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The 18-Electron, Metal−Metal-Bonded Dimers $[\eta^5\text{-}C_5Ph_5Fe(CO)_2]_2$ and $[\eta^5\text{-}C_5Ph_4(p\text{-tolyl})Fe(CO)_2]_2$: Their Proclivity To Undergo Spontaneous, Thermal Homolysis to the Corresponding 17-Electron Monomers

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The known compound $[Cp^{\ddagger}Fe(CO)_2]_2$ and the new, more soluble $[Cp^{\dagger}Fe(CO)_2]_2$ ($Cp^{\ddagger} = \eta^5\text{-}C_5Ph_5$; $Cp^{\dagger} = \eta^5\text{-}C_5Ph_4(p\text{-tolyl})$) are prepared via a new, very effective route involving hydridic hydrogen atom abstraction from the hydrides, $Cp^{\ddagger}Fe(CO)_2H$ and $Cp^{\dagger}Fe(CO)_2H$, by the trityl radical. The dimers dissociate thermally to the corresponding 17-electron monomers, $Cp^{\ddagger}Fe(CO)_2$ and $Cp^{\dagger}Fe(CO)_2$, which probably assume "planar" (C_{2v}) structures with OC−Fe−CO bond angles of ~90°.

There has in recent years been considerable interest in the preparation and characterization of 17-electron, organotransition metal compounds (metal-centered radicals).[1a,b] This class of compounds may be synthesized in a variety of ways[1] and 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 (e.g. CO by tertiary phosphines,[1gi,2] $\eta^5\text{-}C_5H_5$ by $\eta^5\text{-}C_5Me_5$ and $\eta^5\text{-}C_5Ph_5$[1d,j,3]). For many classes of metal−metal-bonded compounds,[4] it has been found that there is a correlation between the proclivity of an 18-electron dimer to undergo thermal homolysis to the corresponding 17-electron species and the length of the metal−metal bond. Thus the chromium−chromium bond of $[CpCr(CO)_3]_2$ (Cp = $\eta^5\text{-}C_5H_5$), which dissociates to the extent of a few percent in solution at room temperature,[1c,d] is much longer (3.281 Å)[1e] than the metal−metal bond of the analogous, much more homolytically stable molybdenum compound (3.235 Å)[1f] but much shorter than the chromium−chromium bonds of $[CpCr(CO)_2P(OMe)_3]_2$ (3.343 Å)[1g] and $[Cp^*Cr(CO)_3]_2$ (3.311 Å, Cp* = $\eta^5\text{-}C_5Me_5$),[1d] both of which dissociate much more extensively in solution.[1d,g] Consistent with the apparent role of steric effects on extent of homolysis, the compounds $CpCr(CO)_2PPh_3$[1h,i] and $\eta^5\text{-}C_5Ph_5Cr(CO)_3$[1j] are completely monomeric in solution and the solid state.

We have recently begun an investigation into the possibility of forming persistent iron-centered radicals of the type $\eta^5\text{-}Cp'Fe(CO)L$ (Cp′ = Cp, substituted Cp; L = bulky phosphines).[6] The 17-electron compounds $CpFe(CO)_2$ and $Cp^*Fe(CO)_2$ can be generated photochemically from the corresponding dimers and have been investigated using time-resolved IR spectroscopy, but are exceedingly reactive and recombine rapidly to form the corresponding 18-electron dimers (eq 1).[7] Attempts

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

to stabilize substituted monomeric iron compounds with sterically demanding phosphines have generally failed. For instance, while abstraction of the hydridic hydrogen atom from $CpFe(CO)(PPh_3)H$ with the trityl radical almost certainly forms $CpFe(CO)(PPh_3)$, the latter and

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[1] (a) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217 and references therein. (b) Trogler, W. C., Ed. *Organometallic Radical Processes*; J. Organomet. Chem. Library 22; Elsevier: New York, 1990; p 49 and references therein. (c) McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643. (d) Watkins, W. C.; Jaeger, T.; Kidd, C. E.; Fortier, S.; Baird, M. C.; Kiss, G.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1992**, *114*, 907. (e) Adams, R. D.; Collins, D. E.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749. (f) Adams, R. D.; Collins, D. E.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086. (g) Goh, L.-Y.; D'Aniello, M. J.; Slater, S.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Frederich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192. (h) Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 2563. (i) Fortier, S.; Baird, M. C.; Preston, K. F.; Morton, J. R.; Ziegler, T.; Jaeger, T. J.; Watkins, W. C.; MacNeil, J. H.; Watson, K. A.; Hensel, K.; Le Page, Y.; Charland, J.-P.; Williams, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 542. (j) Hoobler, R. J.; Hutton, M. A.; Dillard, M. M.; Castellani, M. P.; Rheingold, A. R.; Rieger, A. L.; Rieger, P. H.; Richards, T. C.; Geiger, W. E. *Organometallics* **1993**, *12*, 116.

[2] (a) McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982,** *104*, 7496. (b) Kidd, D. R.; Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1978,** *100*, 4103. (c) Walker, H. W.; Rattinger, G. B.; Belford, R. L.; Brown, T. L. *Organometallics* **1983,** *2*, 775. (d) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* **1985,** *4*, 42. (e) Hanckel, J. M.; Lee, K.-W.; Rushman, P.; Brown, T. L. *Inorg. Chem.* **1986,** *25*, 1852. (f) Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986,** *5*, 2563. (g) Cooley, N. A.; MacConnachie, P. T. F.; Baird, M. C. *Polyhedron* **1988**, *7*, 1965. (h) Watkins, W. C.; Jaeger, T.; Kidd, C. E.; Fortier, S.; Baird, M. C.; Kiss, G.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1992,** *114*, 907.

[3] (a) Broadley, K.; Lane, G. A.; Connelly, N. G.; Geiger, W. E. *J. Am. Chem. Soc.* **1983,** *105*, 2486. (b) Connelly, N. G.; Geiger, W. E.; Lane G. A.; Raven, S. J.; Rieger, P. H. *J. Am. Chem. Soc.* **1986,** *108*, 6219. (c) Connelly, N. G.; Raven, S. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1613. (d) Connelly, N. G.; Raven, S. J.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1987**, 467. (e) Lane, G. A.; Geiger, W. E.; Connelly, N. G. *J. Am. Chem. Soc.* **1987,** *109*, 402. (f) DeGray, J. A.; Geiger, W. E.; Lane, G. A.; Rieger, P. H. *Inorg. Chem.* **1991**, *30*, 4100. (g) Fei, M.; Sur, S. K.; Tyler, D. R. *Organometallics* **1991**, *10*, 419.

[4] Exceptions are fulvalene complexes, many of which exhibit no inclination to undergo homolysis in spite of containing extraordinarily long metal−metal bonds.[5]

[5] (a) Kovács, I.; Baird, M. C. *Organometallics* **1995**, *14*, 4074 and references therein. (b) Kovács, I.; Baird, M. C. *Organometallics* **1995**, *14*, 4084. (c) Kovács, I.; Baird, M. C. *Organometallics* **1995**, *14*, 5469. (d) Kovács, I.; Baird, M. C. *Organometallics* **1996**, *15*, 3588. (e) McGovern, P. A.; Vollhardt, K. P. C. *Synlett* **1990**, 493. (f) McGovern, P. A.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun.* **1996**, 1593.

[6] (a) Kuksis, I.; Baird, M. C. *Organometallics* **1994**, *13*, 1551. (b) Kuksis, I.; Baird, M. C. *J. Organomet. Chem.* **1996**, *512*, 253. (c) Kuksis, I.; Baird, M. C. *J. Organomet. Chem.*, in press.

[7] (a) Moore, B. D.; Simpson, M. B.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1984**, 972. (b) Moore, B. D.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986,** *108*, 1819. (c) Bloyce, P. E.; Campen, A. K.; Hooker, R. H.; Rest, A. J.; Thomas, N. R.; Bitterwolf, T. E.; Shade, J. E. *J. Chem. Soc., Dalton Trans.* **1990**, 2833. (d) Dixon, A. J.; George, M. W.; Hughes, C.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1992,** *114*, 1719.

