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Reactions of the 17-Electron Iron-Centered Radicals $\{\eta^5\text{-}C_5Ph_5\}Fe(CO)_2^{\bullet}$ and $\{\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(CO)_2^{\bullet}$ with Organic Halides and Lewis Bases

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The 18-electron dimers $[Cp'Fe(CO)_2]_2$ ($Cp' = \eta^5\text{-}C_5Ph_5$, $\eta^5\text{-}C_5Ph_4(p\text{-tolyl})$), which undergo only very slight thermal dissociation to the corresponding 17-electron monomers $Cp'Fe(CO)_2^{\bullet}$, nonetheless exhibit reactivity patterns which reflect the chemistry of the monomers. Thus, reactions with several organic halides RX give $Cp'Fe(CO)_2R$ and $Cp'Fe(CO)_2X$, consistent with initial halogen atom abstraction by $Cp'Fe(CO)_2^{\bullet}$ followed by coupling of the resulting carbon-centered radical with a second molecule of $Cp'Fe(CO)_2^{\bullet}$. Reactions of $[(\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(CO)_2]_2$ with small phosphines L result in displacement of $\eta^5\text{-}C_5Ph_4(p\text{-tolyl})$ radicals rather than formation of isolable 17-electron compounds $[\{\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(CO)L^{\bullet}$, while reaction with the isonitrile *t*-BuNC results in disproportionation to the salt $[\{\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(t\text{-BuNC})_3][\{\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(CO)_2]$, possibly via the substituted species $(\eta^5\text{-}C_5Ph_4(p\text{-tolyl})Fe(CO)(t\text{-BuNC})^{\bullet}$. Reactions of $[\{\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(CO)_2]_2$ with phosphites $P(OR)_3$ do give the substituted radical species $\{\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(CO)\{P(OR)_3\}^{\bullet}$, but Arbuzov products such as $\{\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(CO)_2Me$, $\{\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(CO)_2\{P({=}O)(OMe)_2\}$, and $\{\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(CO)\{P(OMe)_3\}\{P({=}O)(OMe)_2\}$ are the major products formed when R = Me and, to a lesser extent, Et. The Arbuzov reaction is hindered when R is large, and the compound $\{\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(CO)\{P(O\text{-}i\text{-}Pr)_3\}^{\bullet}$ is a persistent radical which has been characterized by, *inter alia*, EPR spectroscopy. The EPR spectrum of a frozen solution in benzene can be analyzed in terms of a uniaxial **g** matrix ($g_{\parallel} = 1.993$, $g_{\perp} = 2.103$) with isotropic ^{31}P hyperfine coupling of 37 G (3.7 mT), typical of d^7 organometallic radicals in which the unpaired electron is essentially confined to a metal d_{z^2} orbital.

Major advances have been made, in recent years, in gaining an understanding of the chemical and physical properties of 17-electron organotransition-metal compounds (metal-centered radicals).[1a,b] This class of compounds may often be stabilized with respect to dimerization to the 18-electron metal−metal-bonded analogues by substitution of small ligands by more sterically demanding ligands, and of relevance here is substitution of CO by tertiary phosphines[1,2] and of $\eta^5\text{-}C_5H_5$ by $\eta^5\text{-}C_5Ph_5$.[3] In some cases, such substitutions result in facile thermal homolysis of the metal−metal bond of an 18-electron dimer to the corresponding 17-electron species,[4] and thus $[CpCr(CO)_3]_2$ ($Cp = \eta^5\text{-}C_5H_5$) dissociates to the extent of a few percent in solution at room temperature[1c,d] while $[CpCr(CO)_2P(OMe)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$)[1d] dissociate much more extensively[1d,g] and $CpCr(CO)_2PPh_3^{\bullet}$ [1h,i] and $(\eta^5\text{-}C_5Ph_5)$-

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$Cr(CO)_3^{\bullet}$ [1j] are completely monomeric in solution and the solid state. Similarly, the compound $[(\eta^5\text{-}C_5Ph_5)Mo(CO)_3]_2$ also dissociates in solution, unusual among metal−metal-bonded dimers of the heavier transition metals.[3g]

Until recently,[5] the iron triad had yet to yield examples of persistent metal-centered radicals, and we therefore initiated an investigation into the chemistry of iron-centered radicals of the type $\eta^5\text{-}Cp''Fe(CO)L^{\bullet}$ ($Cp'' = Cp$, substituted Cp; L = bulky ligands).[6] It was known that the 17-electron compounds $CpFe(CO)_2^{\bullet}$ and $Cp^*Fe(CO)_2^{\bullet}$ may be formed photochemically from the corresponding dimers as in eq 1, but they are exceedingly reactive and recombine rapidly to form the corresponding 18-electron dimers (eq 1).[7] Our attempts to

$$[Cp'Fe(CO)_2]_2 \overset{h\nu}{\rightleftharpoons} 2Cp'Fe(CO)_2^{\bullet} \qquad (1)$$

stabilize substituted monomeric iron compounds with sterically demanding phosphines have also failed. For instance, abstraction of the hydridic hydrogen atom from $CpFe(CO)(PPh_3)H$ with trityl radical yielded not the persistent $CpFe(CO)(PPh_3)^{\bullet}$ but the diiron compound $Cp_2Fe_2(CO)_3(PPh_3)$, presumably via $CpFe(CO)(PPh_3)^{\bullet}$ (eq 2).[6a,c]

$$2CpFe(CO)(PPh_3)H + 2Ph_3C^{\bullet} \rightarrow 2CpFe(CO)(PPh_3)^{\bullet} \rightarrow Cp_2Fe_2(CO)_3(PPh_3) \qquad (2)$$

In view of the effectiveness with which the $\eta^5\text{-}C_5Ph_5$ ligand stabilizes the persistent metal-centered radicals $(\eta^5\text{-}C_5Ph_5)M(CO)_3^{\bullet}$ (M = Cr, Mo),[1j,3g] we have more recently turned our attention to compounds in the analogous $\eta^5\text{-}C_5Ph_5$−iron system.[8] As entries to the iron system, we have developed an improved synthetic route to the dimer $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]_2$ (henceforth the $\eta^5\text{-}C_5Ph_5$ group will be denoted $Cp^{\ddagger}$)[8a−c,j] and a route to the new analogue $[\{\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(CO)_2]_2$ (henceforth the $\eta^5\text{-}C_5Ph_4(p\text{-tolyl})$ group will be denoted $Cp^{\dagger}$).[6d] The latter was expected to be more soluble than $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]_2$ but in fact exists in unusual high- and low-solubility, diastereomeric forms, the apparent differences between the two being whether the relative canting of the five aryl groups on the five-membered rings is the same or different.[6d] We have previously shown that both $[Cp^{\ddagger}Fe(CO)_2]_2$ and $[Cp^{\dagger}Fe(CO)_2]_2$ undergo slight thermal homolysis in solution to the corresponding dicarbonyl radical species,[6d] and we now describe experiments designed to probe reactions of these 17-electron species with organic halides.

As has been previously established, many metal-centered radicals readily abstract halogen atoms from alkyl halides (eq 3).[1a,b,2d,e,9] When L_nM is present in

$$L_nM^{\bullet} + RX \rightarrow L_nMX + R^{\bullet} \qquad (3)$$

sufficiently high concentrations that bimolecular coupling reactions of L_nM and R become competitive, the corresponding alkylmetal compounds L_nMR may also be formed. Then the net overall reaction is

$$2L_nM^{\bullet} + RX \rightarrow L_nMX + L_nMR \qquad (4)$$

In general, rates of reaction increase as the strength of the R−X bond decreases, i.e. RI > RBr > RCl, *t*-BuX > *i*-PrX > EtX > MeX; benzylic and allylic halides also react relatively quickly.

We also describe experiments designed to probe reactions of $[\{\eta^5\text{-}C_5Ph_4(p\text{-tolyl})\}Fe(CO)_2]_2$ with Lewis bases, which are expected to involve CO substitution via bimolecular processes.[1a,b] We anticipated enhancing the extent of homolysis of the dimers on substitution of a CO ligand with sterically more demanding ligands such as phosphines, isonitriles, and phosphites, thus possibly resulting in the formation of persistent metal-centered radicals. Although ultimately successful (see below), this line of research has been complicated, since *every* reaction attempted has resulted in different types of products. Preliminary reports of aspects of this work have appeared.[6a,b]

Experimental Section

Experiments were conducted under an inert atmosphere of oxygen-free-grade nitrogen, further purified through a heated BASF catalyst and molecular sieves. Manipulations of air-sensitive materials followed standard Schlenk line techniques and included the use of a Vacuum Atmospheres glovebox. The solvents benzene, toluene, tetrahydrofuran, hexanes, and diethyl ether were dried and distilled over alkali metals. CH_2Cl_2 was dried and distilled over CaH_2. Solvents were thoroughly deoxygenated prior to use by saturation with N_2 or repeated freeze−thaw cycles. Chromatographic separations were typically carried out in a cold-water-jacketed column using alumina or silica gel. Chemicals were obtained from Aldrich, BDH, Fischer, Strem, and Fluka and were used as received.

Infrared spectra were acquired on Bruker 85 IFS FT-IR and Bruker IFS 25 FT-IR spectrometers; IR data are presented in Table 1. NMR spectra were obtained on Bruker ACF 200 (200.1 MHz, ^1H; 50.3 MHz, $^{13}C\{^1H\}$) and AM 400 (400.1 MHz, ^1H; 100.6 MHz, $^{13}C\{^1H\}$) FT-NMR spectrometers using benzene-d_6 unless stated otherwise. The residual proton and the carbon resonances of deuterated solvents served as internal references

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Table 1. IR Data for the Compounds Cp‡Fe(CO)$_2$X and Cp†Fe(CO)$_2$X

Cp‡Fe(CO)$_2$X		Cp†Fe(CO)$_2$X	
X	ν_{CO} (cm^{-1})	X	ν_{CO} (cm^{-1})
H	2008, 1951	H	2007, 1951
Br	2033, 1993^{c}	Br	2033, 1992^{c}
I	2027, 1988	I	2026, 1986
Me	2002, 1948^{b}	Me	2000, 1947
Et	1994, 1942	Et	1993, 1941
i-Pr	~1989, 1938	*i*-Pr	1993, 1940
allyl	~1997, 1948	allyl	1998, 1948
benzyl	~1998, 1949	benzyl	1998, 1949
		PO(OMe)$_2$	2027, 1981
		PO(OEt)$_2$	2025, 1980
		PO(O-*i*-Pr)$_2$	2021, ~1972

[a] All spectra were recorded in benzene unless otherwise noted. [b] Recorded in CH$_2$Cl$_2$. [c] Recorded in THF.

for ^{1}H and ^{13}C resonances, respectively. ^{31}P NMR spectra were run on the AM 400 (162 MHz) spectrometer on solutions in benzene-d_6 and were referenced externally to 85% H$_3$PO$_4$. EPR spectra were recorded on a Varian E-12 X-band spectrometer equipped with a Bruker ER035M gauss meter for magnetic field measurements and a Systron-Donner microwave frequency counter. A thermostated Dewar assembly held samples at the center of the resonant rectangular cavity for spectra run at 96 K.

Mass spectra were acquired on a Fisons VG Quattro instrument utilizing a direct insertion probe in the CI mode with isobutane as reagent gas and flow injection analysis with pneumatically assisted electrospray ionization. FAB positive measurements utilizing *m*-NBA as matrix were acquired on an Autospec Fisons high-resolution spectrometer at Fisons. Elemental analyses for carbon, hydrogen, and nitrogen were carried out by Canadian Microanalytical Services, Delta, British Columbia, Canada.

Solutions of trityl radical in benzene were prepared by the zinc reduction of Ph$_3$CCl,[10,11] while Cp‡Fe(CO)$_2$Br,[8d] Cp‡Fe(CO)$_2$H,[8a] Cp†Fe(CO)$_2$Br,[8d] [Cp‡Fe(CO)$_2$]$_2$,[6d] and [Cp†Fe(CO)$_2$]$_2$[6d] were prepared by literature methods, the dimers by hydridic hydrogen abstraction by trityl radical from the corresponding hydrides.[6d]

Reactions of [Cp‡Fe(CO)$_2$]$_2$ with Organic Halides. IR scale reactions of organic halides with [Cp‡Fe(CO)$_2$]$_2$ were normally conducted in the dark using 10−35 mg of the dimer suspended in 5 mL of benzene and 3−7 μL (4× excess) of organic halide, which were injected directly into the solution. IR spectra of the solutions were taken prior to organic halide addition and at various time intervals afterwards. Usually, the reactions were complete within 35 min (IR), at which time the dark green cloudy suspension had largely disappeared. The solvent was then removed in vacuo, and the residue was dissolved in C$_6$D$_6$ and filtered through Celite into an NMR tube, and a ^{1}H NMR spectrum was recorded. NMR scale reactions of [Cp‡Fe(CO)$_2$]$_2$ with organic halides were normally conducted using 11−17 mg of the dimer, suspended in ~1.5−2.0 mL of C$_6$D$_6$, and a 4× excess of organic halide in an NMR tube. Spectra of the occasionally shaken reaction mixtures were run periodically as required, and IR spectra of the solutions were obtained after the final NMR spectra were acquired to confirm completion of the reactions.

