removal of a brown precipitate form of yellow solution. Gas chromatographic analysis of the yellow solution indicated that the following products were present (yields): COD, bromobenzene, TMEDA, ferrocene (18%), and biphenyl (22%); GC–MS (*m/z*) 195 (M + 41), 183 (M + 29), 155 (M + 1), 154 (M).

Reaction of 1 with Diiodomethane. In a 2-dram vial were placed **1** (0.039 g, 0.11 mmol) and benzene (5 mL). As this solution was gently swirled diiodomethane (25.4 μL, 0.22 mmol) was added with a pipettor. The color of the solution immediately turned very dark red. After 1 h the solution had a pale brown appearance. The solution was exposed to air and centrifuged resulting in a clear yellow solution. Gas chromatographic analysis of the reaction solution indicated that the following products were present (yields): COD (23%), TMEDA, ferrocene (38%); diiodomethane, and 1-methyl-1,5-cyclooctadiene (44%); GC–MS (*m/z*) 1-methyl-1,5-cyclooctadiene 123 (M + 1), 122 (M), 107 (M – 15), 94 (M – 28), 93 (M – 29), 81 (M – 41), 79 (M – 43), 68 (M – 54); 1-methyl-1,5-cyclooctadiene was isolated by gas chromatography and further characterized by ^{1}H NMR (ppm) 1.71 (s, 3 H), 2.34 (m, 8 H), 5.35 (b, 1 H), 5.57 (b, 2 H); $^{13}C\{^1H\}$ NMR (ppm) 26.1, 27.2, 27.3, 28.5, 33.0, 122.6, 128.6, 135.7; $^{13}C\{GATED\}$ (ppm) 26.1 (q, *J* = 121 Hz), 27.2 (t, *J* = 124 Hz), 28.5 (t, *J* = 122 Hz), 33.0 (t, *J* = 128 Hz), 122.6 (d, *J* = 146 Hz), 128.6 (d, *J* = 152 Hz), 135.7 (s).

Reaction of 1 with Benzal Bromide. In a 25-mL, round-bottom flask equipped with a magnetic stir bar were placed **1** (0.106 g, 0.301 mmol) and benzene (17.2 mL). As this solution was stirred, benzal bromide (99.61 μL, 0.601 mmol) in benzene (2.3 mL) was added dropwise. The solution was stirred for 20 min and then exposed to air. Precipitate formed upon exposure to air. The solution was centrifuged, resulting in the separation of yellow solution and brown precipitate. Gas chromatographic analysis of the reaction solution indicated that the following products were present (yields): COD (14%), TMEDA, ferrocene (50%), benzal bromide, bicyclo[6.1.0]nonane-4-enyl-9-phenyl (26%), and stilbene (<1%); GC–MS (*m/z*) bicyclo[6.1.0]nonane-4-enyl-9-phenyl 199 (M + 1), 198 (M), 121 (M – 77); stilbene 209 (M + 29), 181 (M + 1), 180 (M); bicyclo[6.1.0]nonane-4-enyl-9-phenyl was isolated by preparatory gas chromatography and characterized by ^{1}H NMR and ^{13}C NMR spectroscopy; ^{1}H NMR (ppm) 1.30 (mb, 5 H), 2.05 (mb, 6 H), 5.5 (t, *J* = 4.0 Hz, 2 H), 6.95 (mb, 5 H); $^{13}C\{^1H\}$ NMR (ppm) 27.0, 28.9, 29.4, 31.3, 124.9, 125.3, 128.2, 130.2, 144.3; $^{13}C\{GASPE\}$ (ppm) 27.0 (+J), 28.9 (–J), 29.4 (+J), 31.3 (–J), 124.9 (–J), 125.3 (–J), 128.2 (–J), 130.2 (–J), 144.3 (+J).