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its dimer are both unstable and only the diiron compound $\mathrm{Cp_2Fe_2(CO)_3(PPh_3)}$ is formed (eq 2).[6a,c]

$$\begin{tikzcd} \mathrm{2CpFe(CO)(PPh_3)H + 2Ph_3C^{\bullet}} \arrow[r] & \mathrm{2CpFe(CO)(PPh_3) + 2Ph_3CH} \arrow[d, "\mathrm{CO}"] \\ & \mathrm{Cp_2Fe_2(CO)_3(PPh_3)} \end{tikzcd} \qquad (2)$$

In view of the effectiveness with which the η^5-$\mathrm{C_5Ph_5}$ ligand stabilizes the persistent metal-centered radicals η^5-$\mathrm{C_5Ph_5M(CO)_3}$ (M = Cr, Mo),[1j,3g] we turned to compounds in the analogous η^5-$\mathrm{C_5Ph_5}$–iron system.[8] Of these, relevant here are the known $[\eta^5\text{-}\mathrm{C_5Ph_5Fe(CO)_2}]_2$,[8a–c,j] η^5-$\mathrm{C_5Ph_5Fe(CO)_2Br}$,[8a,c] η^5-$\mathrm{C_5Ph_5Fe(CO)_2H}$,[8a] $\mathrm{K}[\eta^5\text{-}\mathrm{C_5Ph_5Fe(CO)_2}]$,[8f] η^5-$\mathrm{C_5Ph_5Fe(CO)_2Me}$,[8b] η^5-$\mathrm{C_5Ph_5Fe(CO)_2Et}$,[8f] $[\eta^5\text{-}\mathrm{C_5Ph_5Fe(CO)_2L}]^+$ (L = CO, phosphines, $\mathrm{C_2H_4}$),[8h] and η^5-$\mathrm{C_5Ph_5Fe(CO)LX}$ (X = Br, Et, EtCO; L = phosphine).[8h] An analogous series of substituted derivatives of iron, containing the η^5-$\mathrm{C_5Ph_{5-\mathit{n}}Ar_\mathit{n}}$ (Ar = *p*-alkylphenyl) ligands, has also been reported,[8d,g,i] as has an analogous ruthenium compound.[8k]

We now describe an improved synthetic route to $[\eta^5\text{-}\mathrm{C_5Ph_5Fe(CO)_2}]_2$[8a–c,j] and to the new, more soluble analogue, $[\eta^5\text{-}\mathrm{C_5Ph_4}(p\text{-tolyl})\mathrm{Fe(CO)_2}]_2$ (henceforth the η^5-$\mathrm{C_5Ph_5}$ and η^5-$\mathrm{C_5Ph_4}$(*p*-tolyl) groups will be denoted $\mathrm{Cp}^{\ddagger}$ and $\mathrm{Cp}^{\dagger}$, respectively). We also describe routes to the hydrides, $\mathrm{Cp^{\ddagger}Fe(CO)_2H}$ and $\mathrm{Cp^{\dagger}Fe(CO)_2H}$, and to the new series of substituted hydrides $\mathrm{Cp^{\dagger}Fe(CO)LH}$ (L = $\mathrm{PMe_3}$, $\mathrm{PMe_2Ph}$, $\mathrm{PMePh_2}$, $\mathrm{PPh_3}$), all potential precursors to new 17-electron compounds of the type $\mathrm{Cp'Fe(CO)L}$. We find that both $[\mathrm{Cp^{\ddagger}Fe(CO)_2}]_2$ and $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ undergo slight thermal homolysis in solution to give the monomeric species $\mathrm{Cp^{\ddagger}Fe(CO)_2}$ and $\mathrm{Cp^{\dagger}Fe(CO)_2}$, respectively, identified by spectroscopy and by chemical reactions, characteristic of 17-electron compounds,[1a,b] which will be described in a subsequent paper. A preliminary report of aspects of this work has appeared.[6a]

Experimental Section

Except where noted, experiments were conducted under an inert atmosphere of oxygen-free nitrogen, further purified through columns containing 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; $\mathrm{CH_2Cl_2}$ was dried and distilled over $\mathrm{CaH_2}$. Solvents were thoroughly deoxygenated prior to use by saturation with $\mathrm{N_2}$ 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, Fisher, Strem, and Fluka and were used as received.

Table 1. IR Data

compd	ν_{CO} (cm^{-1})
$\mathrm{Cp^{\ddagger}Fe(CO)_2H}$	2008, 1951 (benzene)
$\mathrm{Cp^{\ddagger}Fe(CO)_2Br}$	2033, 1993 (THF)
$\mathrm{Cp^{\dagger}Fe(CO)_2H}$	2007, 1951 (benzene)
$\mathrm{Cp^{\dagger}Fe(CO)_2Br}$	2033, 1992 (THF)
$[\mathrm{CpFe(CO)_2}]_2$ (*cis*)	2004, 1792 (cyclohexane)[7a,b]
$[\mathrm{CpFe(CO)_2}]_2$ (*trans*)	1960, 1792 (cyclohexane)[7a,b]
$[\mathrm{Cp^{*}Fe(CO)_2}]_2$ (*cis*)	1981, 1756 (cyclohexane)[7a,b]
$[\mathrm{Cp^{*}Fe(CO)_2}]_2$ (*trans*)	1928, 1765 (cyclohexane)[7a,b]
$[\mathrm{Cp^{\ddagger}Fe(CO)_2}]_2$ (*trans*)	~1951, 1781/1788 (benzene)
$[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ (*trans*)	1957, 1780 (benzene)
$\mathrm{CpFe(CO)_2^{\bullet}}$	2004, 1938 (cyclohexane)[7a]
$\mathrm{Cp^{*}Fe(CO)_2^{\bullet}}$	1984, 1915 (cyclohexane)[7b]
$\mathrm{Cp^{\ddagger}Fe(CO)_2^{\bullet}}$	1990, 1921 (benzene)
$\mathrm{Cp^{\dagger}Fe(CO)_2^{\bullet}}$	1989, 1921 (benzene)
$\mathrm{CpFe}(\mu\text{-}\mathrm{CO})_3\mathrm{FeCp}$	1823 (cyclohexane)[7a]
$\mathrm{Cp^{*}Fe}(\mu\text{-}\mathrm{CO})_3\mathrm{FeCp^{*}}$	1790 (cyclohexane)[7b]
$\mathrm{Cp(CO)_2Fe\text{-}Fe(CO)_2Cp}$	2015, 1973, 1938 (heptane)[15]

Infrared spectra were acquired on Bruker 85 IFS FT-IR and Bruker IFS 25 FT-IR spectrometers; IR data are presented in Table 1. Raman spectra were run on a Bruker RFS-100 FT-Raman spectrometer utilizing a near-infrared Nd:YAG laser, while NMR spectra were obtained on Bruker ACF 200 (200.1 MHz ^{1}H, 50.3 MHz ^{13}C{^{1}H}) and AM 400 (400.1 MHz ^{1}H, 100.6 MHz ^{13}C{^{1}H}) NMR spectrometers. The residual proton and the carbon resonances of deuterated solvents served as internal references for ^{1}H and ^{13}C resonances, respectively. ^{31}P NMR spectra were run on an AM 400 (162 MHz) NMR spectrometer and were referenced to external 85% $\mathrm{H_3PO_4}$.

Ultraviolet–visible spectra were acquired on a Hewlett Packard 8452A diode array spectrophotometer in quartz sample cells with a 1 cm path length. Mass spectra were acquired on a Fisons VG Quattro instrument. EPR spectroscopy was conducted by Dr. K. F. Preston at the National Research Council, Ottawa. Elemental analyses for carbon and hydrogen were carried out by Canadian Microanalytical Services, Delta, British Columbia, Canada.

Solutions of trityl in benzene were prepared by the zinc reduction of $\mathrm{Ph_3CCl}$,[9] $\mathrm{Cp^{\ddagger}Fe(CO)_2Br}$,[8d] $\mathrm{Cp^{\ddagger}Fe(CO)_2H}$,[8a] and $\mathrm{Cp^{\dagger}Fe(CO)_2Br}$[8d] by literature methods.