Methyl Iodide. A suspension of 0.035 g of [Cp‡Fe(CO)$_2$]$_2$ (3.1×10^{-5} mol) in 7 mL of benzene was treated with 0.1 mL of MeI (1.61×10^{-3} mol), and the reaction was monitored by IR spectroscopy. Within 30 min, the bands of the starting material had disappeared and new bands at 2028, 2001, and 1988 cm^{-1} had appeared. The solvent was removed in vacuo, and the residue was dissolved in methylene chloride. The IR spectrum exhibited CO bands attributable to Cp‡Fe(CO)$_2$I and Cp‡Fe(CO)$_2$Me.[8b] See Table 1.

Ethyl Iodide. A suspension of 0.01 g of [Cp‡Fe(CO)$_2$]$_2$ (9.0×10^{-6} mol) in 5 mL of benzene was treated with 3.1 μL of EtI (3.9×10^{-5} mol), and the reaction was monitored by IR spectroscopy. Within 10 min, the bands of the starting material had disappeared and new bands attributable to Cp‡Fe(CO)$_2$I and Cp‡Fe(CO)$_2$Et[8f] (Table 1) had appeared. ^{1}H NMR (C$_6$D$_6$): δ 1.71 (t, CH$_2$CH_3) and 2.37 (q, CH_2CH$_3$).

Isopropyl Iodide. A suspension of 0.014 g of [Cp‡Fe(CO)$_2$]$_2$ (1.3×10^{-5} mol) in 5 mL of benzene was treated with 5.0 μL of *i*-PrI (5.0×10^{-5} mol), and the reaction was monitored by IR spectroscopy. Within 15 min, the bands of the starting material had been replaced by two bands attributable to Cp‡Fe(CO)$_2$I and one band tentatively attributable to Cp‡Fe(CO)$_2$(*i*-Pr) (the other CO band would be obscured by the band at 1988 cm^{-1}; see Table 1). The solvent was removed in vacuo, and the residue was dissolved in C$_6$D$_6$. ^{1}H NMR (C$_6$D$_6$): δ 1.78 (d, CH*Me*$_2$), 3.43 (m, C*H*Me$_2$). The NMR assignments were corroborated by an NMR experiment involving 0.017 g of [Cp‡Fe(CO)$_2$]$_2$ (1.5×10^{-5} mol) and 6.2 μL of *i*-PrI (6.2×10^{-5} mol) in ~1.5 mL of C$_6$D$_6$. ^{1}H NMR (C$_6$D$_6$): δ 1.77 (d, CH*Me*$_2$), ~3.42 (m, C*H*Me$_2$). Resonances of propane at δ 0.85 (m, Me) and 1.25 (m, CH$_2$) and of propylene at δ 1.54 (d, Me), ~4.95 (m), ~5.02 (s), and ~5.7 (m) were also observed. An IR spectrum of the NMR solution exhibited strong CO bands attributable to Cp‡Fe(CO)$_2$I at 2027 and 1988 cm^{-1} and a significantly weaker band attributable to Cp‡Fe(CO)$_2$CHMe$_2$ at 1938 cm^{-1}.

Benzyl Bromide. A suspension of 0.015 g of [Cp‡Fe(CO)$_2$]$_2$ (1.35×10^{-5} mol) in 5 mL of benzene was treated with 6.5 μL of benzyl bromide (5.5×10^{-5} mol), and the reaction was monitored by IR spectroscopy. Within 6 min, the bands of the starting material had been replaced by two bands attributable to Cp‡Fe(CO)$_2$Br[8d] and a weak band tentatively attributable to Cp‡Fe(CO)$_2$(CH$_2$Ph) (Table 1; the other CO band would be obscured by the band at 1998 cm^{-1}). The solvent was removed in vacuo, and the residue was dissolved in C$_6$D$_6$. ^{1}H NMR (C$_6$D$_6$): δ 3.65 (s, CH$_2$). The NMR assignments were confirmed by an NMR experiment involving 0.014 g of [Cp‡Fe(CO)$_2$]$_2$ (1.3×10^{-5} mol) and 6 μL of PhCH$_2$Br (5.0×10^{-5} mol) in ~2 mL of C$_6$D$_6$. ^{1}H NMR (C$_6$D$_6$): δ 3.65 (s, FeCH$_2$), 2.73 (s, bibenzyl).

Allyl Bromide. A suspension of 0.02 g of [Cp‡Fe(CO)$_2$]$_2$ (1.6×10^{-5} mol) in 5 mL of benzene was treated with 6 μL of allyl bromide (6.9×10^{-5} mol), and the reaction was monitored by IR spectroscopy. Within 34 min, the bands of the starting material had been replaced by new bands attributable to Cp‡Fe(CO)$_2$Br[8d] and a weak band tentatively attributable to Cp‡Fe(CO)$_2$(η^1-C$_3$H$_5$) (Table 1; the other CO band would be obscured by the band at 1998 cm^{-1}). The solvent was removed in vacuo, and the residue was dissolved in C$_6$D$_6$. ^{1}H NMR (C$_6$D$_6$): δ 3.06 (d, J_{HH} 9 Hz, 2H, FeCH$_2$), 5.03 (dd, J_{HH} 10 Hz, 1H, =CH$_2$), 5.37 (dd, J_{HH} 17 Hz, 1H, =CH$_2$), 6.57 (m, 1H, CH=). The NMR assignments were confirmed by an NMR experiment involving 0.011 g of [Cp‡Fe(CO)$_2$]$_2$ (1.3×10^{-5} mol) and 3.5 μL of allyl bromide (4.0×10^{-5} mol) in ~2 mL of C$_6$D$_6$. The above-mentioned resonances of Cp‡Fe(CO)$_2$(η^1-C$_3$H$_5$) were all observed, in addition to resonances of 1,5-hexadiene at δ 1.99 (s) and 4.95 (m); the third resonance was obscured by a resonance of allyl bromide.

Reactions of [Cp†Fe(CO)$_2$]$_2$ with Organic Halides. Reactions of [Cp†Fe(CO)$_2$]$_2$ with organic halides were carried out with both suspensions of the insoluble form and solutions of the soluble form, all in benzene, following the procedures described above for [Cp‡Fe(CO)$_2$]$_2$.

Methyl Iodide. A solution of 0.05 g of the soluble form of [Cp†Fe(CO)$_2$]$_2$ (4.5×10^{-5} mol) in 125 mL of benzene was treated with 111 μL of MeI (1.8×10^{-3} mol). After 100 min, the solution was a clear, dark yellow-brown, and an IR spectrum exhibited only bands attributable to Cp†Fe(CO)$_2$I and

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$Cp^{\dagger}Fe(CO)_2Me$ (Table 1), all strong and all of comparable intensity. Column chromatography, on alumina equilibrated with hexanes, and elution with increasing concentrations of toluene in hexanes removed a yellow fraction and a brown fraction. An IR spectrum in benzene of the yellow fraction exhibited CO bands attributable to $Cp^{\dagger}Fe(CO)_2Me$, prepared and characterized below, while a ^1H NMR spectrum (C_6D_6) exhibited resonances reasonably attributable to $Cp^{\dagger}Fe(CO)_2Me$: δ 1.07, (s, FeMe), 1.91 (s, tolyl *Me*), 6.66 (d, aryl H), 7.25−6.69 (m, aryl H).

The brown fraction was recrystallized from toluene and hexanes to give pure $Cp^{\dagger}Fe(CO)_2I$; a ^1H NMR spectrum (toluene-d_8) exhibited resonances at δ 1.91 (s, tolyl Me), 2.12 (s), 6.6−7.4 (aryl H). $^{13}C\{^1H)$ NMR ($CDCl_3$): δ 21.22 (tolyl Me), 100.18, 101.16 ($Cp^{\dagger}$ ring C), 126.38, 127.56, 127.65, 128, 128.29, 128.96, 129.78, 129.99, 132.45, 132.53, 132.59, 138.33 (aryl C), 215.30 (CO). Anal. Calcd for $C_{38}H_{27}FeIO_2$: C, 65.35; H, 3.90. Found: C, 64.72; H, 4.20. The same compound was obtained on treating $[Cp^{\dagger}Fe(CO)_2]_2$ with iodine in benzene.

Further confirmation of the identification of $Cp^{\dagger}Fe(CO)_2Me$ was obtained by synthesizing it by treating 0.75 g $Cp^{\dagger}Fe(CO)_2Br$ (1.2×10^{-3} mol) in 25 mL of THF at 0 °C with 0.6 mL of a 3.0 M ethyl ether solution of MeMgBr (1.8×10^{-3} mol). After 45 min, the IR spectrum of the solution exhibited only the bands of the product (2000, 1947 cm^{-1}); the volume of solvent was reduced in vacuo to ~1.5 mL, and the resulting mixture was transferred to the top of an *n*-hexane-equilibrated alumina column with an additional 3 mL of THF. Elution with THF in *n*-hexane (1:12 THF−hexane) resulted in the removal of a yellow band containing the product. The solution was taken to dryness, and the resulting residue was recrystallized from *n*-hexane−CH_2Cl_2 to give 0.22 g of yellow powder (32.5%). Anal. Calcd for $C_{39}H_{30}FeO_2$: C, 79.87; H, 5.16. Found: C, 79.74; H, 5.27. ^1H NMR (C_6D_6): δ 1.07 (s, FeMe), 1.91 (s, tolyl Me), 6.66 (d, J_{HH} 7.8 Hz, aryl H), ~6.89 (m, aryl H), 7.10 (d, J_{HH} 8.2 Hz, aryl H), 7.20 (m, aryl H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −6.87 (FeMe), 20.98 (tolyl Me), 102.14, 102.64, 103.14 ($Cp^{\dagger}$ ring C), 127.73, 128.09, 128.30, 128.87, 129.05, 129.82, 132.32, 132.43, 132.56, 132.82, 133, 137.47 (aryl C; some resonances may have been obscured by those of the solvent), 218.47 (CO).

Ethyl Iodide. A suspension of 0.017 g of $[Cp^{\dagger}Fe(CO)_2]_2$ (1.5×10^{-5} mol) in 5 mL of benzene was treated with 3.4 μL of EtI (4.25×10^{-5} mol). The reaction was completed within 15 min (IR), the reaction mixture becoming yellow, and the IR spectrum exhibited CO bands attributable to $Cp^{\dagger}Fe(CO)_2I$ and $Cp^{\dagger}Fe(CO)_2Et$ (Table 1). The solvent was removed in vacuo, and the sample was dissolved in methylene chloride. Attempts to isolate the ethyl compound pure were unsuccessful, but a chemical ionization mass spectrum (isobutane as a carrier gas) exhibited very weak peaks for $Cp^{\dagger}Fe(CO)_2Et$ (MW 600.5): $[M]^+$ 600.2; $[M - 1]^+$ 599.3, $[M - CO]^+$ (MW 572.5) 572.3.

In an NMR experiment, a suspension of 0.016 g of $[Cp^{\dagger}Fe(CO)_2]_2$ (1.4×10^{-5} mol) in ~1 mL of C_6D_6 was treated with 4.5 μL of EtI (5.6×10^{-5} mol), and the reaction was monitored for 1.5 h as the mixture changed from dark green to a clear brown. The ^1H NMR spectra exhibited resonances attributable to $Cp^{\dagger}Fe(CO)_2Et$ at δ 2.37 (q, -CH_2CH_3), 1.72 (t, -CH_2CH_3), and 1.92 (s, tolyl Me) and to $Cp^{\dagger}Fe(CO)_2I$ at δ 1.88 (s, tolyl Me). Integration of the two tolyl methyl resonances showed that ~17% more iodo product was present. Both ethane (δ 0.79 (s)) and ethylene (δ 5.25 (s)) were observed as minor components. An IR spectrum of the solution exhibited approximately equal-intensity CO bands for $Cp^{\dagger}Fe(CO)_2Et$ and $Cp^{\dagger}Fe(CO)_2I$.