Reaction of 1 with Dichlorodiphenylmethane. In a 2-dram vial were placed **1** (0.033 g, 0.094 mmol) and benzene (5 mL). As the solution was gently swirled, dichlorodiphenylmethane (36 μL, 0.066 mmol) was added with a pipettor. The color of the solution immediately turned brown. After 20 min the solution was exposed to air and centrifuged resulting in a clear brown solution. Gas chromatographic analysis of the reaction solution indicated that the following products were present (yields): COD (100%), TMEDA, ferrocene (50%), dichlorodiphenylmethane, and tetraphenylethylene (49%); GC–MS (*m/z*) tetraphenylethylene 333 (M + 1), 332 (M), 255 (M – 77).

Stoichiometric Reactions of 1 with Benzyl Halides. In Benzene. In a typical reaction, **1** (0.080 g, 0.227 mmol) and benzene-d_6 (1.0 mL) were placed in a 2-dram vial resulting in the formation of a yellow solution with some undissolved **1** at the bottom of the solution. As the solution was gently swirled, a solution of benzyl bromide (27.01 μL, 0.227 mmol) in benzene-d_6 (0.5 mL) was added dropwise over a period of 4 min. This resulted in the formation of a red solution. This solution was immediately transferred to a NMR tube and sealed with an air-tight septum. The reaction solution was examined by ^{1}H NMR using a +125 to –125 ppm sweep width: ^{1}H NMR 111.7 (6 H), 95.6 (2 H), 30.5 (2 H), 5.5 (4 H), 2.3–1.8 (16 H), –42.3 (2 H), and –64.5 (1 H).

In THF. In typical reaction, **1** (0.022 g, 0.063 mmol) and THF-d_8 (0.25 mL) were placed in a 2-dram vial. This resulted in the formation of a red solution. As this solution was gently swirled, a solution of benzyl chloride (7.19 μL, 0.063 mmol) in THF-d_8 (0.25 mL) was added dropwise. This resulted in the formation of a slightly darkened red solution. This solution was immediately transferred to a NMR tube and sealed with an air-tight septum. The reaction solution was examined by ^{1}H NMR spectroscopy. The following paramagnetically shifted resonances due to **3** (66% yield vs $PhCH_2Cl$) were observed: 113.3, 99.1, 30.2, –42.6, and –65.0 ppm in a 6:2:2:2:1 ratio. Paramagnetically shifted resonances due to **12** (9% yield) were also observed: 31.5, –50.2, –78.0 ppm in a 2:2:1 ratio. A resonance due to the phenyl groups of toluene and bibenzyl (25% combined yield) was observed at 7.2 ppm. Several broad overlapping resonances were observed from 0–5.5 ppm with peaks centered at 5.5 (COD), 4.1 ($FeCp_2$), 3.58 (THF), 2.3 (TMEDA, COD), 1.73 (THF).

Stoichiometric Reaction of 2 with Benzyl Bromide. In a 2-dram vial were placed **2** (0.038 g, 0.127 mmol) and benzene (1.0 mL). This resulted in the formation of a yellow solution with some undissolved **2** at the bottom of the solution. As this solution was gently swirled, a solution of benzyl bromide (10.54 μL, 0.089 mmol) in benzene (0.5 mL) was added dropwise. This resulted in the formation of a red solution. The solution was immediately transferred to an NMR tube and sealed with an air-tight septum. The reaction solution was examined by ^{1}H NMR spectroscopy. The following resonances due to the formation of **3** were observed: 111.7, 95.6, 30.5, –42.3, and 64.5 ppm in a 6:2:2:2:1 ratio. The resonances in the region from 0–10 ppm were significantly broadened with the resonances centered at 7.15 (benzene-d_5), 5.3 ($CH_2{=\!=}CH_2$), 4.0 ($FeCp_2$), and 2.2 (TMEDA).

Synthesis of (TEMDA)$_x$FeCl$_2$. Ferrous chloride (1.50 g, 11.8 mmol) and TMEDA (8 mL, 53.0 mmol) were placed in an 100 mL, round-bottom flask. The flask was sealed with a septum. The solution was stirred for 24 h. The solid was then collected on a frit, rinsed with pentane (3 × 20 mL), and dried under high vacuum overnight at room temperature yielding a fluffy salmon colored solid.