$[\mathrm{Cp^{\ddagger}Fe(CO)_2}]_2$.[8a] A mixture of 0.845 g of $\mathrm{Ph_3CCl}$ (3.04×10^{-3} mol) and 0.672 g of zinc metal (1.03×10^{-2} mol) in 65 mL of benzene was sonicated for 1 h and then stirred overnight for 16 h. Stirring was stopped, the mixture was allowed to settle for 1 h, and 10 mL of benzene was added to a flask containing 0.422 g (7.60×10^{-4} mol) of $\mathrm{Cp^{\ddagger}Fe(CO)_2H}$. About 62 mL of the trityl solution was cannulated onto the hydride, and the reaction was complete within 56 min (IR). A dark green, cloudy solution had formed, and strong IR bands were observed at 1952 and 1788 cm^{-1}. The green suspension was collected by filtration, washed, and dried under reduced pressure. Yield: 0.32 g (76%). IR of the green product (Nujol): 1953 (s), 1788 (s) cm^{-1} (lit. IR 1954, 1774 cm^{-1} (Nujol)[8b]).

A similar experiment, run under conditions of greater dilution, was monitored by IR spectroscopy. A yellow solution of 0.55 g (9.83×10^{-4} mol) of $\mathrm{Cp^{\ddagger}Fe(CO)_2H}$ in 200 mL of benzene (IR bands 2008 and 1951 cm^{-1}) was cannulated into an aluminum foil wrapped flask containing 0.96 g (1.97×10^{-3} mol) of trityl dimer. Approximately 5 min after addition, the reaction mixture was a clear, emerald green. The solution still exhibited bands in the IR spectrum corresponding to $\mathrm{Cp^{\ddagger}Fe(CO)_2H}$, as well as new, weak bands at 1990 and 1921 cm^{-1}. An intense band at 1781 cm^{-1}, attributable to the bridging carbonyls of $[\mathrm{Cp^{\ddagger}Fe(CO)_2}]_2$,[8b,j] was also present, although the terminal CO band of this compound overlaps a CO band

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[8] (a) McVey, S.; Pauson, P. L. *J. Chem. Soc.* **1965**, 4312. (b) Connelly, N. G.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1989**, 283. (c) Field, L. D.; Hambley, T. W.; Lindall, C. M.; Masters, A. F. *Polyhedron* **1989**, *8*, 2425. (d) Field, L. D.; Ho, K. M.; Lindall, C. M.; Masters, A. F.; Webb, A. G. *Aust. J. Chem.* **1990**, *43*, 281. (e) Brown, K. N.; Field, L. D.; Lay, P. L.; Lindall, C. M.; Masters, A. F. *J. Chem. Soc., Chem. Commun.* **1990**, 408. (f) Brégaint, P.; Hamon, J.-R.; Lapinte, C. *J. Organomet. Chem.* **1990**, *398*, C25. (g) Field, L. D.; Hambley, T. W.; Lay, P. L.; Lindall, C. M.; Masters, A. F. *J. Chem. Soc., Dalton Trans.* **1991**, 1499. (h) Brégaint, P.; Hamon, J.-R.; Lapinte, C. J. *Organometallics* **1992**, *11*, 1417. (i) Field, L. D.; Masters, A. F.; Gibson, M.; Latimer, D. R.; Hambley, T. W.; Buys, I. E. *Inorg. Chem.* **1993**, *32*, 211. (j) Aroney, M. J.; Buys, I. E.; Dennis, G. D.; Field, L. D.; Hambley, T. W.; Lay, P. A.; Masters, A. F. *Polyhedron* **1993**, *12*, 2051. (k) Colbran, S. B.; Harrison, W. M.; Saadeh, C. *Organometallics* **1994**, *13*, 1061.

[9] (a) Drake, P. R.; Baird, M. C. *J. Organomet. Chem.* **1989**, *363*, 131. (b) Koeslag, M. D.; Baird, M. C. *Organometallics* **1994**, *13*, 11. (c) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1980**, *193*, 383. (d) Turaki, N. N.; Huggins, J. M. *Organometallics* **1986**, *5*, 1703. (e) Edidin, R. T.; Hennessy, K. M.; Moody, A. E.; Okrasinski, S. J.; Norton, J. R. *New J. Chem.* **1988**, *12*, 475. (f) Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4888.

of the hydride and a band of the benzene solvent at 1960 cm^{-1}, and thus its intensity could not be estimated with certainty. A green precipitate developed after ~0.5 h, and an IR spectrum of the solution exhibited only two strong bands, the terminal CO band at 1951 cm^{-1} of $[Cp^{\ddagger}Fe(CO)_2]_2$ and a bridging CO band at 1787 cm^{-1}, the latter of equal intensity to and ~6 cm^{-1} higher in frequency than the band which had originally been observed at 1781 cm^{-1}. The bands of $Cp^{\ddagger}Fe(CO)_2H$ and those initially at 1990 and 1921 cm^{-1} had essentially disappeared. The green precipitate was collected by filtration, washed four times with cold benzene and then with *n*-hexane and pentane, and dried. Yield: 0.36 g (66%). Anal. Calcd for $C_{74}H_{50}Fe_2O_4$: C, 79.72; H, 4.52. Found: C, 79.12; H, 4.48.

On stirring of a suspension of the dimer in benzene, a small amount dissolved and the CO bands at 1951 and 1781 cm^{-1} reappeared.

$Cp^{\dagger}Fe(CO)_2H$. Synthesis of this hydride was based on the method of McVey and Pauson for their preparation of $Cp^{\ddagger}Fe(CO)_2H$.[8a] A solution of 5.02 g of $Cp^{\dagger}Fe(CO)_2Br$[8d] (7.71×10^{-3} mol) in 80 mL of THF was treated with a solution of 0.50 g (1.32×10^{-2} mol) of $NaBH_4$ in 25 mL of distilled water over 7 min. The red solution turned lighter in color, some bubbling was noticed, and eventually the solution appeared green due to the presence of a black solid in the yellow liquid. The mixture was stirred for 75 min (covered with aluminum foil) and then filtered through Celite to give an orange-yellow solution. The solvent was removed in vacuo, and the yellow solid was dissolved in 60 mL of benzene, washed 3 times with distilled water, and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo to give 3.62 g (82%) of product. Anal. Calcd for $C_{38}H_{28}FeO_2$: C, 79.73; H, 4.93. Found: C, 80.44; H, 5.09. IR (benzene): 2008, 1951 cm^{-1}. IR (THF): 2006, 1952 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.34−7.26 (m, 8H, aryl H), 7.20 (d, J_{HH} 7.96, 2H, aryl H), 6.91−6.77 (m, 12 H, aryl H), 6.65 (d, J_{HH} 7.98, 2H, aryl H), 1.90 (s, 3H, Me), −10.35 (s, 1H, Fe−H). ^{13}C NMR (C_6D_6): δ 21.0 (s, Me), 102.7, 102.8, 103.0 ($Cp^{\dagger}$ ring C), 129.2, 127.5−132.9 (other peaks at ~δ 128 may be obscured by solvent resonances), 132.4, 132.5, 137.4 (aryl C), 216.4 (CO).

$[Cp^{\dagger}Fe(CO)_2]_2$. This compound was synthesized in the dark as described above for $[Cp^{\ddagger}Fe(CO)_2]_2$, using variable amounts of $Cp^{\dagger}Fe(CO)_2H$ and approximately 2-fold excesses of trityl dimer. After addition of the solvent, the reactions were monitored by IR spectroscopy. In a typical preparative reaction, 160 mL of benzene was added to a mixture of 1.56 g of $Cp^{\dagger}Fe(CO)_2H$ (2.72×10^{-3} mol) and 0.97 g of trityl dimer (1.99×10^{-3} mol) in an aluminum foil wrapped flask. The mixture turned to an emerald green solution within 15 min, with some green solid present. The IR spectrum exhibited a band at 2007 cm^{-1} (m) attributable to $Cp^{\dagger}Fe(CO)_2H$ (the other CO band was obscured by a product band at 1956 cm^{-1}), as well as bands at 1989 (w), 1921 (w), 1956 (vs), and 1779 cm^{-1} (s), the latter two attributable to $[Cp^{\dagger}Fe(CO)_2]_2$. The reaction was essentially complete after 45 min. The final IR spectrum, taken after 75 min, exhibited CO bands at 1957 (s), 1779 (s), 1989 (w), and 1921 cm^{-1} (w). The reaction mixture at this point was a dark green solution containing some solid material. The solvent was removed in vacuo, the residue was stirred with 20 mL of cold benzene, and then the mixture was filtered to give a green solid and a clear, very dark emerald green filtrate. The green solid was washed 5 times with cold benzene and dried in vacuo to give 1.21 g (78%) of product, $[Cp^{\dagger}Fe(CO)_2]_2$. This material exhibits rather low solubility in benzene, but an IR spectrum of a suspension of 0.02 g in 10 mL of benzene (pale green solution) exhibited CO bands at 1957 (s), 1780 (s), 1989 (w), and 1921 cm^{-1} (w), while a ^{1}H NMR spectrum (C_6D_6) indicated that no trityl dimer was present. A Nujol mull IR spectrum of the solid exhibited strong bands at 1956 and 1780 cm^{-1}. Raman spectra of both pure, powdered samples and samples in Nujol exhibited CO bands at 1971 (m) and 1599 (vs) cm^{-1}.