Isopropyl Iodide. A suspension of 0.45 g of $[Cp^{\dagger}Fe(CO)_2]_2$ (4.0×10^{-4} mol) in 40 mL of benzene was treated with 160 μL of 2-iodopropane (1.6×10^{-3} mol). The mixture became a clear brown solution within ~10 min, and an IR spectrum exhibited the bands of $Cp^{\dagger}Fe(CO)_2I$ (Table 1) in addition to a weaker band at 1940 cm^{-1}, tentatively attributable to $Cp^{\dagger}Fe(CO)_2CHMe_2$. The solvent was removed in vacuo, the residue was dissolved in a minimum of THF, and this solution was chromatographed on an *n*-hexane-equilibrated column with 25% THF in *n*-hexane. The yellow fraction initially eluted was collected, the solvent was removed, and the residue was recrystallized from CH_2Cl_2−pentane at 195 K to give a small amount of rather unstable material which exhibited CO bands in the IR spectrum (benzene) at 1993 and 1940 cm^{-1}. A chemical ionization mass spectrum using a direct-insertion probe and isobutane as the carrier gas exhibited peaks for $[M]^+$ and $[M + H]^+$. $Cp^{\dagger}Fe(CO)_2CHMe_2$ (MW 614.6 g/mol): $[M]^+ =$ 614.4, $[M + 1]^+ = 615.4$. A second, darker yellow fraction was identified as $Cp^{\dagger}Fe(CO)_2I$.

In a ^1H NMR experiment, a suspension of 0.016 g of $[Cp^{\dagger}Fe(CO)_2]_2$ (1.40×10^{-5} mol) in ~1.5 mL of C_6D_6 was treated with 5.6 μL (5.6×10^{-5} mol) of 2-iodopropane. A ^1H NMR spectrum, run after ~35 min, exhibited the tolyl methyl resonance of $Cp^{\dagger}Fe(CO)_2I$ at δ 1.88, as well as resonances attributable to $Cp^{\dagger}Fe(CO)_2CHMe_2$ at δ 3.44 (m, CH), 1.92 (s, tolyl Me), and 1.80 (d, J_{HH} 6.4 Hz, Me). Integration of the tolyl methyl resonances showed that $Cp^{\dagger}Fe(CO)_2I$ was present in ~2.5 times greater quantity than $Cp^{\dagger}Fe(CO)_2CHMe_2$. The resonances of propylene at δ 5.02 (m, CH_2), 4.96 (m, CH), and 1.54 (d, J_{HH} 6.4 Hz, Me) and of propane at δ 1.27 (m, CH_2) and 0.86 (t, J_{HH} 7.2 Hz, Me) were also observed, the ratio of propylene to propane being ~1.2:1. An IR spectrum of the solution showed that the carbonyl band of $Cp^{\dagger}Fe(CO)_2CHMe_2$ at 1938 cm^{-1} was about half as intense as that of $Cp^{\dagger}Fe(CO)_2I$ at 2026 cm^{-1}.

***tert*-Butyl Iodide.** A suspension of 0.02 g of $[Cp^{\dagger}Fe(CO)_2]_2$ (1.84×10^{-5} mol) in 10 mL of benzene was treated with 4.5 μL (3.9×10^{-5} mol) of *tert*-butyl iodide. The dark green solution turned dark golden yellow in ~2 min, and an IR spectrum exhibited bands of $Cp^{\dagger}Fe(CO)_2I$ in addition to much weaker bands of $Cp^{\dagger}Fe(CO)_2H$. In an NMR study, a suspension of 0.014 g of $[Cp^{\dagger}Fe(CO)_2]_2$ (1.23×10^{-6} mol) in ~2 mL of C_6D_6 was treated with 3 μL (2.6×10^{-5} mol) of *tert*-butyl iodide. A ^1H NMR spectrum of the resulting orange solution was rather broad after 15 min but much sharper after 45 min, and the tolyl methyl resonance of $Cp^{\dagger}Fe(CO)_2I$ was evident at δ 1.88. Isobutylene formation was also indicated by resonances at δ 4.74 (br s) and ~1.6 (overlapped) as was isobutane by resonances at δ 0.86 (d) and ~1.6 (overlapped). The proportion of isobutylene to isobutane was found to be 3:4 on the basis of integration. A very weak Fe−H resonance for $Cp^{\dagger}Fe(CO)_2H$ was observed at δ −10.4.

Slightly different results were obtained when the reaction was carried out using the soluble form of $[Cp^{\dagger}Fe(CO)_2]_2$. A solution of 0.024 g of $[Cp^{\dagger}Fe(CO)_2]_2$ (2.10×10^{-5} mol) in 10 mL of benzene was treated with 5 μL (4.2×10^{-5} mol) of *tert*-butyl iodide. The solution quickly turned yellow, and an IR spectrum exhibited strong bands of $Cp^{\dagger}Fe(CO)_2I$ and $Cp^{\dagger}Fe(CO)_2H$ (Table 1). The latter set was only slightly less intense than the former.

Benzyl Bromide. A suspension of 0.016 g of $[Cp^{\dagger}Fe(CO)_2]_2$ (1.4×10^{-5} mol) in 5 mL of benzene was treated with 6.6 μL (5.55×10^{-5} mol) of $PhCH_2Br$. The reaction mixture turned golden yellow within 8 min, and an IR spectrum exhibited the bands of both $Cp^{\dagger}Fe(CO)_2Br$ and, tentatively, $Cp^{\dagger}Fe(CO)_2CH_2Ph$ (Table 1). Electrospray, FAB, and chemical ionization mass spectrometry experiments on the residue obtained after removal of solvent yielded no useful information.

In an NMR experiment, a suspension of 0.016 g of $[Cp^{\dagger}Fe(CO)_2]_2$ (1.4×10^{-5} mol) in ~1.5 mL of C_6D_6 was treated with 6.6 μL of $PhCH_2Br$ (5.55×10^{-5} mol). The reaction mixture had become an orange-brown solution within 15 min, and a ^1H NMR spectrum exhibited resonances of both $Cp^{\dagger}Fe(CO)_2Br$ (tolyl methyl resonance at δ 1.88) and $Cp^{\dagger}Fe(CO)CH_2Ph$ (tolyl methyl resonance at δ 1.92, CH_2 resonance at δ 3.66). The ratio of $Cp^{\dagger}Fe(CO)_2Br$ to $Cp^{\dagger}Fe(CO)CH_2Ph$ was 1.3:1, on the basis of integration of the methyl resonances, while an IR of the solution showed the carbonyl bands of the two products to be of comparable intensities.

Allyl Iodide. A solution of 0.019 g of the soluble form of $[Cp^{\dagger}Fe(CO)_2]_2$ (1.66×10^{-5} mol) in 10 mL of benzene was treated with 5 μL of $CH_2{=}CHCH_2I$ (5.5×10^{-5} mol). The solution instantly turned to moss green, and an IR spectrum

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run within 2 min exhibited only bands, of comparable intensity, attributable to $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{I}$ and (tentatively) to $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{CH}_2\text{CH}{=}\text{CH}_2$ (Table 1). A similar experiment, involving a suspension of 0.019 g of the insoluble form of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ and 5 μL of $\text{CH}_2{=}\text{CHCH}_2\text{I}$ in 10 mL benzene, turned moss green within 2 min but orange-brown within 6 min. While strong IR bands of $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{I}$ were present, only a weak, high-frequency shoulder at 1986 cm^{-1} and a weak band at 1949 cm^{-1} indicated the presence of $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{CH}_2\text{CH}{=}\text{CH}_2$. No IR bands corresponding to $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ were evident.

In an NMR experiment, a suspension of 0.014 g of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ (1.22×10^{-5} mol) in 2 mL of C_6D_6 was treated with 4.5 μL (4.9×10^{-5} mol) of allyl iodide. After ~20 min, the ^{1}H NMR spectrum of the brown solution exhibited resonances of $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{I}$, the major product, at δ 1.88 (s, tolyl Me) and of $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{CH}_2\text{CH}{=}\text{CH}_2$, the minor product, at δ 1.92 (s, tolyl Me), ~3.06 (d, $-\text{CH}_2$) and ~5.02 (m, $=\text{CH}_2$). Additional resonances for the allyl group, expected at ~δ 5.34 and ~6.57 compared with those observed for $\text{Cp}^{\ddagger}\text{Fe(CO)}_2\text{CH}_2\text{CH}{=}\text{CH}_2$ (see above), were either barely discernable at ~δ 5.35 or completely obscured by aryl resonances at ~δ 6.61. 1,5-Hexadiene was identified by resonances at δ 2.00 (m, CH_2), 4.95 (m, $\text{C}{=}\text{CH}_2$), 5.00 (s, $\text{C}{=}\text{CH}_2$), and ~5.72 (m, partially overlapped, $\text{CH}{=}$). An IR spectrum of the solution verified that the major product was $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{I}$, only weak bands being attributable to $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{CH}_2\text{CH}{=}\text{CH}_2$. A chemical ionization mass spectrometry experiment yielded no useful information.

Attempts To Form Substituted Compounds $\text{Cp}^{\dagger}\text{Fe(CO)L}$: Reactions of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ with ^{13}CO, PMe_3, and *t*-BuNC. Reactions of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ with ^{13}CO. A stream of ^{13}CO was bubbled through a solution of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ in benzene for 15 s. The solution was stirred for 30 min and then treated with a stream of ^{13}CO for a further 15 s. An IR spectrum of the reaction mixture showed that the ^{12}CO bands at 1955, 1780, 1989, and 1921 cm^{-1} had been completely replaced by bands at 1911, 1740, 1942, and 1876 cm^{-1}, respectively.

Reactions of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ with PMe_3. A solution of 0.10 g of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ (8.8×10^{-5} mol) in 20 mL of benzene was treated with 36 μL (3.48×10^{-4} mol) of PMe_3 at room temperature, and the reaction mixture was monitored by IR spectroscopy for 2.5 h. Within 10 min, the IR spectrum showed a significant decrease in the intensity of the bridging CO band of the dimer at 1780 cm^{-1} and the growth of a band at 1874 cm^{-1} attributable to $\text{Fe(CO)}_3(\text{PMe}_3)_2$.[12] An additional 8 mL of PMe_3 was added to consume all remaining dimer, and ultimately the IR spectrum exhibited only strong bands attributable to $\text{Fe(CO)}_3(\text{PMe}_3)_2$ and $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{H}$ (2007, 1954 cm^{-1}). The same products were obtained on treating $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{H}$ with PMe_3 and trimethylamine oxide in THF. There was no IR evidence in the latter reaction for the formation of $\text{Cp}^{\dagger}\text{Fe(CO)(PMe}_3\text{)H}$, although a ^{1}H NMR spectrum of the products formed exhibited a weak hydride doublet resonance at δ -13.35 (J_{PH} 88 Hz).

A solution of 0.05 g of $\text{Cp}^{\dagger}\text{Fe(CO)(PMe}_2\text{Ph)H}$ (7.46×10^{-5} mol) in 10 mL of benzene was wrapped with aluminum foil and treated with a 4-fold excess of trityl radical in 7 mL of benzene solution. The reaction was monitored by IR spectroscopy, but there was no apparent reaction after stirring for 16 h at room temperature followed by 3 h of refluxing.

Reactions of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ with *tert*-BuNC. A suspension of 0.09 g of the insoluble form of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ (8.0×10^{-5} mol) in 10 mL of benzene was treated with 20 μL of *t*-BuNC (1.77×10^{-4} mole, 2.2 fold excess). An IR spectrum taken 25 min after addition exhibited new bands at 2178, 2147, 1863, and 1794 cm^{-1}. After 84 min, the solution had turned brown, but bands attributable to $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ were still evident and an additional 5 μL of *t*-BuNC (4.42×10^{-5} mol) was added. The solution turned orange-red after another 30 min, and an IR spectrum showed that the reaction was complete. The solvent was removed in vacuo to give $[\text{Cp}^{\dagger}\text{Fe}(t\text{-BuNC})_3][\text{Cp}^{\dagger}\text{Fe(CO)}_2]$. Difficulties were experienced trying to purify the compound, and the suggested formulation is based on spectroscopic and chemical evidence. IR (benzene): 2178, 2147, 1863, 1794 cm^{-1}. ^{1}H NMR (C_6D_6): δ 2.04 (s, 3H, tolyl Me), 1.95 (s, 3H, tolyl Me), 1.30 (br s, 27H, *t*-Bu).