Reaction of (TMEDA)$_x$FeCl$_2$ with Benzyllithium. In a 2-dram vial were placed benzyllithium (0.016 g, mmol) and benzene-d_6 (0.5 mL). As the solution was gently swirled, a solution of (TMEDA)$_x$FeCl$_2$ (0.030 g) in benzene-d_6 (1.0 mL) was added in a dropwise manner. Upon completion of the addition the solution had a red color. Some of the solution was rapidly placed in a 5-mm NMR tube which was sealed with a rubber septum. ^{1}H NMR spectroscopy using a sweep width of 125 to –125 ppm was used to examine the solution for the presence of **3**. Resonances characteristic of **3** were observed at 111.7, 95.6, 30.5, –42.3, and 64.5 ppm in a ratio of 6:2:2:2:1. The solution was not stable, and significant decomposition was observed after a few hours as the solution turned black.

Variable-Temperature NMR of 3. **1** (0.040 g, 0.119 mmol) and toluene (1.0 mL) were placed in a 2-dram vial. This resulted in the formation of a yellow solution with some undissolved **1** at the bottom of the solution. As this solution was gently swirled, a solution of benzyl-d_7 chloride (13.28 μL, 0.119 mmol) and toluene (0.5 mL) was added dropwise. This resulted in the formation of a red solution. A portion of this solution (0.2 mL) was immediately transferred to a 4-mm coaxial NMR tube and sealed with an air-tight septum. This tube was then placed in a 5-mm NMR tube containing a methanol solution made according to the method of Van Gleet.[32] The solution was examined by ^{2}H NMR spectroscopy. Spectra were recorded at approximate 10° interval from 173–293 K.

Reaction of 3-d_{14} with Excess Benzyl Bromide. **3**-d_{14} was generated in benzene by the reaction of **1** (0.036 g, 0.10 mmol) with 1 equiv of benzyl-d_7 chloride (11.38 μL, 0.10 mmol). The reaction of the solution was examined by ^{2}H NMR spectroscopy to see if any bibenzyl-d_{14} had already formed. No bibenzyl-d_{14} was detected, and then an excess of benzyl bromide (60.78 μL, 0.51 mol) was added to the reaction solution.

The solution turned yellow and was stirred for 1 h. A small amount of white precipitate was visible. The solution was exposed to air, and the volatiles were removed in vacuo. CH_2Cl_2 (2 mL) was added to the residue, and the solution was centrifuged and then extracted with H_2O. The resulting yellow solution was analyzed by GC/MS for bibenzyl. Bibenzyl-d_0, -d_7, and -d_{14}, were identified by their molecular ion peaks and the relative amount of each was determined by single ion scans: 35% bibenzyl-d_0, 39% bibenzyl-d_7, and 26% bibenzyl-d_{14}.