The filtrate was taken down to dryness and then suspended in benzene, and the resulting mixture was placed on a column of hexanes-equilibrated silica gel. Beginning with 10% benzene in hexanes and using increasing proportions of benzene in hexanes as eluent, first a yellow solution containing trityl products and then a green fraction was obtained. On removal of solvent, there was obtained 0.11 g (7%) of *benzene-soluble* $[Cp^{\dagger}Fe(CO)_2]_2$. Addition of 0.02 g of this material to 10 mL of benzene resulted in ready dissolution to give a clear, emerald green solution exhibiting IR bands at 1957, 1780, 1989, and 1921 cm^{-1}, all of comparable intensity. The material was recrystallized from benzene/n-hexane with mixed success. Anal. Calcd for $C_{76}H_{54}Fe_2O_4$: C, 79.87; H, 4.76. Found: C, 77.62; H, 4.99. A chemical ionization MS investigation using isobutane as carrier gas was carried out on a benzene solution of $[Cp^{\dagger}Fe(CO)_2]_2$ (MW 1143.97 g/mol). While the molecular ion could not be observed at 298, 423, or 673 K, a peak at *m*/*z* 571.7 is attributed to $[Cp^{\dagger}Fe(CO)_2]^+$ (MW 571.5 g/mol). IR (Nujol): 1953, 1777 cm^{-1}. IR (benzene): 1955, 1780, 1989, 1921 cm^{-1}. IR (THF): 1956, 1781, 1988, 1920 cm^{-1}. The ^{1}H NMR spectrum in C_6D_6 was difficult to assess. Although multiplets in the phenyl region (δ 6.5−7.5) were obvious, there were no resonances in the aryl methyl region which could be unambiguously attributed to the tolyl methyl group.

In a reaction monitored by ^{1}H NMR spectroscopy, 0.01 g of $Cp^{\dagger}Fe(CO)_2H$ (1.92×10^{-5} mol) was dissolved in a small amount of C_6D_6 and an NMR spectrum was run; the tolyl methyl resonance at δ 1.90 (s) and the hydride resonance at δ −10.30 were clearly observed. The sample was then treated with 0.01 g of trityl dimer (2.05×10^{-5} mol), and the solution turned green within a few minutes. The NMR spectrum showed a significant decrease in the intensity of the methyl resonance at δ 1.90 and strong growth of a new resonance at δ 5.42, attributable to Ph_3CH. Distinguishable trityl dimer peaks were also present at δ 6.48 (d, J_{HH} 2 Hz), 6.42 (br), 5.95 (d, J_{HH} 4.0 Hz), 5.90 (d, J_{HH} 4.0 Hz), and 4.92 (s, br),[10] and a rather weak, broad resonance centered at δ 2.08 appeared. The residual hydride resonance was by now very weak, and the reaction was essentially complete. A significant amount of green solid precipitated from solution over the next 0.5 h. In a similar reaction carried out using a deficiency of trityl dimer, no residual trityl dimer resonances were observed when all of the hydride had reacted.

On heating of a suspension of 0.036 g of $[Cp^{\dagger}Fe(CO)_2]_2$ in 10 mL of benzene (CO bands at 1956 (s), 1780 (s), 1989 (vw), and 1919 cm^{-1} (vw) at room temperature) to ~70 °C, all of the solid dissolved to give a dark yellow solution. A sample syringed out of the hot flask appeared green in the syringe barrel, but an IR spectrum acquired immediately exhibited very strong CO bands at 1989 and 1919 cm^{-1}, in addition to those at 1956, and 1780 cm^{-1}. When the solution in the flask was cooled to room temperature, the color changed to a clear, emerald green. The bands at 1989, 1919, 1956 and 1780 cm^{-1} were still present.

The temperature-dependent changes in the $[Cp^{\dagger}Fe(CO)_2]_2$ system were also investigated by UV−visible spectroscopy. A clear, green solution of 0.003 g (2.62×10^{-6} mol) of the soluble form of $[Cp^{\dagger}Fe(CO)_2]_2$ in 3 mL of benzene was placed in a quartz cell equipped with a stirring bar and allowed to equilibrate at 298 K. The instrument was equipped with a no. 3 filter in the beam to absorb light of wavelengths <295 nm. Before and after measurements, the beam was blocked completely. The spectrum of $[Cp^{\dagger}Fe(CO)_2]_2$ at 298 K was obtained, and the cell was covered with a black cloth as the temperature was increased to 328 K, where the spectrum was run again. The temperature of the sample was then decreased, still covered with a black cloth, to 298 K. The experiment was repeated using the insoluble form of $[Cp^{\dagger}Fe(CO)_2]_2$, dissolved in hot benzene.

Reactions of $[Cp^{\dagger}Fe(CO)_2]_2$ with ^{13}CO and PMe_3. A solution of 0.032 g of $[Cp^{\dagger}Fe(CO)_2]_2$ (2.8×10^{-5} mol) in 10 mL of benzene, exhibiting CO bands 1955 (s), 1780 (s), 1989 (w) and 1921 (w) cm^{-1}, was treated with ^{13}CO for 30 s at 1 atm. The IR spectrum run after ~30 min exhibited CO bands at

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[10] (a) Smith, W. B. *J. Chem. Educ.* **1970**, *47*, 535. (b) Lankamp, H.; Nauta, W. T.; MacLean, C. *Tetrahedron Lett.* **1968**, 249.

1911 (s), 1740 (s), 1942 (w), and 1876 (w) cm^{-1}. A similar experiment using $[CpFe(CO)_2]_2$ resulted in no change in the IR spectrum.

A solution of 0.10 g of $[Cp^{\dagger}Fe(CO)_2]_2$ (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 $Fe(CO)_3(PMe_3)_2$.[11] An additional 8 mL of PMe_3 were added to consume all remaining dimer, and ultimately the IR spectrum exhibited only strong bands attributable to $Fe(CO)_3(PMe_3)_2$ and $Cp^{\dagger}Fe(CO)_2H$.

Reaction of $Cp^{\dagger}Fe(CO)_2H$ with PMe_3. The compound $Fe(CO)_3(PMe_3)_2$ was also obtained on treating $Cp^{\dagger}Fe(CO)_2H$ with PMe_3 and trimethylamine oxide in THF. There was no IR evidence in this reaction for the formation of $Cp^{\dagger}Fe(CO)(PMe_3)H$, although a ^1H NMR spectrum of the crude solid products exhibited a weak hydride doublet resonance at δ −13.35 (J_{PH} 88 Hz).

$Cp^{\dagger}Fe(CO)(PMe_3)Br$. A solution of 0.10 g of $Cp^{\dagger}Fe(CO)_2Br$ (1.54×10^{-4} mol) in acetone (ν_{CO} 2035, 1992 cm^{-1}) was treated with 32 μL of PMe_3 (3.09×10^{-4} mol), the color of the solution changing from dark brown-orange to dark yellow-brown and new bands appearing in the IR spectrum at 2040 and 1996 cm^{-1}. On the addition of 0.018 g (1.62×10^{-4} mol) of trimethylamine oxide$\cdot 2H_2O$, the solution changed to a brown yellow color and the IR spectrum exhibited a new band at 1941 cm^{-1}, corresponding to $Cp^{\dagger}Fe(CO)(PMe_3)Br$ (compare $Cp^{\ddagger}Fe(CO)(PMe_3)Br$: ν_{CO} 1942 cm^{-1} in CH_2Cl_2).[8h] In a more direct procedure, $Cp^{\dagger}Fe(CO)(PMe_3)Br$ was synthesized via the procedure for $Cp^{\ddagger}Fe(CO)(PMe_3)Br$.[8h] A solution of 0.50 g of $Cp^{\dagger}Fe(CO)_2Br$ (7.7×10^{-4} mol) in THF was treated with 100 μL of PMe_3 (9.66×10^{-4} mol). The solution changed color quickly from red to dark yellow-black, a single strong band being observed in the IR spectrum at 1942 cm^{-1}. Various approaches to substitution of the bromide by hydride gave mixtures of products.