A yellow-orange solution of 0.027 g of $[\text{Cp}^{\dagger}\text{Fe}(t\text{-BuNC})_3][\text{Cp}^{\dagger}\text{Fe(CO)}_2]$ (1.99×10^{-5} mol) in 5 mL of benzene was treated with 5 μL (8.03×10^{-5} mol) of MeI, turning pale yellow instantly. The IR spectrum showed that all starting material had reacted, with new bands appearing at 2180, 2149, 2000 and 1946 cm^{-1}. The last two bands are attributed to the known compound $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{Me}$ (Table 1) and those at 2180 and 2149 cm^{-1} to the complex $[\text{Cp}^{\dagger}\text{Fe}(t\text{-BuNC})_3]\text{I}$. Volatiles were removed in vacuo, but attempts at recrystallization from toluene/pentane/hexane were unsuccessful. ^{1}H NMR (C_6D_6) of the reaction mixture exhibited the resonance at δ 1.07 (s, 3H, Fe$-$Me) in addition to a resonance at δ 1.5 (s, 9H, *t*-Bu). A synthesis on a large scale resulted in precipitation of $[\text{Cp}^{\dagger}\text{Fe}(t\text{-BuNC})_3]\text{I}$, which was washed with benzene and pentane. ^{1}H NMR (C_6D_6): δ 1.52 (s, 27H, Me_3C), 1.92 (s, 3H, tolyl Me), 6.70 (d, J_{HH} 8.0 Hz, aryl H), 6.90$-$6.80 (m, aryl H), 7.16 (d, J_{HH} 1.6 Hz, aryl H), 7.26$-$7.22 (m, aryl H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 21.21 (tolyl Me), 30.66 (Me_3C), 59.18 (Me_3CNC), 98.94, 99.30, 99.80 ($\text{Cp}^{\dagger}$ ring C), 127.44, 127.69, 128.16, 128.30, 128.41, 130.81, 130.90, 131.78, 131.97, 138.16 (aryl C), 157.55 ($\text{Me}_3\text{CN}C$). Elemental analyses were inconclusive, but high-resolution mass spectral measurements confirmed the formation of the complex $[\text{Cp}^{\dagger}\text{Fe}(t\text{-BuNC})_3]^+$ (MW 764.85). Fast atom bombardment resulted in the appearance of peaks corresponding to the calculated isotopic distribution for the molecular ion.

Reactions of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ with Phosphites. P(OMe)_3. A suspension of 0.053 g of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ (4.6×10^{-5} mol) in 5 mL of benzene was treated with 12 μL (1.0×10^{-4} mol) of P(OMe)_3. Much of the solid dissolved within 2 min, and strong bands at 2027, 2000, 1981, and 1946 cm^{-1} were present in the IR spectrum as well as a weak band at 1897 cm^{-1}; the bridging CO band of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ (1780 cm^{-1}) had diminished in intensity by ~50%. The reaction was complete within 15 min (yellow solution), and the solvent was removed in vacuo. The IR spectrum of the residue exhibited the strong CO bands mentioned above, attributable to $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{Me}$ and, tentatively, $\text{Cp}^{\dagger}\text{Fe(CO)}_2\{\text{P}({=}\text{O})(\text{OMe})_2\}$ (Table 1), but the weak band at 1897 cm^{-1}, attributable to the substituted radical $\text{Cp}^{\dagger}\text{Fe(CO)}\{\text{P(OMe)}_3\}$ (see below), had disappeared. A ^{1}H NMR spectrum of the reaction mixture (C_6D_6) exhibited three strong singlet tolyl methyl resonances (δ 1.91, 1.89, 1.95; ~1:1:0.5 ratio of intensities, respectively), the iron$-$methyl resonance of $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{Me}$ (δ 1.07), and a doublet at δ 3.64 (J_{PH} 11.0 Hz, OMe), tentatively attributed to $\text{Cp}^{\dagger}\text{Fe(CO)}_2\{\text{P}({=}\text{O})(\text{OMe})_2\}$. Also observed were doublet resonances at δ 3.42 (J_{PH} 10 Hz, OMe), 3.56 (d, J_{PH} 11.0 Hz) and δ 3.77 (d, J_{PH} 10 Hz), tentatively attributed to $\text{Cp}^{\dagger}\text{Fe(CO)}\{\text{P(OMe)}_3\}\{\text{P}({=}\text{O})(\text{OMe}_2)\}$.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibited a singlet at δ 103.8, tentatively attributed to $\text{Cp}^{\dagger}\text{Fe(CO)}_2\{\text{P}({=}\text{O})(\text{OMe})_2\}$, and a doublet of doublets at δ 116.7 and 170.8 (J_{PP} 155 Hz), tentatively attributed to $\text{Cp}^{\dagger}\text{Fe(CO)}\{\text{P(OMe)}_3\}\{\text{P}({=}\text{O})(\text{OMe}_2)\}$. If we assume similar extinction coefficients for the CO bands of $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{Me}$ and $\text{Cp}^{\dagger}\text{Fe(CO)}_2\{\text{P}({=}\text{O})(\text{OMe})_2\}$ and utilize the ^{31}P integrations, the ratio of the reaction products formed is ~1:1:0.7 for $\text{Cp}^{\dagger}\text{Fe(CO)}_2\text{Me}$, $\text{Cp}^{\dagger}\text{Fe(CO)}_2\{\text{P}({=}\text{O})(\text{OMe})_2\}$, and $\text{Cp}^{\dagger}\text{Fe(CO)}\{\text{P(OMe)}_3\}\{\text{P}({=}\text{O})(\text{OMe}_2)\}$, reasonably consistent with the tolyl methyl integrations in the ^{1}H NMR spectrum.

A minor species present in the reaction mixture gave rise to an apparent virtual triplet in the OMe region at δ 3.26 and a partially obscured triplet at δ 1.12 (J_{PH} 6 Hz) in the ^{1}H NMR spectrum, as well as a singlet at δ 172.4 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

In an attempt to separate the products by column chromatography, a reaction mixture of 0.20 g of $[\text{Cp}^{\dagger}\text{Fe(CO)}_2]_2$ and 45 μL of P(OMe)_3 in 20 mL of benzene was stirred for 30 min, by which time the mixture had become a yellow solution. The

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[12] Bigorgne, M. *J. Organomet. Chem.* **1970**, *24*, 211.

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solvent was removed under reduced pressure, and the residue was dissolved in a minimum of toluene and this solution placed on a silica gel column. Elution with hexanes resulted in the removal of $Cp^{\dagger}Fe(CO)_2Me$ (ν_{CO} 2000, 1948 cm^{-1}; δ 1.91 (s, 3H, tolyl Me), 1.07 (s, 3 H, FeMe)), contaminated with small amounts of other materials. Elution with 1:1 hexanes−toluene then removed a second yellow band containing a mixture of materials, including $Cp^{\dagger}Fe(CO)_2Me$, and a previously undetected compound (ν_{CO} 1920 (br), 1605 (m) cm^{-1}; δ 3.24 (d, J_{HP} 10.2 Hz, POMe), 2.10 (s, tolyl Me)), while elution with toluene removed a small amount of $Cp^{\dagger}Fe(CO)_2\{P(=O)(OMe)_2\}$ (ν_{CO} 2027, 1981 cm^{-1}; δ 3.63 (d, J_{HP} 10.8 Hz, 6 H, POMe), 1.89 (s, 3 H, tolyl Me)). Considerable colored material remained at the top of the column, even after an attempt to elute with acetone.

$P(OEt)_3$. A suspension of 0.052 g (4.55 × 10^{-5} mol) of $[Cp^{\dagger}Fe(CO)_2]_2$ in 5 mL of benzene was treated with 16 μL (9.33 × 10^{-5} mol) of $P(OEt)_3$, and the reaction was monitored by IR spectroscopy. Within ~2 min, a band at 1894 cm^{-1} became strong relative to the bands of the dimer and, after ~3 h, there had also appeared very weak bands at 2025, 1994, 1980, and 1941 cm^{-1}. Addition of more $P(OEt)_3$ (~50 μL) over 1 h resulted in formation of a dark yellow solution and in a dramatic increase of the band at 1894 cm^{-1}. Essentially all the starting dimer had disappeared after 9 h.

By analogy with the $P(OMe)_3$ system, the weak bands at 1941 and 1994 cm^{-1} are tentatively attributed to $Cp^{\dagger}Fe(CO)_2Et$ and those at 2025 and 1980 cm^{-1} to $Cp^{\dagger}Fe(CO)_2\{P(=O)(OEt)_2\}$. The strong band at 1894 cm^{-1}, on the other hand, is reasonably attributed to the substituted radical $Cp^{\dagger}Fe(CO)\{P(OEt)_3\}^{\bullet}$ (see below). The solvent was removed in vacuo, and a ^1H NMR spectrum run in C_6D_6 was too complex to be interpreted. The $^{31}P\{^1H\}$ spectrum (C_6D_6) of a similar reaction mixture indicated the presence of products similar to those formed in the reaction with $P(OMe)_3$, *i.e.* a singlet at δ 100.3 tentatively attributed to $Cp^{\dagger}Fe(CO)_2\{P(=O)(OEt)_2\}$, a doublet of doublets at δ 112.4 and 163.8 (d, J_{PP} 156 Hz) tentatively attributed to $Cp^{\dagger}Fe(CO)\{P(OEt)_3\}\{P(O)(OEt)_2\}$, and a very weak singlet at δ 165.0 tentatively attributed to $Cp^{\dagger}Fe\{P(OEt)_3\}_2Et$. A relatively strong, very broad resonance was observed at ~δ 142; the $^{31}P\{^1H\}$ resonance of free $P(OEt)_3$ is observed at δ 139.4.

$P(O\text{-}i\text{-}Pr)_3$. A suspension of 0.052 g of $[Cp^{\dagger}Fe(CO)_2]_2$ (4.55 × 10^{-5} mol) in 5 mL of benzene was treated with 23 μL (9.32 × 10^{-5} mol) of $P(O\text{-}i\text{-}Pr)_3$. Reaction was very slow, and even after several hours, the only new band of significant intensity was observed at 1886 cm^{-1}, tentatively attributed to $Cp^{\dagger}Fe(CO)\{P(O\text{-}i\text{-}Pr)_3\}^{\bullet}$. Resonances in the ^1H NMR spectrum (C_6D_6) were broad, as was a very strong resonance at δ 139.8 in the $^{31}P\{^1H\}$ NMR spectrum (C_6D_6); the $^{31}P\{^1H\}$ resonance of free $P(OEt)_3$ is observed at δ 139.4.

The EPR spectrum of a similar reaction mixture in benzene at 96 K exhibited the spectrum shown below, but no resonance was detected in liquid benzene at 293 K. Although the presumed $Cp^{\dagger}Fe(CO)\{P(O\text{-}i\text{-}Pr)_3\}$ remained in solution for several hours, all attempts to grow crystals failed.

Results and Discussion

Pentaarylcyclopentadienyl ligands have been receiving increased attention in recent years as extensions of the better known $\eta^5\text{-}C_5H_5$ (Cp) and $\eta^5\text{-}C_5Me_5$ (Cp*) ligands,[13] their exceptional size often providing considerable steric hindrance and thus providing kinetic stability to complexes such as 17-electron compounds.[1j,3] In addition, their chiral structures, in which the aryl rings are canted (see above), have provided much impetus for the investigation of ring rotation dynamics.[13,14] In general, we find that the reactions of $[Cp^{\ddagger}Fe(CO)_2]_2$ and $[Cp^{\dagger}Fe(CO)_2]_2$ with various reagents give comparable products, and we therefore combine discussion of analogous chemistry of the two iron compounds. Hereafter we use Cp′ to denote $Cp^{\ddagger}$ and $Cp^{\dagger}$ collectively.