Reaction of 3 with Allyl Bromide. In a typical reaction, in a 25 mL, round-bottom flask equipped with a magnetic stirring bar were placed **1** (0.033 g, 0.094 mmol) and benzene (3 mL). As this solution was rapidly stirred, a solution of benzyl chloride (10.78 μL, 0.094 mmol) in benzene (1 mL) was added over a period of 5 min. The solution turned red and was stirred for an additional 25 min, and then allyl bromide (8.11 μL, 0.094 mmol) in benzene (1 mL) was added. The solution became slightly darker. Stirring was continued for 1.5 h, and then the contents of the flask were exposed to air. The solution turned brown as precipitate formed and was centrifuged. This resulted in the separation of yellow solution from brown precipitate. Gas chromatographic analysis of the reaction solution indicated that the following products were present (yields vs **1**): COD (100%), benzyl bromide (1%), 3-butenylbenzene (44%), bibenzyl (11%), 1,5-hexadiene (26%), ferrocene (49%), TMEDA. A GC/MS (EI) analysis of a similar reaction solution using benzyl-d_7 chloride (in place of $C_6H_5CH_2Cl$) was used to facilitate identification of the products. The relevant ion peaks (*m/z*) for $C_6D_5CD_2CH_2CH{=}CH_2$ were 139 (M), 98 (M − 41), 70 (M − 69). 3-Butenylbenzene was also isolated by gas chromatography and further characterized by ^{1}H NMR and ^{13}C NMR spectroscopy: ^{1}H NMR 2.22 (t d, *J* = 7.8, 6.6, Hz, 2 H), 2.56 (t, *J* = 7.8 Hz, 2 H), 4.85 (m, 2 H), 5.70 (m, 1 H), 7.05 (m, 5 H); ^{13}C{^{1}H} NMR 35.5, 35.5, 114.9, 125.8, 128.3, 128.4, 138.1, 141.8; ^{13}C-{GATED} 35.4 (t, *J* = 127 Hz), 35.5 (t, *J* = 127 Hz), 114.9 (t, *J* = 155 Hz), 125.8 (d, *J* = 160 Hz), 128.2 (d, *J* = 159 Hz), 128.3 (d, *J* = 159 Hz), 138.1 (d, *J* = 151 Hz), 141.8 (s).

Reactions of 1 with Benzyl Halides in the Presence of DIPHOS. Benzyl Bromide. In a 2-dram vial were placed **1** (0.083 g, 0.24 mmol), DIPHOS (0.106 g, 0.266 mmol), and benzene-d_6 (1.0 mL) resulting in the formation of a yellow solution with some undissolved **1** at the bottom of the solution. As this solution was gently swirled a solution of benzyl bromide (28 μL, 0.24 mmol) and benzene-d_6 (0.5 mL) was added dropwise over a period of 5 min. This resulted in the formation of a red solution. This solution was transferred to a NMR tube and sealed with an air-tight septum. The reaction solution was then analyzed by ^{31}P NMR spectroscopy. Resonances were observed at 109.8, CpFe (DIPHOS)CH_2Ph, **4** (93.9% yield based on **1**); 98.7 [CpFe(DIPHOS)(Br)] (2.8% yield): and −12.2 ppm, DIPHOS. Crystals, suitable for a single crystal X-ray diffraction study, were grown by slow evaporation of benzene from a similar reaction solution.

Benzyl Chloride. This reaction was done in an analogous manner to the reaction of **1** with benzyl bromide and DIPHOS using 0.065 g (0.18 mmol) of **1**, 0.087 g (0.22 mmol) of DIPHOS, and 20 μL (0.18 mmol) of benzyl chloride: ^{31}P NMR 109.8, CpFe(DIPHOS) (CH_2Ph), **7** (98.2% yield based on **1**); 98.2, CpFe(DIPHOS)Cl (1.8%); and −12.2 ppm, DIPHOS.