$Cp^{\dagger}Fe(CO)(PMe_3)H$. A solution of 0.49 g of $Cp^{\dagger}Fe(CO)_2H$ (8.50×10^{-4} mol in 125 mL of THF was treated with 132 μL of PMe_3 (1.28×10^{-3} mol). The solution, in a water-cooled quartz vessel, was photolyzed with a 250 W Hanovia UV lamp for 4.5 h, during which time an additional 50 μL of PMe_3 (4.83×10^{-4} mol) was added. IR spectra showed the gradual disappearance of the CO bands of $Cp^{\dagger}Fe(CO)_2H$ (2006, 1952 cm^{-1}) and the growth of new bands at 1915 (s) and 1888 cm^{-1} (sh). Following the photolysis, the solvent was removed in vacuo, and the residue was chromatographed on hexanes-equilibrated alumina using increasing concentrations of diethyl ether in hexanes to elute $Cp^{\dagger}Fe(CO)(PMe_3)H$ as a yellow band. The yield was 0.10 g (17.4%), which was recrystallized from ethyl ether/hexanes. Increasing the concentrations, using a 2.5-fold excess of PMe_3 and irradiating for a longer period, resulted in a yield of 55%. Anal. Calcd for $C_{40}H_{37}FeOP$: C, 77.42; H, 6.01. Found: C, 76.84; H, 6.14. IR (THF): 1915, 1888 (sh) cm^{-1}. (Nujol): 1919, ∼1880 (sh) cm^{-1}. Raman (solid): 1916, 1877 cm^{-1}. ^1H NMR (benzene-d_6): δ 7.46−7.41 (m, 8H, aryl H), 7.32 (d, J_{HH} 8.3 Hz, 2H, aryl H), 6.92−6.8 (m, 12H, aryl H), 6.71 (d, J_{HH} 7.63 Hz, 2H, aryl H), 1.94 (s, 3H, aryl Me), 1.15 (d, J_{PH} 8.6 Hz, ∼9H, PMe), −13.36 (d, J_{PH} 85 Hz, 1H, Fe−H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 21.0 (s, aryl Me), 21.6 (d, J_{PC} 29.0 Hz, PMe), 99.2, 99.4 ($Cp^{\dagger}$ ring C), 127.5−133.4, 131.9, 135.1, 135.3, 136.3 (aryl C; some resonances may be partially obscured by solvent), 221.8 (d, J_{PC} 32 Hz, CO). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 29.4.

$Cp^{\dagger}Fe(CO)(PMe_2Ph)H$. A solution of 0.23 g of $Cp^{\dagger}Fe(CO)_2H$ (3.97×10^{-4} mol) and 114 μL of PMe_2Ph (8.01×10^{-4} mol) in 100 mL of THF was photolyzed as above for 2.5 h to give an orange solution. The solvent was removed in vacuo, and two batches of crude product prepared in this way were combined and chromatographed on an alumina column equilibrated with hexanes. Gradually increasing quantities of diethyl ether in hexanes resulted in elution of an orange band of the product; yield 53%. The product was recrystallized from ethyl ether−hexanes. Anal. Calcd for $C_{45}H_{39}FeOP$: C, 79.18; H, 5.76. Found: C, 78.49; H, 5.73. IR (ethyl ether, hexanes): 1915, 1890 cm^{-1} (sh). IR (benzene, THF): 1914, ∼1887 (sh) cm^{-1}. Raman (solid): 1916, 1882 cm^{-1}. ^1H NMR (C_6D_6): δ 7.54−7.49 (m, 2H, aryl H), 7.41−7.34 (m, 10H, aryl H), 7.27 (d, J_{HH} 7.97 Hz, 3H, aryl H), 7.01−6.94 (m, 4H, aryl H), 6.93−6.82 (m, 14H, aryl H), 6.69 (d, J_{HH} 7.97 Hz, ∼2H, aryl H), 1.94 (s, 3H, aryl-*Me*) 1.43 (d, J_{PH} 8.62 Hz, 3H, P*Me*), 1.38 (d, J_{PH} 8.9 Hz, 3H, P*Me*), −13.17 (d, J_{PH} 86.3 Hz, ∼1H, Fe−H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.9 (d, J_{PC} 28.7 Hz, P*Me*), 21.0 (s, aryl-*Me*), 23.0 (d, J_{PC} 35.2 Hz, P*Me*), 99.2, 99.4, 99.6, 99.7 ($Cp^{\dagger}$ ring C), 128.9 (d, P*Ph*), 128.9−133.4 (aryl C; some resonances may be partially obscured by solvent), 130.7 (d, J_{PC} 8.90 Hz, P*Ph*), 131.5, 134.7, 134.8, 134.9, 136.3 ($Cp^{\dagger}$ phenyl C), ∼141 (d, J_{PC} 27 Hz, P*Ph*), 222.5 (d, J_{PC} 30.6 Hz, CO). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 39.7 at 298 K. δ 39.4, 39.3 at 240 K; both resonances with shoulders.

$Cp^{\dagger}Fe(CO)(PMePh_2)H$. A solution of 0.80 g of $Cp^{\dagger}Fe(CO)_2H$ (1.4×10^{-3} mol) and 2.0 mL of $PMePh_2$ (4.3×10^{-3} mol) in 180 mL of THF was photolyzed as above for 11 h to give an orange solution. The final IR spectrum exhibited a new band at 1915 cm^{-1}, as well as bands attributable to the hydride at 2006 and 1950 cm^{-1}. The reaction mixture was worked up as for $Cp^{\dagger}Fe(CO)(PMe_2Ph)H$ to give 0.205 g (18%) of dark red product which was recrystallized from ethyl ether/hexanes. Anal. Calcd for $C_{50}H_{41}FeOP$: C, 80.64; H, 5.50. Found: C, 79.90; H, 5.62. IR (THF): ∼1914 (br) cm^{-1}. IR (Nujol): 1919, 1890 (sh) cm^{-1}. ^1H NMR in benzene-d_6: δ 7.74−7.70 (m, ∼1H, aryl H), 7.67−7.62 (m, 2H, aryl H), 7.43−7.37 (m, ∼8H, aryl H), 7.29 (d, J_{HH} 7.55 Hz, ∼2H, aryl H), 7.08−6.95 (m, ∼6H, aryl H), 6.87−6.81 (m, ∼12H, aryl H), 6.67 (d, J_{HH} 8.13 Hz, 2H, aryl H), 1.93 (s, 3H, aryl *Me*), 1.67 (d, J_{PH} 8.40, 3H, P*Me*), −12.48 (d, J_{PH} 82.68 Hz, ∼1H, Fe−H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 20.08 (d, J_{PC} 28.4 Hz, P*Me*), 21.0 (s, Ph *Me*), 99.4, 99.6, 99.7, 99.8, 100.0 ($Cp^{\dagger}$ ring C), 129.3 (P*Ph*), 129.5 (P*Ph*), 132.4 (d, J_{PC} 8.56 Hz, P*Ph*), 132.8 (d, J_{PC} 8.96 Hz, P*Ph*), 136.3−127.4 (aryl, some resonances may be obscured by solvent), 138.3 (d, J_{PC} 35.62 Hz, P*Ph*), 141.4 (d, J_{PC} 47.5 Hz, P*Ph*), 222.0 (d, J_{PC} 32.20 Hz, CO). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 60.8.