Reactions of $[Cp^{\ddagger}Fe(CO)_2]_2$ and $[Cp^{\dagger}Fe(CO)_2]_2$ with Organic Halides. It has been shown previously that the chemistry of the 18-electron, dimeric compound $[CpCr(CO)_3]_2$ reflects the relatively high reactivity of the 17-electron monomer $CpCr(CO)_3^{\bullet}$, even though homolysis of the dimer is slight and the monomer constitutes only a few percent of the total chromium in solution at room temperature.[1c,d,9f−h] The two dimeric iron compounds discussed behave similarly; $[Cp^{\ddagger}Fe(CO)_2]_2$ and $[Cp^{\dagger}Fe(CO)_2]_2$ both dissociate slightly in solution,[6d] and both react with organic halides to give the products anticipated on the basis of halogen abstraction by the corresponding 17-electron radical monomers, as in eq 5.[1a,b,9]

$$[Cp'Fe(CO)_2]_2 + RX \rightarrow Cp'Fe(CO)_2R + Cp'Fe(CO)_2X \qquad (5)$$

Thus, reactions of $[Cp^{\ddagger}Fe(CO)_2]_2$ and $[Cp^{\dagger}Fe(CO)_2]_2$ with methyl iodide resulted in the formation of $Cp'Fe(CO)_2Me$ and $Cp'Fe(CO)_2I$. The compound $Cp^{\ddagger}Fe(CO)_2Me$ (ν_{CO} 2002, 1948 cm^{-1}) has been reported previously and was characterized by comparisons with spectroscopic data in the literature.[8b] The compound $Cp^{\dagger}Fe(CO)_2Me$, however, is new and was characterized by elemental analyses and IR (ν_{CO} 2000, 1947 cm^{-1}) and ^1H NMR (δ_{CMe} 1.91, δ_{FeMe} 1.07) spectroscopy. The same compound was prepared via reaction of $Cp^{\dagger}Fe(CO)_2Br$ with MeMgBr. The iodo compound $Cp^{\dagger}Fe(CO)_2I$ is also new and was characterized by elemental analysis, IR spectroscopy (ν_{CO} 2026, 1986 cm^{-1}), and comparison with an authentic sample formed by reaction of $[Cp^{\dagger}Fe(CO)_2]_2$ with iodine.

The chemistry of eq 5 undoubtedly proceeds via two steps, iodine atom abstraction from methyl iodide by $Cp'Fe(CO)_2^{\bullet}$ followed by coupling of the resulting methyl radical with a second molecule of $Cp'Fe(CO)_2^{\bullet}$ (eqs 6 and 7). A ^1H NMR study in C_6D_6, using $[Cp^{\dagger}Fe(CO)_2]_2$, showed that the methyl and iodo products formed to comparable extents on the basis of integrations of the respective tolyl methyl resonances, but neither methane nor coupling products derived from the carbon-centered radicals were observed. These results are as previously found for reactions of $[CpCr(CO)_3]_2$ with methyl iodide.[9f−h]

$$Cp'Fe(CO)_2^{\bullet} + MeI \rightarrow Cp'Fe(CO)_2I + Me^{\bullet} \qquad (6)$$

$$Cp'Fe(CO)_2^{\bullet} + Me^{\bullet} \rightarrow Cp'Fe(CO)_2Me \qquad (7)$$

In a similar fashion, reactions of $Cp'Fe(CO)_2^{\bullet}$ and EtI resulted in the formation of comparable quantities of $Cp'Fe(CO)_2Et$ and $Cp'Fe(CO)_2I$, on the basis of relative intensities of the carbonyl stretching bands in IR spectra of reaction mixtures. The ethyl compounds could not be obtained analytically pure, but $Cp^{\ddagger}Fe(CO)_2Et$ has been reported,[8f] and the carbonyl stretching bands are not only very similar but compare well with data for the methyl analogues (Table 1).

A ^1H NMR investigation indicated that $Cp^{\dagger}Fe(CO)_2I$ formed to a somewhat greater extent (~17%) than did the ethyl complex, on the basis of integrations of the tolyl resonances. Interestingly, small quantities of ethylene and ethane were also detected, as was observed

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previously with $[CpCr(CO)_3]_2$.[9f−h] The ethylene may not have been formed via β-elimination from the ethyl compound, as ethane but no hydride, $Cp^{\dagger}Fe(CO)_2H$, was observed. Instead, the hydrocarbon products may have been formed via the secondary reactions shown in eqs 8−10.

$$Cp'Fe(CO)_2^{\bullet} + EtI \rightarrow Cp'Fe(CO)_2I + Et^{\bullet} \tag{8}$$

$$Cp'Fe(CO)_2^{\bullet} + Et^{\bullet} \rightarrow Cp'Fe(CO)_2H + C_2H_4 \tag{9}$$

$$Cp'Fe(CO)_2H + Et^{\bullet} \rightarrow Cp'Fe(CO)_2^{\bullet} + C_2H_6 \tag{10}$$

Thus, while some ethyl compound is formed via direct coupling of $Et^{\bullet}$ and $Cp'Fe(CO)_2^{\bullet}$, the ratio of ethyl to iodo product is less than 1 because some of the ethyl groups are diverted as in eqs 9 and 10.

Formation of alkane and alkene was much more extensive in the reactions of $Cp'Fe(CO)_2^{\bullet}$ with isopropyl iodide and, although a significant amount of iodo compound formed, a much smaller quantity of isopropyl compound was produced. The latter could not be isolated pure but was readily identified by the carbonyl stretching bands in IR spectra of reaction mixtures, which are similar to those of the iron methyl and ethyl complexes (Table 1), and by its ^1H NMR spectrum, which exhibited isopropyl resonances at δ 3.44 (m, CH) and 1.80 (d, J_{HH} 6.4 Hz, Me) and a tolyl methyl resonance at 1.92 (s, tolyl Me). A ^1H NMR spectrum of a reaction mixture involving $[Cp^{\dagger}Fe(CO)_2]_2$ clearly exhibited resonances of both propane and propylene but not of $Cp^{\dagger}Fe(CO)_2H$, and a sequence of reactions analogous to those of eqs 8−10 again seems to be occurring.

Reaction of the low-solubility form[6d] of $[Cp^{\dagger}Fe(CO)_2]_2$ with *tert*-butyl iodide produced $Cp^{\dagger}Fe(CO)_2I$ as the major iron-containing product; in addition, a small amount of $Cp^{\dagger}Fe(CO)_2H$ was evident in the IR spectrum of a reaction mixture. An NMR experiment showed that isobutane and isobutylene were also formed, in comparable amounts, suggesting a sequence of reactions as outlined above for the ethyl and isopropyl systems. There were no resonances which could be attributed to $Cp^{\dagger}Fe(CO)_2CMe_3$. In contrast, a reaction of the soluble form[6d] of $[Cp^{\dagger}Fe(CO)_2]_2$ with *tert*-butyl iodide turned yellow very quickly and an IR spectrum showed that comparable amounts of $Cp^{\dagger}Fe(CO)_2I$ and of $Cp^{\dagger}Fe(CO)_2H$ had formed. The latter result implies that the relative contributions of eqs 9 and 10 have altered. In contrast to the reaction with a suspension of the low-solubility form of $[Cp^{\dagger}Fe(CO)_2]_2$, where the steady-state concentration of $Cp^{\dagger}Fe(CO)_2^{\bullet}$ would be very low, reaction of *tert*-butyl iodide with the high-solubility form of $[Cp^{\dagger}Fe(CO)_2]_2$ would proceed in the presence of a relatively high steady-state concentration of $Cp^{\dagger}Fe(CO)_2^{\bullet}$ (eqs 11−13). In the latter case, the rate of hydrogen atom abstraction by iron from the t-$Bu^{\bullet}$ radical (eq 12) might well be greater than the rate of the hydrogen abstraction reaction from $Cp'Fe(CO)_2H$ (eq 12), resulting in the formation of a higher proportion of hydride.

$$Cp'Fe(CO)_2^{\bullet} + t\text{-}BuI \rightarrow Cp'Fe(CO)_2I + t\text{-}Bu^{\bullet} \tag{11}$$

$$Cp'Fe(CO)_2^{\bullet} + t\text{-}Bu^{\bullet} \rightarrow Cp'Fe(CO)_2H + Me_2C{=}CH_2 \tag{12}$$

$$Cp'Fe(CO)_2H + t\text{-}Bu^{\bullet} \rightarrow Cp'Fe(CO)_2^{\bullet} + Me_3CH \tag{13}$$

The proportions of alkyl−iron products relative to iodo product decrease in the order Me > Et > $CHMe_2$ > CMe_3. This trend is probably a result (a) of increasing steric hindrance to coupling of the very bulky iron-centered radical with the organic radicals as the size of the latter increases (Me < Et < $CHMe_2$ < CMe_3), (b) of decreasing Fe−C bond strengths in the order Me > Et > $CHMe_2$ > CMe_3, and (c) of competition from increasingly more favorable hydrogen atom abstractions from aliphatic fragments with increasing numbers of available β-hydrogen atoms. Since the expected coupling products of the organic radicals $Me^{\bullet}$, $Et^{\bullet}$, i-$Pr^{\bullet}$, and t-$Bu^{\bullet}$ were not observed, olefin disproportionation reactions[15] were not a factor.

Consistent with halogen abstraction being the initial step, treatment of $[Cp'Fe(CO)_2]_2$ with n-butyl chloride and bromide did not result in the type of chemistry described above. The carbon−halogen bonds in these cases are relatively strong,[16] making halogen abstraction reactions energetically much less feasible.

In contrast, reaction of suspensions of $[Cp'Fe(CO)_2]_2$ with benzyl bromide readily yielded the products $Cp'Fe(CO)_2Br$ and $Cp'Fe(CO)_2CH_2Ph$. The IR data obtained for $Cp'Fe(CO)_2Br$ (Table 1) are comparable with those obtained previously for these compounds,[8d] while IR data for $Cp'Fe(CO)_2CH_2Ph$ (1998 and 1949 cm^{-1}) compare favorably with literature values for the Cp analogue (2009 and 1958 cm^{-1})[17] and for the compounds $Cp'Fe(CO)_2Me$ (Table 1). The benzyl methylene resonances were identified (δ ~3.65) in ^1H NMR experiments, integration of the tolyl methyl resonances in the $Cp^{\dagger}$ system indicating that ~32% more $Cp^{\dagger}Fe(CO)_2Br$ (δ 1.88) than $Cp^{\dagger}Fe(CO)_2CH_2Ph$ (δ 1.92) had formed, although an IR spectrum of the same NMR solution exhibited product bands which were of comparable intensities. In a ^1H NMR experiment carried out with $[Cp^{\ddagger}Fe(CO)_2]_2$, some bibenzyl was shown to have also formed as a result of coupling of the benzyl radicals formed during reaction.

Similar to the benzyl system, reaction of a suspension of $[Cp^{\ddagger}Fe(CO)_2]_2$ with allyl bromide yielded both $Cp^{\ddagger}Fe(CO)_2Br$[8d] and $Cp^{\ddagger}Fe(CO)_2CH_2CH{=}CH_2$. Although the latter, a very minor product, could not be isolated pure, its carbonyl stretching bands in IR spectra compare well with those of the methyl and ethyl analogues (Table 1) and a ^1H NMR spectrum exhibited resonances at δ 3.06 (d, J_{HH} 9 Hz, CH_2), 5.03 (dd, J_{HH} 10 Hz, $=CH_2$), 5.37 (dd, J_{HH} 17 Hz, $=CH_2$), and 6.57 (m, CH=). These chemical shifts and coupling constants are very similar to those of $CpCr(CO)_3CH_2CH{=}CH_2$, formed via reaction of allyl halides with $[CpCr(CO)_3]_2$,[9f] and are characteristic of a σ-allyl group. Resonances of 1,5-hexadiene, the product of allyl radical coupling,[9f] were also observed.