Reactions of 1 with Benzyl Halides in the Presence of *S,S*-Chiraphos. (*R*)-Benzyl-α-d_1 Chloride. In a 2-dram vial were placed **1** (0.019 g, 0.054 mmol), *S,S*-chiraphos (0.036 g, 0.084 mmol), and benzene-d_6 (0.57 mL) resulting in the formation of a yellow solution with some undissolved **1** at the bottom of the solution. As this solution was gently swirled a solution of (*R*)-benzyl-α-d_1 chloride 93.5 ee (6.2 μL, 0.054 mmol) in benzene-d_6 (0.4 mL) was added dropwise over a period of 4 min. This resulted in the formation of a red solution. This solution was transferred to a 50-mL, round-bottom flask equipped with a magnetic stir bar. The volatiles were removed in vacuo (10^{-3} mmHg). This residue was dissolved in benzene-d_6. The resultant solution was transferred to a NMR tube and sealed with an air-tight septum. In addition to resonances due to COD and TMEDA which had been partially removed in vacuo, the following compounds were identified by ^{1}H NMR: excess chiraphos, 1.36 (m, 6 H relative to other chiraphos integrals), 2.74 (m, 2 H), 6.9–7.5 (m, 20 H); FeCp_2, 4.0 ppm (1.6% yield vs CpFe (*S,S*-chiraphos) (CDHPh)); CpFe(*S,S*-chiraphos) (CDHPh), 0.90 (m, 6 H relative to other integrals of **8**-d_1, CHC*H*$_3$), 1.12 (d, *J* = 15.3 Hz, 0.595 H, (*S*)-CHD*H*Ph), 1.70 (d, *J* = 13.0 Hz, 0.405 H, (*R*)-CD*H*Ph), 2.00 (m, 2 H, C*H*CH$_3$), 3.87 (s, 5 H, C$_5$*H*$_5$), 6.38 (d, 2 H, phenyl), 6.90–7.35 (m, 16 H, phenyls), 7.8 (d, 2 H, phenyl); ^{31}P{^{1}H} NMR CpFe (*S,S*-chiraphos)Cl, 1.2% yield vs **1**, 91.1 (d, *J* = 43 Hz), 102 (d, *J* = 43 Hz) ppm; CpFe(*S,S*-chiraphos) (CDHPh), 94.0% yield, 110.0 (d, *J* = 40 Hz), 112.42 (d, *J* = 40 Hz), 112.48 (d, *J* = 40 Hz) ppm; *S,S*-chiraphos, −9.7 ppm. ^{1}H NMR integrals of the benzylic protons indicated that CpFe(*S,S*-chiraphos) (*S*-benzyl-α-d_1) was formed in 19.0 de. Thus, after correcting for 93.5 ee (*R*)-benzyl-α-d_1 chloride; 79.7% of the product is formed with racemization at the chiral carbon.

Table 7. Positional Parameters and Their Estimated Standard Deviations for Compound **4**[a]

atom	*x*	*y*	*z*	*B*(A2)
Fe	0.71592(4)	0.40318(4)	0.68187(3)	2.87(1)
P1	0.57033(8)	0.48155(7)	0.70597(5)	3.14(2)
P2	0.77279(8)	0.41042(7)	0.80019(5)	3.09(2)
C1	0.7366(3)	0.3559(3)	0.5758(2)	4.2(1)
C2	0.7027(3)	0.4488(3)	0.5709(2)	3.9(1)
C3	0.7852(3)	0.5013(3)	0.6161(2)	3.6(1)
C4	0.8696(3)	0.4406(3)	0.6483(2)	4.3(1)
C5	0.8393(3)	0.3501(3)	0.6235(2)	4.3(1)
C6	0.5639(3)	0.4826(3)	0.8074(2)	4.1(1)
C7	0.6446(3)	0.4110(3)	0.8465(2)	3.4(1)
C11	0.5707(4)	0.6044(3)	0.6798(2)	3.4(1)
C12	0.5221(4)	0.6316(3)	0.6092(2)	4.6(1)
C13	0.5365(4)	0.7205(3)	0.5838(3)	5.8(1)
C14	0.5992(4)	0.7833(3)	0.6287(3)	5.8(1)
C15	0.6445(4)	0.7589(3)	0.6993(3)	5.4(1)
C16	0.6309(3)	0.6699(3)	0.7247(2)	4.4(1)
C21	0.4244(3)	0.4512(3)	0.6661(2)	3.4(1)
C22	0.4048(3)	0.3894(3)	0.6074(2)	4.3(1)
C23	0.2954(4)	0.3667(3)	0.5763(3)	5.7(1)
C24	0.2056(4)	0.4059(4)	0.6036(3)	6.1(1)
C25	0.2228(3)	0.4685(3)	0.6608(3)	5.7(1)
C26	0.3320(3)	0.4908(3)	0.6917(2)	4.5(1)
C31	0.8482(3)	0.5117(3)	0.8441(2)	3.3(1)
C32	0.8698(4)	0.5184(3)	0.9211(2)	4.4(1)
C33	0.9172(4)	0.5974(3)	0.9552(2)	5.1(1)
C34	0.9444(4)	0.6708(3)	0.9132(2)	5.1(1)
C35	0.9252(4)	0.6647(3)	0.8373(2)	5.2(1)
C36	0.8775(3)	0.5859(3)	0.8033(2)	4.2(1)
C41	0.8615(3)	0.3181(3)	0.8469(2)	3.3(1)
C42	0.9732(3)	0.3117(3)	0.8340(2)	4.3(1)
C43	1.0430(4)	0.2417(3)	0.8650(2)	5.4(1)
C44	1.0025(4)	0.1765(3)	0.9095(2)	5.3(1)
C45	0.8927(4)	0.1815(3)	0.9231(2)	5.0(1)
C46	0.8230(3)	0.2521(3)	0.8924(2)	4.2(1)
C50	0.6399(3)	0.2742(3)	0.7080(2)	3.3(1)
C51	0.6602(3)	0.1939(3)	0.6612(2)	3.9(1)
C52	0.5785(4)	0.1636(3)	0.6035(2)	5.1(1)
C53	0.5971(5)	0.0890(3)	0.5601(2)	7.7(1)
C54	0.6951(5)	0.0410(3)	0.5730(3)	8.9(1)
C55	0.7781(4)	0.0683(3)	0.6295(3)	7.8(1)
C56	0.7610(4)	0.1442(3)	0.6737(3)	5.5(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\,(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