$Cp^{\dagger}Fe(CO)(PPh_3)H$. A solution of 0.72 g of $Cp^{\dagger}Fe(CO)_2H$ (1.3×10^{-3} mol) and 0.41 g of PPh_3 (1.6×10^{-3} mol) in THF was photolyzed as above for 14 h to give an orange solution. The final IR spectrum exhibited a new band at 1920 cm^{-1}, as well as weak bands attributable to the hydride at 2006 and 1950 cm^{-1}. The solvent was removed in vacuo, and the resulting solid was extracted with ethyl ether, filtered off, and dried. The yield of crude product was 0.20 g (18.3%), which was recrystallized from toluene−hexanes. Anal. Calcd for $C_{55}H_{43}FeOP$: C, 81.99; H, 5.25. Found: C, 79.90; H, 5.62. IR (THF): 1920 (br) cm^{-1}. IR (Nujol): 1924, 1900 (sh) cm^{-1}. Raman (solid): 1928, 1897 cm^{-1}. ^1H NMR in benzene-d_6: δ 7.64−7.59 (m, ∼10H, aryl H), 7.38−7.29 (m, 8H, aryl), 7.23 (d, J_{PH} 8.06 Hz, 2H, aryl H), 7.12−6.77 (m, ∼25H, aryl H, some resonances may be obscured by solvent), 6.63 (d, J_{PH} 8.04 Hz, 2H, aryl H) 2.10 (s, 2.4 H, aryl *Me*), 1.91 (s, 3H, aryl *Me*), −11.98 (d, J_{PH} 83.53 Hz, 1H, Fe−H). A variable-temperature ^1H NMR study showed that the resonances at δ 1.91 and 2.10 neither coalesced nor moved together between 298 and 343 K. Also no loss of the phosphorus−hydride coupling was observed. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 57.7.

Results and Discussion

Pentaarylcyclopentadienyl ligands have been much investigated as extensions of the better known η^5-C_5H_5 (Cp) and η^5-C_5Me_5 (Cp*) ligands, and there has in recent years been increased interest in their coordination to metal ions.[12] Their exceptional size provides consider-

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(11) Bigorgne, M. *J. Organomet. Chem.* **1970**, *24*, 217.

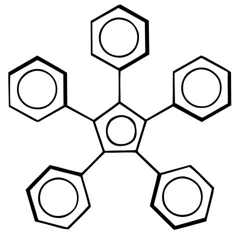

Figure 1. One possible enantiomeric structure of the C_5-Ph_5 group.

able steric protection, thus shielding otherwise reactive metal centers from other reagents and conferring kinetic stability to complexes such as 17-electron compounds.[1j,3] In addition, their chiral structures, in which the aryl rings are canted relative to the five-membered ring (Figure 1),[13] have provided much impetus for the investigation of ring rotation dynamics.[14] The neutral, purple pentaphenylcyclopentadienyl species is itself a persistent radical which can be observed in solution and exhibits ESR resonance at $\{g\} = 2.003 \pm 0.001$.[3g]

The first report of metal coordination by a pentaarylcyclopentadienyl ligand involved the synthesis of Cp‡-$Fe(CO)_2Br$;[8a] the crystal structure of this compound was then reported in 1989.[8c] The compound assumes the expected piano stool structure, with Br−Fe−CO and OC−Fe−CO angles of 86.6(1) and 89.8(2)°, respectively. The C_5 ring of the Cp‡ ligand is planar, but the *ipso*-carbon atoms of each of the phenyl rings sit 0.05−0.23 Å above the plane. The phenyl rings are oriented between 49.09 and 142.84° to the C_5 frame in a conformation of much less regular structure than that depicted in Figure 1, while the Fe atom is not found directly below the centroid of the Cp ring but is rather shifted slightly off-center.

Formation and Characterization of [Cp‡Fe-$(CO)_2]_2$ and [Cp†$Fe(CO)_2]_2$. Although the reactions of Cp‡Br and Cp†Br with $Fe(CO)_5$ to produce Cp‡Fe-$(CO)_2Br$[8a,c,d] and Cp†$Fe(CO)_2Br$[8a,d] are the only procedures used to date in the literature to synthesize these compounds, we have found that the use of $Fe_2(CO)_9$ instead of $Fe(CO)_5$ greatly improved the efficiency of the reaction as reaction times were reduced to 2−3 h and product yields were generally higher (54% for Cp‡Fe-$(CO)_2Br$ and as high as 83% for Cp†$Fe(CO)_2Br$). The compound Cp†$Fe(CO)_2H$ is new and was prepared as was the Cp‡ analogue, reported in 1965.[8a]

Hydrogen atom abstraction reactions of Cp″$Fe(CO)_2H$ (Cp″ = Cp‡, Cp†) by the trityl radical proceed in benzene as found for other metal hydrides,[9] yielding triphenylmethane and, presumably, the 17-electron compounds Cp″$Fe(CO)_2$. The latter rapidly couple to give the green dimers [Cp″$Fe(CO)_2]_2$, which are generally the major iron-containing products of the reactions (eq 3). [Cp‡-$Fe(CO)_2]_2$ has previously been synthesized via the reduction of Cp‡$Fe(CO)_2Br$ with sodium amalgam[8a] and cobaltocene,[8b] but the very low solubility and apparently high reactivity of this compound seem to have discouraged further investigations. Aroney *et al.*[8j] also inadvertently synthesized the compound during synthesis of Cp‡$Fe(CO)_2Br$, but the procedure was not reproducible and was not pursued. In contrast, although a new route to [Cp‡$Fe(CO)_2]_2$ was not our original intention, the chemistry of eq 3 does indeed provide a very convenient, high-yield method for its synthesis.

$$2\mathrm{Cp''Fe(CO)_2H} + 2\mathrm{Ph_3C^{\bullet}} \rightarrow [\mathrm{Cp''Fe(CO)_2}]_2 + 2\mathrm{Ph_3CH} \quad (3)$$

IR spectroscopy has been used to monitor hydrogen atom abstraction from Cp‡$Fe(CO)_2H$ and clearly shows diminution of the CO bands of the hydride and the concomitant growth of a strong bridging CO band at 1781 cm^{-1}. The reaction mixture initially changes from yellow to a clear emerald green solution, but within 0.5 h, a green suspension forms, the solution turns light green, and the bridging CO band shifts to 1787 cm^{-1}. The terminal CO band of the product at ∼1951 cm^{-1} overlaps the hydride band at 1951 cm^{-1} as well as a benzene solvent band at 1960 cm^{-1}, and thus the relative intensity and exact position of this band cannot be discerned over the course of the reaction. Since [Cp‡-$Fe(CO)_2]_2$ was the sole product formed and exhibits very low solubility, the compound was readily filtered and washed to remove trityl products and residual hydride. Its low solubility precluded recrystallization, but elemental analyses were found to be satisfactory.

The bands at ∼1951 and 1781−1788 cm^{-1} are consistent with a centrosymmetric trans isomer of the dimer,[8b,j] in accord with the trend to the trans configuration with increasing size of the η^5-ligands in these iron compounds. Thus while [$CpFe(CO)_2]_2$ forms a mixture of *cis* and *trans* isomers in solution, [Cp*Fe-$(CO)_2]_2$ is predominantly found in the trans configuration,[7a,b,15] and it is thus anticipated that [Cp‡Fe-$(CO)_2]_2$ will also exist as the *trans* isomer. Furthermore, since IR spectra of *cis*−*trans* mixtures of isomers exhibit differences of 40−50 cm^{-1} between the terminal CO stretching frequencies of the *cis* and *trans* forms (Table 1), our observation of two different bridging CO bands in spectra of [Cp‡$Fe(CO)_2]_2$ clearly cannot be rationalized in these terms.

However, the phenyl groups of the C_5Ph_5 ligands are expected to be canted relative to the five-membered ring (Figure 1), and thus the C_5Ph_5 ligands are chiral.[8j,13,14] It therefore seems reasonable that the bands at 1781 and 1787 cm^{-1} are attributable to different diastereomers in which the pairs of C_5Ph_5 ligands in each molcule of dimer have the same or opposite chirality. Although dynamic processes involving the Cp‡ ligand in rather similar Cp‡Fe compounds have been studied,[14] thefactors influencing the conversion of the bridging CO band between positions at 1781 and 1788 cm^{-1} are not understood and the phenomenon we describe has not been noted previously.[8a,b,j]

In an effort to find more soluble compounds of the type [$\{C_5(aryl)_5\}Fe(CO)_2]_2$, Field *et al.*[8i] have synthesized [$\{C_5$(*p*-tolyl)$_5\}Fe(CO)_2]_2$ by reduction of $\{C_5$(*p*-tolyl)$_5$Fe-$(CO)_2Br$ with zinc metal but have commented only briefly on its properties and chemistry. We prepared

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[12] Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291.