Similar results were found in reactions of $[Cp^{\dagger}Fe(CO)_2]_2$ with allyl iodide although, interestingly, reaction of the insoluble form of the dimer produced significantly

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less of the σ-allyl product relative to the amount of iodo product than did the soluble form. The mechanism of these reactions is expected to occur as in eqs 14–16.

$$\mathrm{Cp'Fe(CO)_2^{\bullet} + XCH_2CH{=}CH_2 \rightarrow Cp'Fe(CO)_2X + {}^{\bullet}CH_2CH{=}CH_2} \quad (14)$$

$$\mathrm{Cp'Fe(CO)_2^{\bullet} + {}^{\bullet}CH_2CH{=}CH_2 \rightarrow Cp'Fe(CO)_2CH_2CH{=}CH_2} \quad (15)$$

$$\mathrm{2{}^{\bullet}CH_2CH{=}CH_2 \rightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2} \quad (16)$$

The relative proportions of the $\mathrm{Cp'Fe(CO)_2CH_2CH{=}CH_2}$ and 1,5-hexadiene formed therefore depend on the concentration of the radical species $\mathrm{Cp'Fe(CO)_2^{\bullet}}$ available in solution. When the steady-state concentration of iron-centered radical is low, as when $\mathrm{[Cp^{\ddagger}Fe(CO)_2]_2}$ or the insoluble form of $\mathrm{[Cp^{\dagger}Fe(CO)_2]_2}$ was used, then the bimolecular process involved in coupling of the iron-centered and allyl radicals is not competitive with allyl radical self-coupling to form 1,5-hexadiene. On the other hand, the greater steady-state concentration of $\mathrm{Cp'Fe(CO)_2^{\bullet}}$ obtained through use of the soluble dimer permits more extensive coupling of the iron and allyl radicals, giving rise to a higher proportion of the allyliron product. Radical coupling is observed only in the allyl and benzyl systems because of the greater stabilities of the benzyl and allyl radicals.[16]

Substitution Reactions of $\mathbf{Cp^{\dagger}Fe(CO)_2}$: Attempted Syntheses of $\mathbf{Cp^{\dagger}Fe(CO)L}$ (L = Phosphorus Donor). The substitutional lability of 17-electron complexes has long been recognized, and it is well-known that many neutral metal-centered radicals undergo facile substitution reactions with CO and with phosphines and phosphites, L, to produce substituted radicals.[1a,b] The products undergo a variety of bimolecular secondary reactions, including coupling, unless stabilized by substitution with sterically demanding ligands.[1]

Reactions of $\mathbf{[Cp^{\dagger}Fe(CO)_2]_2}$ with $\mathbf{^{13}CO}$. In order to establish substitutional lability of the 17-electron compounds under consideration here, the reaction of $\mathrm{[Cp^{\dagger}Fe(CO)_2]_2}$ with ^{13}CO was investigated. As anticipated, rapid and complete substitution into both radical and dimer occurred, as indicated by the 40–47 cm^{-1} decrease in the position of the IR bands from the nonsubstituted ^{12}CO species. Thus, the CO bands of $\mathrm{Cp^{\dagger}Fe(^{12}CO)_2}$ and $\mathrm{[Cp^{\dagger}Fe(^{12}CO)_2]_2}$, at 1989, 1921 cm^{-1} and 1955, 1780 cm^{-1}, respectively, were converted to bands at 1942, 1876 cm^{-1} and 1911, 1740 cm^{-1}, respectively. The changes are as predicted theoretically[18] and are also as observed in the analogous Cp iron system.[19]

Interestingly, we find that $\mathrm{[CpFe(CO)_2]_2}$ is inert to CO substitution under thermal conditions, although photochemical substitution, presumably via the monomer, is facile.[19] Thus, typical of the behavior of many 17-electron metal-centered radicals,[1,19] ^{13}CO substitution occurred readily into $\mathrm{Cp^{\dagger}Fe(CO)_2^{\bullet}}$, present in relatively small concentrations in the solution (eqs 17–19). Similar but slower ^{13}CO substitution has also been observed in $\mathrm{CpCr(CO)_3^{\bullet}}$, which is in thermal equilibrium with $\mathrm{[CpCr(CO)_3]_2}$.[1c,d] Substitution is expected to occur via an associative mechanism, and it is possible, in spite of the bulky Cp† group, that the iron of $\mathrm{Cp^{\dagger}Fe(CO)_2^{\bullet}}$ is less sterically hindered than is the metal of $\mathrm{CpCr(CO)_3^{\bullet}}$, with three coordinated carbonyl groups.

$$\mathrm{[Cp^{\dagger}Fe(CO)_2]_2 \rightleftarrows 2Cp^{\dagger}Fe(CO)_2^{\bullet}} \quad (17)$$

$$\mathrm{Cp^{\dagger}Fe(CO)_2^{\bullet} + 2\,^{13}CO \rightarrow Cp^{\dagger}Fe(^{13}CO)_2^{\bullet} + 2CO} \quad (18)$$

$$\mathrm{2\ Cp^{\dagger}Fe(^{13}CO)_2^{\bullet} \rightleftarrows [Cp^{\dagger}Fe(^{13}CO)_2]_2} \quad (19)$$

Attempts To Prepare Phosphine-Substituted Radicals. In an attempt to form more stable iron-centered radicals, phosphine substitution reactions of $\mathrm{Cp^{\dagger}Fe(CO)_2^{\bullet}}$ were attempted. It was found, however, that treatment of suspensions of $\mathrm{[Cp^{\dagger}Fe(CO)_2]_2}$ in benzene or toluene with $\mathrm{PMe_3}$ at room temperature resulted primarily in the slow formation of a small amount of $\mathrm{Fe(CO)_3(PMe_3)_2}$[12] as a consequence of Cp† ring displacement from the metal atom. Very small amounts of $\mathrm{Cp^{\dagger}Fe(CO)_2H}$ were also formed, possibly via hydrogen atom abstraction by $\mathrm{Cp^{\dagger}Fe(CO)_2^{\bullet}}$ from decomposition products. The same products were obtained when the reaction was carried out using a solution containing the monomer and dimer in equilibrium in hot benzene.

In a variation of this approach, a mixture of $\mathrm{Cp^{\dagger}Fe(CO)_2H}$ and $\mathrm{PMe_3}$ was treated with trityl radical to give $\mathrm{[Cp^{\dagger}Fe(CO)_2]_2}$, $\mathrm{Fe(CO)_3(PMe_3)_2}$, and unidentified products exhibiting two bands in the IR spectrum at 1943 and 2035 cm^{-1}. Neither of these latter bands may be attributed to the anticipated product $\mathrm{Cp^{\dagger}Fe(CO)(PMe_3)}$, which would be expected to exhibit a carbonyl stretching band at a frequency comparable with that reported for $\mathrm{CpFe(CO)\{P(OMe)_3\}}$ (1907 cm^{-1})[20a] or for compounds of the type CpFe(CO)LX (L = phosphine, phosphite; X = H, Cl), the CO stretching bands of which also occur at much lower frequencies.[20b]

Attempts at hydrogen atom abstraction from $\mathrm{Cp^{\dagger}Fe(CO)(PMe_2Ph)H}$ using trityl radical were also unsuccessful in producing $\mathrm{Cp^{\dagger}Fe(CO)(PMe_2Ph)^{\bullet}}$. To our surprise and disappointment, $\mathrm{Cp^{\dagger}Fe(CO)(PMe_2Ph)H}$ did not react with trityl radical, even on extended stirring and heating. Hydrogen atom abstraction was probably ineffective because of steric hindrance imposed on the metal center by the large, coordinated ligands, which would not allow access of the central carbon atom of the organic radical, itself a large molecule, sufficiently close to the coordinated hydrogen atom.

Reactions of $\mathbf{[Cp^{\dagger}Fe(CO)_2]_2}$ with Isonitriles. Although reactions of $\mathrm{[Cp^{\dagger}Fe(CO)_2]_2}$ with *t*-BuNC in benzene were expected to result in simple substitution to form the neutral, 17-electron compound $\mathrm{Cp^{\dagger}Fe(CO)(\mathit{t}\text{-}BuNC)^{\bullet}}$, the result was, instead, the ionic product of disproportionation, $\mathrm{[Cp^{\dagger}Fe(\mathit{t}\text{-}BuNC)_3][Cp^{\dagger}Fe(CO)_2]}$. Attempts to recrystallize the compound failed, and it was therefore characterized spectroscopically and chemically. IR spectra of clear, orange-red reaction mixtures exhibited only the CN stretching bands of the cation (2178, 2147 cm^{-1}) and the CO stretching bands of the anion (1863, 1794 cm^{-1}), consistent with reported IR data for similar Cp iron salts such as $\mathrm{[CpFe(\mathit{t}\text{-}BuNC)_3]}$-

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Br (ν_{CN} 2175, 2135 cm^{-1})[21a] and [Bu_4N][$CpFe(CO)_2$] (ν_{CO} 1864, 1787).[21b] In addition, ^{1}H NMR spectra of the salt showed clearly the presence of two types of Cp† groups, there being two equal-intensity tolyl methyl resonances, at δ 2.04 and 1.95.

Also, as anticipated, a red solution of [Cp†Fe(*t*-BuNC)$_3$][Cp†Fe(CO)$_2$] was found to react readily with methyl iodide to give, within 10 min, the compound Cp†Fe(CO)$_2$Me (ν_{CO} 2000, 1946 cm^{-1}), which has been synthesized by other routes (see above). The byproduct of this reaction was [Cp†Fe(*t*-BuNC)$_3$]I (ν_{CN} 2180, 2149 cm^{-1}), characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. A high-resolution FAB mass spectrum of [Cp†Fe(*t*-BuNC)$_3$]I exhibited a very strong signal for [Cp†Fe(*t*-BuNC)$_3$]$^+$ (MW 764.85), exhibiting the peaks corresponding to the calculated isotopic distribution for this ion.

The mechanism of disproportionation may involve either initial addition to or substitution of Cp†Fe(CO)$_2^\bullet$ by *t*-BuNC to give a 19-electron intermediate[22a] or a 17-electron intermediate,[22b] respectively (eq 20 or 21). The

$$\mathrm{Cp^\dagger Fe(CO)_2^\bullet} + t\text{-BuNC} \rightarrow \mathrm{Cp^\dagger Fe(CO)_2}(t\text{-BuNC})^\bullet \tag{20}$$

$$\mathrm{Cp^\dagger Fe(CO)_2^\bullet} + t\text{-BuNC} \rightarrow \mathrm{Cp^\dagger Fe(CO)}(t\text{-BuNC})^\bullet + \mathrm{CO} \tag{21}$$

electron-rich 19-electron species of eq 20 could then reduce a molecule of Cp†Fe(CO)$_2^\bullet$ and proceed to the cationic product as in eqs 22 and 23, while the 17-electron species of eq 21 could similarly reduce a molecule of Cp†Fe(CO)$_2^\bullet$ and proceed to products as in eqs 24 and 25.

$$\mathrm{Cp^\dagger Fe(CO)_2}(t\text{-BuNC})^\bullet + \mathrm{Cp^\dagger Fe(CO)_2^\bullet} \rightarrow [\mathrm{Cp^\dagger Fe(CO)_2}(t\text{-BuNC})]^+ + [\mathrm{Cp^\dagger Fe(CO)_2}]^- \tag{22}$$

$$[\mathrm{Cp^\dagger Fe(CO)_2}(t\text{-BuNC})]^+ + 2t\text{-BuNC} \rightarrow [\mathrm{Cp^\dagger Fe}(t\text{-BuNC})_3]^+ \tag{23}$$

$$\mathrm{Cp^\dagger Fe(CO)}(t\text{-BuNC})^\bullet + \mathrm{Cp^\dagger Fe(CO)_2^\bullet} \rightarrow [\mathrm{Cp^\dagger Fe(CO)}(t\text{-BuNC})]^+ + [\mathrm{Cp^\dagger Fe(CO)_2}]^- \tag{24}$$

$$[\mathrm{Cp^\dagger Fe(CO)}(\ t\text{-BuNC})]^+ + 2t\text{-BuNC} \rightarrow [\mathrm{Cp^\dagger Fe}(t\text{-BuNC})_3]^+ + \mathrm{CO} \tag{25}$$

In contrast, [CpFe(CO)$_2$]$_2$ reacts with isonitriles under thermal conditions to form mono-, di-, and trisubstituted neutral dimers.[23] Since the cyclopentadienyl and pentaarylcyclopentadienyl ligands are expected to be similar with respect to electronic properties,[24] it seems possible that the bulkiness of the pentaarylcyclopentadienyl ligand may inhibit comproportionation, thereby stabilizing the ionic products.

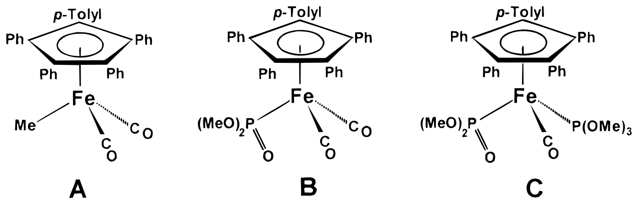

Figure 1. Structures of the Arbuzov products **A**–**C**.

Reactions of [Cp†Fe(CO)$_2$]$_2$ with Phosphites: Arbuzov Rearrangements and Syntheses of Cp†Fe(CO)L (L = P(OMe)$_3$, P(OEt)$_3$, P(O-*i*-Pr)$_3$). In spite of our inability to prepare monocarbonyl radicals by direct substitution of Cp†Fe(CO)$_2^\bullet$ with phosphines and isonitriles, we carried out a similar series of reactions of [Cp†Fe(CO)$_2$]$_2$ with phosphites. We began with the relatively small P(OMe)$_3$ and found that the reaction of [Cp†Fe(CO)$_2$]$_2$ with P(OMe)$_3$ resulted in the formation of three major Arbuzov[25] products, Cp†Fe(CO)$_2$Me (**A**), Cp†Fe(CO)$_2${P(=O)(OMe)$_2$} (**B**), and Cp†Fe(CO){P(OMe)$_3$}{P(=O)(OMe)$_2$} (**C**) (see Figure 1), as indicated by the presence of three tolyl methyl resonances and several OMe resonances in the carefully integrated ^{1}H NMR spectrum of the reaction mixture. While little success was achieved in separating the products (see below), all are known or are very similar to known compounds, and all were satisfactorily characterized by spectroscopic means.