(*S*)-Benzyl-α-d_1 Bromide. In a 2-dram vial were placed **1** (0.024 g, 0.068 mmol), *S,S*-chiraphos (0.068 g, 0.033 mmol), and benzene-d_6 (1.0 mL) resulting in the formation of a yellow solution with some undissolved **1** at the bottom of the solution. As this solution was gently swirled, a solution of (*S*)-benzyl-α-d_1 bromide (47.8 ee, 8.10 μL, 0.068 mmol) in benzene-d_6 (0.5 mL) was added dropwise over period of 5 min. This resulted in the formation of a red solution. This solution was immediately transferred to an NMR tube and sealed with an air-tight septum. The reaction solution was then analyzed by ^{1}H NMR spectroscopy. In addition to resonances due to COD, TMEDA, and *S,S*-chiraphos the following resonances were observed: FeCp_2, 4.0 ppm (1.7% yield vs CpFe(*S,S*-chiraphos)(CDHPh)); CpFe(*S,S*-chiraphos)(CDHPh), 0.90 (m, 6 H relative to other integrals of **8**-d_1, CHC*H*$_3$), 1.12 (d, *J* = 15.3 Hz, 0.5 H, (*S*)-CD*H*Ph), 1.70 (d, *J* = 13.0 Hz, 0.5 H, (*R*)-CD*H*Ph), 2.00 (m, 2 H, C*H*CH$_3$), 3.87 (s, 5 H, C$_5$*H*$_5$), 6.38 (d, 2 H, phenyl), 6.90–7.35 (m, 16 H, phenyls), 7.8 (d, 2 H, phenyl); ^{31}P{^{1}H} NMR CpFe(*S,S*-chiraphos)-(CDHPh), 98% yield vs **1**, 110.0 (d, *J* = 40 Hz), 112.40 (d, *J* = 40 Hz), 112.46 (d, *J* = 40 Hz); CpFe(*S,S*-chiraphos) Br, 2% yield, 95.1 (d, *J* = 37 Hz), 101.0 (d, *J* = 37 Hz); *S,S*-chiraphos, −9.7 ppm. The integrals of the benzylic protons indicated that this reaction went with complete racemization. However, the low enantiotopic excess of (*S*)-benzyl-α-d_1 bromide (47.8 ee) resulted in an increase in the experimental uncertainty of the result. Thus the reaction proceeded with >95% racemization of the benzyl group.