[13] (a) Chambers, J. W.; Baskar, A. J.; Bott, S. G.; Atwood, J. L.; Rausch, M. D. *Organometallics* **1986**, *5*, 1635. (b) Adams, H.; Bailey, N. A.; Browning, A. F.; Ramsden, J. A.; White, C. *J. Organomet. Chem.* **1990**, *387*, 305. (c) Ramsden, J. A.; Milner, D. J.; Hempsread, P. D.; Bailey, N. A.; White, C. *J. Chem. Soc., Dalton Trans.* **1995**, 2101.

[14] Li, L.; Decken, A.; Sayer, B. G.; McGlinchey, M. J.; Bregaint, P.; Thepot, J.-Y.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1994**, *13*, 682.

[15] (a) Fischer, R. D.; Vogler, A.; Noack, K. *J. Organomet. Chem.* **1967**, *7*, 135. (b) Bullitt, J. G.; Cotton, F. A.; Marks, T. J. *Inorg. Chem.* **1972**, *11*, 671. (c) Noack, K. *J. Organomet. Chem.* **1967**, *7*, 151. (d) Bullitt, J. G.; Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1970**, *92*, 2155.

$[Cp^{\dagger}Fe(CO)_2]_2$ for the same reason but via the reaction of $Cp^{\dagger}Fe(CO)_2H$ with trityl radical. The dimeric $[Cp^{\dagger}Fe(CO)_2]_2$ was readily formed as in eq 3, and its CO bands were observed at 1958 and 1780 cm^{-1}, neither shifting as the reaction progressed. It is possible either that the two diastereomers have coincident CO bands or that only one diastereomer is formed during the reaction. Interestingly, however, $[Cp^{\dagger}Fe(CO)_2]_2$ was obtained in two forms, one which exhibits very low solubility in cold benzene or toluene but does dissolve when heated, and another which is sufficiently soluble in benzene at room temperature that it can be purified by column chromatography. The insoluble variety is generally the major product of eq 3, especially if formed in large-scale reactions (~1 g). Nujol mull IR spectra of the two forms exhibit identical CO stretching bands, leading to the suggestion that the origin of the solubility differences is again the type of diastereoisomerism that is apparently observed for $[Cp^{\ddagger}Fe(CO)_2]_2$, although it is strange that the two forms do not interconvert readily.

IR spectra of the solid materials exhibited strong CO bands at 1956 and 1780 cm^{-1}, while Raman spectra of both pure, powdered samples and samples in Nujol exhibited CO bands at 1971 (m) and 1599 (vs) cm^{-1}. The noncoincidence of the IR and Raman spectra provides clear evidence for the centrosymmetric *trans* structure suggested above. The Raman spectra also exhibited bands at 215 and 115 cm^{-1}, either of which may correspond to the Fe−Fe bond stretching mode which has been reported at 225 cm^{-1} in the Raman spectrum of $[CpFe(CO)_2]_2$[16a] but at 140−154 cm^{-1} in the spectrum of $[Cp^{*}Fe(CO)_2]_2$.[16b]

Using purified trityl dimer, it was possible to monitor the synthesis of $[Cp^{\dagger}Fe(CO)_2]_2$ in C_6D_6 by ^1H NMR spectroscopy and to show that the reaction does indeed proceed with the stoichiometry shown in eq 3. It was found that, on addition of trityl dimer to a C_6D_6 solution of $Cp^{\dagger}Fe(CO)_2H$, the yellow color changed to green with the consequent decrease in the intensity of the tolyl methyl resonance of the hydride at δ 1.90 and the growth of the Ph_3CH resonance at δ 5.42.

Also noted during the course of the hydrogen atom abstraction reactions of $Cp''Fe(CO)_2H$ was the appearance of relatively weak IR bands at ~1990 and ~1920 cm^{-1} (Table 1), which were not present in spectra of the solid products ultimately isolated. Although not noted previously by workers with these types of compounds, the bands reappeared when solid dimers $[Cp''Fe(CO)_2]_2$ were redissolved and were eventually attributed to the 17-electron monomers $Cp''Fe(CO)_2^{\bullet}$, the initial products of hydrogen atom abstraction and presumably in equilibrium with the dimers (eq 4). IR spectra of the

$$[Cp''Fe(CO)_2]_2 \rightleftarrows 2Cp''Fe(CO)_2^{\bullet} \qquad (4)$$

analogous species $CpFe(CO)_2^{\bullet}$ (2004, 1939 cm^{-1}) and $Cp^{*}Fe(CO)_2^{\bullet}$ (1984, 1915 cm^{-1}) have been observed by time-resolved IR spectroscopy and matrix isolation studies,[7a−c] and the CO stretching bands of both are in close correspondence with those observed for $Cp''Fe(CO)_2^{\bullet}$. The assignments seem particularly reasonable since IR bands for C_5Ph_5 compounds normally lie between those of the Cp and Cp* analogues,[3a,13] as is the case here.

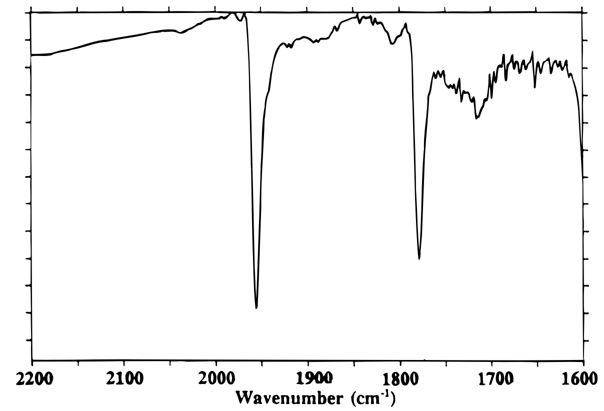

Figure 2. Nujol mull IR spectrum of $[Cp^{\dagger}Fe(CO)_2]_2$.

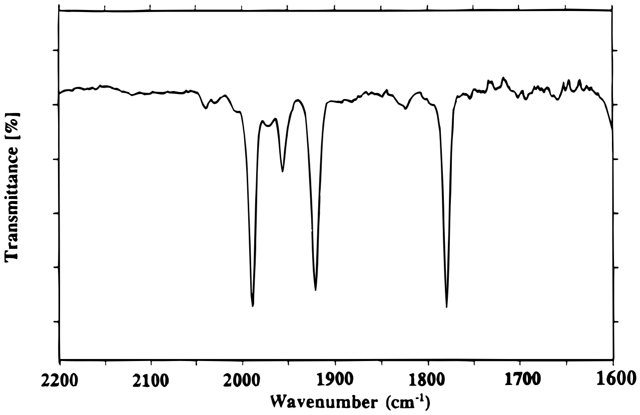

Figure 3. IR spectrum of $[Cp^{\dagger}Fe(CO)_2]_2$ (1.8×10^{-3} M) in benzene.

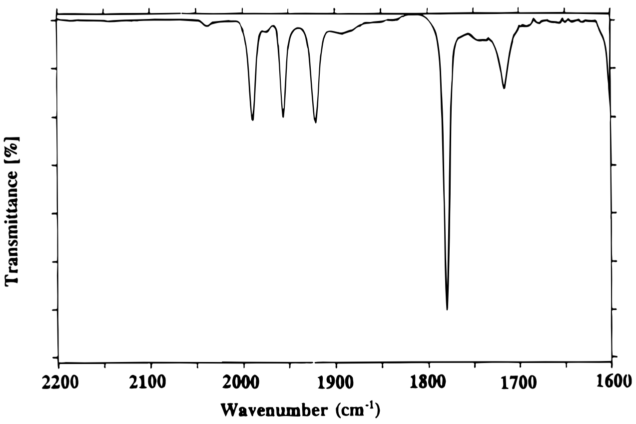

Figure 4. IR spectrum of $[Cp^{\dagger}Fe(CO)_2]_2$ (1.3×10^{-2} M) in benzene.