The presence of **A** was confirmed by comparison of its IR (ν_{CO} 2000, 1946 cm^{-1}) and NMR (^{1}H NMR δ 1.07 (s, FeMe), 1.91 (s, tolyl Me)) spectral data with those of the Cp†Fe(CO)$_2$Me formed from the reaction of [Cp†Fe(CO)$_2$]$_2$ with MeI (see above). The IR spectrum of **B** (ν_{CO} 2027, 1981 cm^{-1}) is very similar to that of the known Cp‡Fe(CO)$_2${P(=O)(OMe)$_2$} (ν_{CO} 2030, 1983 cm^{-1}), which has been synthesized by the reaction of Cp‡Fe(CO)$_2$Br with P(OMe)$_3$.[14a] In addition, the chemical shift and hydrogen–phosphorus coupling constant of the OMe resonance (δ 3.64, d, J_{PH} 11 Hz) are very similar to those of Cp‡Fe(CO)$_2${P(=O)(OMe)$_2$} (δ 3.70, d, J_{PH} 10 Hz).[14b] A singlet ^{31}P resonance (δ 103.8), attributable to **B**, was observed in the ^{31}P{^{1}H} NMR spectrum of the reaction mixture. The corresponding resonance of Cp‡Fe(CO)$_2${P(=O)(OMe)$_2$} was observed at δ 116.4, in good agreement since a different solvent (CH_2ClCH_2Cl) was used.[14a] Compounds **A** and **B** were formed in approximately equal amounts in this experiment, but the proportions were found to vary in experiments carried out under somewhat different conditions.

No distinct CO band attributable to **C** was observed in the IR spectrum of the reaction mixture, but it should occur 10–15 cm^{-1} lower[24,26] than for the Cp analogue (1967 cm^{-1})[27] and thus overlaps the band of **A** at 1946 cm^{-1}. The ^{1}H NMR spectrum of the reaction mixture exhibits a series of OMe doublet resonances which are completely consistent with the presence of a compound with a structure such as **C**, containing a chiral iron atom. Thus, a methyl resonance observed at δ 3.42 (d, J_{PH} 10 Hz) is assigned to the phosphite OMe group and two methyl resonances at δ 3.56 (d, J_{PH} 11 Hz) and 3.77

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(d, J_{PH} 10 Hz) are assigned to the diastereotopic phosphonate OMe groups; cf. δ 3.68 (d, J_{PH} 12 Hz), 3.53 (d, J_{PH} 11 Hz), 3.57 (d, J_{PH} 11 Hz), respectively, for the Cp analogue.[27] The $^{31}P\{^1H\}$ NMR spectrum provided clear evidence for the formation of **C**, as a distinctive doublet of doublets (AB quartet) at δ 116.7 and 170.8 (J_{PP} 155 Hz) corresponds well with data for the Cp analogue (δ 125.7 and 180.2 (J_{PP} 139 Hz)).[27]

As mentioned in the Experimental Section, the reaction also yielded a minor product, the ^{1}H NMR spectrum of which exhibited an apparent virtual triplet in the OMe region at δ 3.26 and a partially obscured triplet at δ 1.12 (t, J_{PH} 6 Hz). The ^{1}H NMR spectrum of the compound CpFe$\{P(OMe)_3\}_2$Me is reported to exhibit OMe and FeMe resonances at δ 3.73 (t) and 0.20 (t, J_{PH} 5.3 Hz), respectively,[28] and it is tempting to suggest that this compound is Cp†Fe$\{P(OMe)_3\}_2$Me, a reasonable product. While the $^{31}P\{^1H\}$ chemical shift of the putative Cp†Fe$\{P(OMe)_3\}_2$Me (δ 172.4) is quite different from that reported for CpFe$\{P(OMe)_3\}_2$Me (δ 11.42), the latter is well outside the region normally found for phosphite complexes[29] and may be in error.

An attempt to separate the various products on a silica column utilizing hexanes−toluene mixtures as eluant resulted in mixed success. Compound **A** eluted readily and was characterized by IR and ^{1}H NMR spectroscopy, but a band containing a previously undetected compound followed that containing **A**. This unexpected species could not be freed of contaminants, and thus its ^{1}H NMR resonances could not be unambiguously identified. However, the presence of carbonyl bands at 1920 (br) and 1605 (m) cm^{-1} suggest that the compound may be Cp†Fe(CO)$\{P(OMe)_3\}$(COMe); the corresponding CO bands of the Cp analogue are observed at 1939 and 1603 cm^{-1},[27] in reasonable agreement. The ^{1}H NMR spectrum of the eluted mixture exhibited a single POMe doublet resonance at δ 3.63 (d, J_{HP} 10.8 Hz), clearly different from all of the compounds present in the original reaction mixture, but the acetyl resonance could not be unambiguously identified. The corresponding resonances of CpFe(CO)$\{P(OMe)_3\}$(COMe) occur at δ 3.58 (d, J_{PH} 11.3 Hz, CDCl$_3$) and 2.50 (d, J_{PH} 0.5 Hz).[27]

A third compound eluted from the column was **C**, with IR and ^{1}H NMR data corresponding to those inferred from the spectra of the reaction mixture. Although **C** also could not be obtained free of impurities, it clearly was the dominant species in this fraction and the IR and ^{1}H NMR data of this compound are unambiguously correlated. Thus, the chromatography experiment lends credence to the spectroscopic assignments suggested above. However, the appearance, as a product of facile decomposition, of the species exhibiting CO bands at 1920 (br) and 1605 (m) cm^{-1} and a POMe doublet resonance at δ 3.63 underscores the problems inherent in the separation and isolation of the products as analytically pure compounds.

During the course of the reaction of [Cp†Fe(CO)$_2$]$_2$ with P(OMe)$_3$, a weak CO band of an apparent intermediate was observed at 1897 cm^{-1} but was not present at the end of the reaction. This ephemeral band is reasonably attributable to the anticipated substituted radical Cp†Fe(CO)$\{P(OMe)_3\}^\bullet$, since it occurs 10 cm^{-1} lower[24,26] than does the corresponding band of the Cp analogue (1907 cm^{-1}), which has been observed by time-resolved IR spectroscopy.[20a] It is also similar in frequency to the CO band of the paramagnetic isopropyl analogue, discussed below.

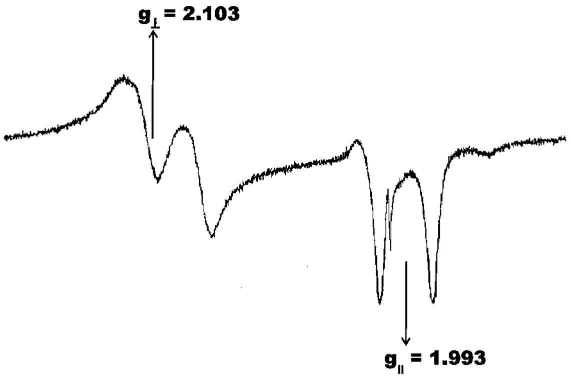

Figure 2. EPR spectrum (9456.8 MHz) of a frozen solution of Cp†Fe(CO)$\{P(O\text{-}i\text{-}Pr)_3\}^\bullet$ in benzene at 96 K.

The reaction of [Cp†Fe(CO)$_2$]$_2$ with P(OEt)$_3$ proceeded relatively slowly to produce low yields of the Arbuzov products Cp†Fe(CO)$_2$Et and Cp†Fe(CO)$_2\{PO(OEt)_2\}$, identified on the basis of IR and $^{31}P\{^1H\}$ NMR spectra of reaction mixtures since the ^{1}H NMR spectra were very complex. The IR spectrum of the ethyl compound exhibited CO bands at 1994 and 1941 cm^{-1}, identical with those of the ethyl compound formed from reaction of [Cp†Fe(CO)$_2$]$_2$ with EtI (see above). The identity of the compound Cp†Fe(CO)$_2\{P({=}O)(OEt)_2\}$ was inferred from its IR spectrum (ν_{CO} 2025, 1980 cm^{-1}), very similar to that of the methyl analogue (see above), while its $^{31}P\{^1H\}$ NMR spectrum exhibited a singlet at δ 100.3. A doublet of doublets at δ 112.36 and 163.83 (J_{HP} ~155.5 Hz) indicated the probable formation of Cp†Fe(CO)$\{P({=}O)(OEt)_2\}\{P(OEt)_3\}$, while a singlet at δ 165.0 may indicate the formation of Cp†Fe$\{P(OEt)_3\}_2$Et.

However, the extent of formation of these products was far from complete, and the IR spectrum was dominated by a CO band at 1894 cm^{-1}, which remained for several hours and which is attributable to the new, iron-centered radical Cp†Fe(CO)$\{P(OEt)_3\}^\bullet$. Consistent with this assignment, the $^{31}P\{^1H\}$ NMR spectrum also exhibited a broad ($\Delta\delta_{1/2}$ ~20 ppm) resonance (δ ~142), which may be reasonably attributed to free phosphite (δ 139) exchanging with coordinated phosphite of the paramagnetic Cp†Fe(CO)$\{P(OEt)_3\}^\bullet$.

Reaction of [Cp†Fe(CO)$_2$]$_2$ with a 17-fold excess of P(O-*i*-Pr)$_3$ proceeded even more slowly and was still incomplete after stirring for 7.5 h. Again the dominant CO band in the IR spectrum was attributable to the substituted radical Cp†Fe(CO)$\{P(O\text{-}i\text{-}Pr)_3\}^\bullet$ (1886 cm^{-1}) and only traces of other products were evident. Although an IR study indicated that Cp†Fe(CO)$\{P(O\text{-}i\text{-}Pr)_3\}^\bullet$ can persist for many hours at least, all attempts to grow crystals failed; slow decomposition occurred instead.

No EPR spectrum was detected in liquid benzene, but an EPR investigation of a frozen benzene solution (96 K) of Cp†Fe(CO)$\{P(O\text{-}i\text{-}Pr)_3\}^\bullet$ revealed the spectrum illustrated in Figure 2. The spectrum observed is clearly that of an electronic doublet ($S = {}^1/_2$) with a uniaxial **g** matrix ($g_\parallel = 1.993$, $g_\perp = 2.103$) and an isotropic ^{31}P hyperfine coupling of 37 G (3.7 mT). The principal g values are typical of d^7 organometallic radicals in which the unpaired electron is essentially

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confined to a metal d_{z^2} orbital.[1a,30] In particular, they resemble the *g* values in the 17-electron Fe(I) species $[Fe(CO)_5]^+$ and $[Fe(CO)_3(PPh_3)_2]^+$.[30b,31a] The small isotropic ^{31}P hyperfine interaction corresponds[31b] to only 0.8% P 3s character and is typical of a phosphorus nucleus vicinal to the spin-bearing metal nucleus in phosphite- or phosphine-substituted transition metal carbonyl radicals.[30b,31c] It undoubtedly arises through bond polarization by the metal d orbital; *i.e.*, there is little or no direct participation of phosphorus valence orbitals in the SOMO. The spectral parameters are certainly consistent with $Cp^\dagger Fe(CO)\{P(O\text{-}i\text{-}Pr)_3\}^\bullet$ as the carrier. However, the uniaxiality of **g** is perplexing *vis-a-vis* the molecular symmetry.

Since the $Cp^\dagger$ ligand is topologically equivalent to three *fac* CO ligands, the radical $CpFe(CO)_2^\bullet$ is isolobal[32] with $[Fe(CO)_5]^+$. It is, therefore, not too surprising that the two such species should have similar metal contributions to their SOMOs and similar principal *g* values, and the unexpected symmetry of **g** for $Cp^\dagger Fe(CO)\{P(O\text{-}i\text{-}Pr)_3\}^\bullet$ may possibly be a result either of an accidental degeneracy of filled orbitals or, alternatively, of rapid internal motions that result in a time-averaged axial symmetry. While extended Hückel calculations for "planar" $CpCo(CO)_2$ do not support the simplistic deduction of a d_{z^2} SOMO for the 17-electron analogue $CpFe(CO)_2^\bullet$, they do point to significant pyramidalization in passing from the 18-electron to the 16-electron species $CpMn(CO)_2$.[33] This, together with a very soft bending mode, could result in a $p_z-d_{z^2}$ hybrid SOMO.