Reaction of 1 with Trityl Chloride. [(Cp-d_5)Fe(COD)][Li(TMEDA)], **1**-d_5, (0.036 g, 0.100 mmol) and toluene (1.1 mL) were placed in a 2-dram vial. This resulted in the formation of a yellow solution with some undissolved **1**-d_5 at the bottom of the solution. As this solution was gently swirled a solution of trityl chloride (0.026 g, 0.093 mmol) in toluene (0.6 mL) was added dropwise. This solution was immediately transferred to a NMR tube and sealed with an air-tight septum. The reaction was examined by ^{2}H NMR spectroscopy (46.1 MHz). A broad resonance due to the formation of [CpFe(COD)]$^\bullet$ was observed at 45.0 ppm.

Reaction of 3 with Allyl-d_2 Bromide. In a 100-mL, round-bottom flask, equipped with a magnetic stir bar, were placed **1** (0.266 g, 0.755 mmol) and benzene (30 mL). As this solution was rapidly stirred, a solution of benzyl bromide (89.92 μL, 0.755 mmol) and benzene (1 mL) was added dropwise. The color of the solution changed from yellow to green (when half of the benzyl bromide/benzene solution was added) to red (when addition was complete). Upon completion of the addition, the solution was allowed to stir for 2 min. Then 5.50 mL of the 0.168 M allyl-d_2 bromide/benzene solution was added in two portions. The solution was brought out of the drybox and exposed to air and was centrifuged. This resulted in the separation of a yellow solution and brown precipitate. The coupled product 3-butenylbenzene-d_2 was isolated by preparatory gas chromatography. This position of the label in this product was determined by ^{2}H NMR (benzene) 2.10 (s, 1.00 D), 4.8 (s, 1.00 D).

Reaction of 3-d_{14} with Benzyl Chloride in the Presence of 1,4-Cyclohexadiene. In a 2-dram vial were placed **1** (0.020 g, 0.057 mmol) and benzene-d_6 (1.0 mL). As this solution was gently swirled a solution of benzyl-d_7 chloride (6.32 μL, 0.057 mmol) in benzene-d_6 (0.5 mL) was added dropwise. Upon completion of the addition, the solution was transferred to a 10-mL, round bottom flask equipped with a stir bar. The solution was stirred 10 min. The volatiles were then removed in vacuo (10^{-3} mmHg), and then 1,4-cyclohexadiene (0.4 g) was added to the residue. As the resulting solution was rapidly stirred, a solution of benzyl chloride (19.6 μL, 0.17 mmol) and 1,4-cyclohexadiene (0.4 g) was added dropwise. The solution was stirred for 10 min and then was exposed to air. An extraction with water (0.5 mL) was done in order to remove metal salts. The layers were separated by centrifugation. The resulting yellow solution was analyzed by GC/MS. The following products, containing the benzyl group, were identified (molar ratios): toluene-d_0 (1.0), toluene-d_7 (1.8), bibenzyl-d_0 (0.03), bibenzyl-d_7 (0.08), bibenzyl-d_{14} (0.09).

Crystal Structure Determination of CpFe(DIPHOS)(CH$_2$Ph). Accurate cell dimensions and a crystal orientation matrix were determined on an Enraf-Nonius CAD-4 diffractometer by a least-squares fit of the setting angles of 25 reflections. Experimental details are provided in Table 6. Data were corrected for Lorentz, polarization, and empirical absorption effects.[42]

The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic temperature factors for the non-hydrogen atoms. At an intermediate stage in the refinement, a difference map revealed maxima consistent with the positions of hydrogen atoms which were included in the subsequent cycles of refinement with fixed isotropic temperature factors. Refinement converged with $R = 0.082$ and $wR = 0.084$. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Mann[43] and Stewart, Davidson, and Simpson,[44] and allowance was made for anomalous dispersion.[45] A difference map calculated at the conclusion of the refinement had no chemically significant features. All computer programs used in this study were from the Enraf-Nonius "Structure Determination Package" (B. A. Frenz & Associates Inc., 1985), and Figure 4 was plotted using Ortep II.[46] The positional parameters are given in Table 7.

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Supplementary Material Available: Tables of observed and calculated structure factors (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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