Our inability to detect an EPR spectrum of the radical in liquid solvent is not too surprising. A number of metal-centered radicals have proven problematic in this regard, notably $Mn(CO)_5$ and $CpCr(CO)_3$.[30a] The proximity of the d orbitals in these species, which results in large displacements of *g* values from free spin, also provides an efficient mechanism for spin relaxation and line broadening to the point of spectral indetectability.

Mechanism of the Reactions with Phosphites. As first observed and studied in organophosphorus chemistry,[34a−c] the Arbuzov rearrangement normally involves the nucleophilic dealkylation of a phosphite and the concurrent formation of a compound containing a phosphorus(V) compound that possesses a PO double bond, as in eq 26. Similar processes have also been observed in reactions of phosphites with complexes of transition metals in positive oxidation states (eq 27).[25]

$$P(OR)_3 + R'X \rightarrow [P(OR)_3R']X \rightarrow (RO)_2P({=}O)R' + RX \quad (26)$$

$$[L_nM\{P(OR)_3\}]X \rightarrow [L_nM\{P({=}O)(OR)_2\}] + RX \quad (27)$$

In both types of reactions, the formation of a cationic species results in activation of the bound phosphite with respect to nucleophilic displacement of the $(RO)_2P({=}O)R'$ or $L_nM\{P({=}O)(OR)_2\}$ fragments from C-1 of the phosphite by halide ion X^-, yielding phosphorus(V) compounds as shown.

Of possibly greater relevance here, there have also been several reports of Arbuzov reactions induced by radicals.[25,34] For instance, in a number of cases, phosphites $P(OR)_3$ have been observed to react with alkyl and alkoxy radicals $^\bullet Y$ as in eq 28. The reactions are believed to involve four-coordinated, phosphorus-centered radicals of type **D**. Depending on the relative stabilities of the radical products $^\bullet R$ and $^\bullet OR$, **D** can undergo homolysis of P−O or O−C bonds (the latter as in eq 28) to give phosphorus(V) compounds and either alkoxy or alkyl radicals.

$$P(OR)_3 + {}^\bullet Y \rightarrow \underset{\mathbf{D}}{{}^\bullet\{P(Y)(OR)_3\}} \rightarrow P({=}O)(OR)_2(Y) + {}^\bullet R \quad (28)$$

Among the very limited number of possibly direct precedents for the chemistry described here is the reaction of $P(OMe)_3$ with $[CpCr(CO)_2\{P(OMe)_3\}]_2$, which exists in thermal equilibrium with its 17-electron monomer $CpCr(CO)_2\{P(OMe)_3\}^\bullet$.[1c,d,g] Reaction of $[CpCr(CO)_3]_2$ with 2 molar equiv of $P(OMe)_3$ proceeds rapidly at temperatures below 25 °C to yield primarily $CpCr(CO)_2\{P(OMe)_3\}^\bullet$, while reaction of the latter with excess $P(OMe)_3$ yields $CpCr(CO)_2\{P(OMe)_3\}Me$ and $CpCr(CO)_2\{P(OMe)_3\}\{P({=}O)(OMe)_2\}$ as the major products.[1g] An Arbuzov rearrangement has also been observed in the high-temperature (refluxing xylene) reaction of $Cp_2Fe_2(CO)_3P(OMe)_3$ with $P(OMe)_3$, which yields $CpFe(CO)_2Me$ and $CpFe(CO)\{P(OMe)_3\}\{P({=}O)(OMe)_2\}$.[27] Although spontaneous homolysis of diiron species such as $[CpFe(CO)_2]_2$ and $Cp_2Fe_2(CO)_3P(OMe)_3$ at ambient temperatures has not been observed,[7d] radical involvement at high temperatures seems likely.

The mechanism originally proposed for the reaction of $CpCr(CO)_2\{P(OMe)_3\}^\bullet$ with excess $P(OMe)_3$ to yield $CpCr(CO)_2\{P(OMe)_3\}Me$ and $CpCr(CO)_2\{P(OMe)_3\}P({=}O)(OMe)_2\}$[1g] involved abstraction of a methyl group from free phosphite by the radical $CpCr(CO)_2\{P(OMe)_3\}^\bullet$ to form $CpCr(CO)_2\{P(OMe)_3\}Me$ and the phosphonate radical intermediate, $OP(OMe)_2^\bullet$. The latter could then couple with a second chromium-centered radical (eqs 29 and 30). This mechanism was subsequently revised to make it more consistent "with the products often encountered when alkyl phosphites react with radicals", as in eq 28[25] (eqs 31 and 32). Here elimination of a

$$CpCr(CO)_2\{P(OMe)_3\}^\bullet + P(OMe)_3 \rightarrow CpCr(CO)_2\{P(OMe)_3\}Me + OP(OMe)_2^\bullet \quad (29)$$

$$CpCr(CO)_2\{P(OMe)_3\}^\bullet + OP(OMe)_2^\bullet \rightarrow CpCr(CO)_2\{P(OMe)_3\}\{P({=}O)(OMe)_2\} \quad (30)$$

$$CpCr(CO)_2\{P(OMe)_3\}^\bullet + P(OMe)_3 \rightarrow CpCr(CO)_2\{P(OMe)_3\}\{P({=}O)(OMe)_2\} + Me^\bullet \quad (31)$$

$$CpCr(CO)_2\{P(OMe)_3\}^\bullet + Me^\bullet \rightarrow CpCr(CO)_2\{P(OMe)_3\}Me \quad (32)$$

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methyl radical from coordinated phosphite is concurrent with or followed by coordination of free phosphite to the 16-electron phosphonate species $\mathrm{CpCr(CO)_2\{P({=}O)(OMe)_2\}}$; coupling of methyl and chromium-centered radicals ensues. A similar mechanism was also proposed for the above-mentioned high-temperature reactions of $\mathrm{Cp_2Fe_2(CO)_3P(OMe)_3}$ with $\mathrm{P(OMe)_3}$.[27]

The reaction under consideration here, in which $\mathrm{[Cp^{\dagger}Fe(CO)_2]_2}$ reacts with $\mathrm{P(OMe)_3}$ to give Arbuzov products **A**−**C**, almost certainly involves initial formation of $\mathrm{Cp^{\dagger}Fe(CO)\{P(OMe)_3\}^{\bullet}}$. The latter then undergoes dealkylation, as in the chromium system, but assisted, presumably, by $\mathrm{Cp^{\dagger}Fe(CO)_2}$ as in eqs 33 and 34. Direct release of a methyl radical as in eq 30 seems very unlikely and would lead to the prediction that similar ethyl and isopropyl compounds would react even more quickly. This is not so (see below). The formation of the 16-electron intermediate $\mathrm{Cp^{\dagger}Fe(CO)\{P({=}O)(OMe)_2\}}$ could not be verified, but it would readily coordinate any free CO or $\mathrm{P(OMe)_3}$ to form $\mathrm{Cp^{\dagger}Fe(CO)_2\{P({=}O)(OMe)_2\}}$ (**B**; eq 35) or $\mathrm{Cp^{\dagger}Fe(CO)\{P({=}O)(OMe)_2\}\{P(OMe)_3\}}$ (**C**; eq 36), respectively, thus rationalizing the formation of these two products.

$$\mathrm{Cp^{\dagger}Fe(CO)_2^{\bullet} + P(OMe)_3 \rightarrow Cp^{\dagger}Fe(CO)\{P(OMe)_3\}^{\bullet} + CO} \qquad (33)$$

$$\mathrm{Cp^{\dagger}Fe(CO)\{P(OMe)_3\}^{\bullet} + Cp^{\dagger}Fe(CO)_2^{\bullet} \rightarrow \underset{\mathbf{A}}{Cp^{\dagger}Fe(CO)_2Me} + Cp^{\dagger}Fe(CO)\{P({=}O)(OMe)_2\}} \qquad (34)$$

$$\mathrm{Cp^{\dagger}Fe(CO)\{P({=}O)(OMe)_2\} + CO \rightarrow \underset{\mathbf{B}}{Cp^{\dagger}Fe(CO)_2\{P({=}O)(OMe)_2\}}} \qquad (35)$$

$$\mathrm{Cp^{\dagger}Fe(CO)\{P({=}O)(OMe)_2\} + P(OMe)_3 \rightarrow \underset{\mathbf{C}}{Cp^{\dagger}Fe(CO)\{P(OMe)_3\}\{P({=}O)(OMe)_2\}}} \qquad (36)$$

The reactions of $\mathrm{[Cp^{\dagger}Fe(CO)_2]_2}$ with $\mathrm{P(OEt)_3}$ and $\mathrm{P(O\text{-}\mathit{i}\text{-}Pr)_3}$ proceed much more slowly to give the substituted radicals $\mathrm{Cp^{\dagger}Fe(CO)\{P(OR)_3\}^{\bullet}}$ (R = Et, *i*-Pr), as anticipated since the reactions are presumably associative.[1] Interestingly, however, the substituted 17-electron compounds are also very stable with respect to conversion to Arbuzov products. Although IR spectra of reaction mixtures suggest the formation of products similar to **A**−**C**, these never appear in quantity even after many hours when the radical species have decomposed. These results are much more consistent with the mechanism of eqs 33 and 34 than in that of eqs 31 and 32, as conversion of the intermediate radical species in an assisted, bimolecular reaction (eq 34) would be retarded for steric reasons and the iron-centered radicals containing the bulkier phosphites should be more stable. Indeed, the relative proclivities of phosphites to undergo Arbuzov rearrangements in this system, i.e. $\mathrm{P(OMe)_3} \gg \mathrm{P(OEt)_3} > \mathrm{P(O\text{-}\mathit{i}\text{-}Pr)_3}$, parallel the relative reactivities observed for the type of ionic process exemplified by eq 27 and, thus, the ease of attack on C-1 of an activated phosphite, whether by nucleophile or by radical. The same steric factors affect the relative reactivities, *i.e.* Me > Et > $^{\mathrm{i}}$Pr > Ph. On the other hand, as noted above, unassisted scission of a carbon−oxygen bond as in eq 30 would not only be very slow, but it should become more facile in the order Me < Et < *i*-Pr. Thus, the compounds $\mathrm{Cp^{\dagger}Fe(CO)\{P(OR)_3\}^{\bullet}}$ (R = Et, *i*-Pr) should be less stable than is $\mathrm{Cp^{\dagger}Fe(CO)\{P(OMe)_3\}^{\bullet}}$, the opposite to what is observed.

Summary. The compounds $\mathrm{[Cp'Fe(CO)_2]_2}$ ($\mathrm{Cp'} = \eta^5\text{-}\mathrm{C_5Ph_5}$, $\eta^5\text{-}\mathrm{C_5Ph_4}$(*p*-tolyl)) dissociate slightly in solution to give the corresponding 17-electron iron-centered radicals $\mathrm{Cp'Fe(CO)_2^{\bullet}}$. The latter take part in a variety of reactions characteristic of 17-electron compounds, reacting with organic halides RX to form $\mathrm{Cp'Fe(CO)_2R}$ and $\mathrm{Cp'Fe(CO)_2X}$ and, in the case of $\mathrm{[Cp^{\dagger}Fe(CO)_2]_2}$, readily with ^{13}CO to form the fully ^{13}CO-labeled compound. The radical $\mathrm{Cp^{\dagger}Fe(CO)_2^{\bullet}}$ is surprisingly inert to CO substitution by phosphines, presumably for steric reasons, because the sterically less demanding *t*-BuNC reacts readily, albeit giving ultimately the product of disproportionation $\mathrm{[Cp^{\dagger}Fe(\mathit{t}\text{-}BuNC)_3][Cp^{\dagger}Fe(CO)_2]}$. The phosphites $\mathrm{P(OR)_3}$ (R = Me, Et, *i*-Pr) do give the anticipated 17-electron species $\mathrm{Cp^{\dagger}Fe(CO)\{P(OR)_3\}^{\bullet}}$ in apparently associative processes, since the rates of formation vary qualitatively in the order Me > Et > *i*-Pr, but the methyl analogue reacts rapidly with free $\mathrm{P(OMe)_3}$ to give products of Arbuzov rearrangements. Attempts to grow single crystals of the persistent radical $\mathrm{Cp^{\dagger}Fe(CO)\{P(O\text{-}\mathit{i}\text{-}Pr)_3\}^{\bullet}}$ failed, but an EPR spectrum of a frozen solution in benzene could readily be obtained and analyzed in terms of a uniaxial **g** matrix ($g_{\parallel} = 1.993$, $g_{\perp} = 2.103$) and an isotropic ^{31}P hyperfine coupling of 37 G (3.7 mT), typical of d^7 organometallic radicals in which the unpaired electron is essentially confined to a metal d_{z^2} orbital.

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