It was found that the relative intensities of the carbonyl stretching bands at ~1990 and ~1922 cm^{-1}, absent in the spectra of the solid (Figure 2), are strongly concentration dependent in benzene solution. Thus the intensities of the monomer bands were relatively high in dilute solutions (1.8×10^{-3} M, Figure 3), comparable with the dimer band at 1780 cm^{-1} (the dimer band at 1958 cm^{-1} coincides with a solvent peak, and its relative intensity cannot be determined reliably) but relatively low in more concentrated solutions (1.3×10^{-2} M, Figure 4), consistent with the thermal equilibrium of eq 4. Also consistent with this hypothesis, it was found that the relative intensities of the monomer bands increased significantly in the more polar solvent THF (1.8×10^{-3} M, Figure 5), again as expected for the

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(16) (a) Markwell, R. D.; Butler, I. S.; Gao, J. P.; Shaver, A. *J. Raman Spectrosc.* **1993**, *24*, 423. (b) Vitale, M.; Lee, K. K.; Hemann, C. F.; Hille, R.; Gustafson, T. L.; Bursten, B. E. *J. Am. Chem. Soc.* **1995**, *117*, 2286.

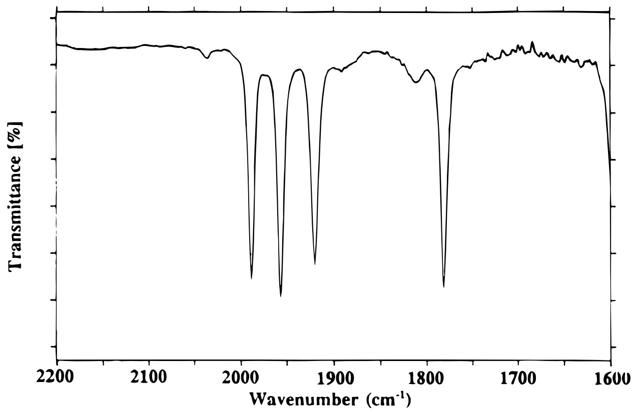

Figure 5. IR spectrum of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ (1.8×10^{-3} M) in THF.

monomer–dimer equilibrium of eq 4 since the centrosymmetric trans dimer would not possess a permanent dipole moment.

Assuming comparable extinction coefficients for the terminal CO stretching bands of the monomer and bridging CO band of the dimer, as is found for the Cp analogue,[7d] K_{eq} was estimated to be $\sim 10^{-3}$ M in benzene at room temperature. Unfortunately, attempts to carry out variable-temperature IR studies on solutions of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ were inconclusive, resulting only in significant decomposition as was shown by weakening of the CO bands. In other solvents, *e.g.* acetone and $\mathrm{CH_2Cl_2}$, decomposition of the dimer was observed at room temperature.

The magnetic susceptibility of a benzene solution of the soluble form of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ was measured using the Evans method,[17] although difficulties in obtaining reproducible results were experienced initially because the monomer concentrations were of necessity very low and the compound is extremely susceptible to oxidation to highly paramagnetic species. Indeed, intentional exposure of solutions of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ to air resulted in ~8-fold increases in the magnetic susceptibilities of the solutions, and thus even slight oxidation could result in misleading values. Reasonable precision was ultimately achieved, however, and reproducible susceptibility shifts of 8.2 ± 0.2 Hz were obtained for $\sim 10^{-3}$ M solutions of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$. After diamagnetic corrections for ligands and solvent, and assuming an equilibrium constant of 10^{-3} for eq 4 (see above), the calculated magnetic moment of the monomer was found to be 2.3 μ_B. This is marginally higher than the expected value for one unpaired electron,[17] possibly because of slight oxidation.

A useful ^{1}H NMR spectrum of the insoluble form of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ could not be obtained, as is the case with $[\mathrm{Cp^{\ddagger}Fe(CO)_2}]_2$, but the ^{1}H NMR spectrum of the soluble form of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ ($\mathrm{C_6D_6}$) was unfortunately also rather uninformative. Although phenyl multiplet resonances were readily apparent, there was no resonance which could be attributed to the methyl of the tolyl group. Since aryl methyl resonances were readily assigned in the spectra of $\mathrm{Cp^{\dagger}Fe(CO)_2H}$ and $\mathrm{Cp^{\dagger}Fe(CO)_2Br}$, it would seem that rapid monomer–dimer exchange in the Cp† system must broaden and perhaps shift the tolyl methyl resonance sufficiently that it cannot be recognized. For presumably the same reason, both liquid and frozen solutions of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ are also EPR inactive. As in other systems,[1i,j,3g] the ESR resonance is broadened in liquid solution, in part because of rapid exchange between the paramagnetic monomer and the diamagnetic dimer, while cooling shifts the equilibrium to the thermodynamically more stable dimer.

The above-mentioned temperature dependence of the changes in the $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ system were also investigated in a UV–visible spectroscopic study. Consistent with the equilibrium of eq 4, a dark green solution of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ in benzene turned yellow on heating from 298 to 328 K, although the solution returned only to a somewhat lighter green on cooling. Similar behavior was observed on heating suspensions of the insoluble form of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$, the mixtures initially turning yellow and then emerald green on cooling. In the latter cases, some precipitation occurred on cooling. Analogous thermochromic behavior has been reported for other systems involving equilibria between monomers and deeply colored dimers.[1c,d,3g] (see below).

Consistent with these observations, the UV–visible spectrum of a benzene solution of the soluble form of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ in a quartz cell at 298 K exhibited very intense, high-energy bands ($>$22 200 cm^{-1}), a shoulder at ~21 000 cm^{-1} and a broad, weak band at 16 200 cm^{-1}. On increase of the temperature to 328 K, it was found that both the shoulder and the band at 16 200 cm^{-1} weakened significantly. However, on decrease of the temperature of the sample to 298 K, the bands at ~21 000 cm^{-1} and 16 200 cm^{-1} returned only to intensities intermediate between those of the previous two spectra. Consistent with this observation, the solution changed to a lighter green than it had been initially. Repetition of this experiment using the insoluble form of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$, dissolved in hot benzene, yielded similar results, and it would seem that the system is thermally unstable under the conditions of the experiments.

To rationalize these results, we note that, by analogy with other systems, the shoulder at ~21 000 cm^{-1} may be attributed to a metal–metal $\sigma \rightarrow \sigma^*$ transition and the band at 16 200 cm^{-1} to a $d\pi \rightarrow \sigma^*$ transition.[1c,3g,7c,18] The corresponding $\sigma \rightarrow \sigma^*$ bands of $[\mathrm{CpFe(CO)_2}]_2$ and $[\mathrm{Cp^{*}Fe(CO)_2}]_2$ are found at ~29 400[18a,b] and ~27 800[19] cm^{-1}, respectively, at higher energies than for $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$ as expected for stronger Fe–Fe bonds (26–32 kcal/mol[20]) which do not undergo thermal dissociation to monomers. The $\sigma \rightarrow \sigma^*$ band of $[\mathrm{CpCr(CO)_3}]_2$, which does undergo spontaneous thermal dissociation in solution,[1] is observed at 22 200 cm^{-1}.[1c] Replacement of Cp by Cp† or Cp‡ would be expected to further decrease the energy of the $\sigma \rightarrow \sigma^*$ transition, and a difference of almost 2800 cm^{-1} is observed between the absorbances of $[(\mathrm{C_5H_4Me})\mathrm{Mo(CO)_3}]_2$ (25 400 cm^{-1}, does not dissociate) and $[\mathrm{Cp^{\ddagger}Mo(CO)_3}]_2$ (22 600 cm^{-1}, dissociates significantly).[3g]

Thus it is reasonable that the $\sigma \rightarrow \sigma^*$ transition and the low-energy $d\pi \rightarrow \sigma^*$ transition at 16 200 cm^{-1}, which gives rise to the green color of solutions of $[\mathrm{Cp^{\dagger}Fe(CO)_2}]_2$,

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(17) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

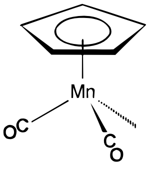
(18) (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; p 143. (b) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187. (c) Abrahamson, H. B.; Palazzotto, M. C.; Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 4123. (d) Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1978**, *17*, 1003.

(19) Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694.

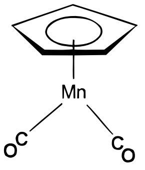
(20) (a) Cutler, A. R.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *120*, 87. (b) Pugh, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 8245.

decreased in intensity upon heating because of dissociation to monomer (eq 4). Similar behavior has been reported for the compounds $[CpCr(CO)_3]_2$[1c] and $[Cp^{\ddagger}Mo(CO)_3]_2$.[3g] The homolysis reaction is at least partially reversible, since cooling of solution resulted in dimerization and a significant return of the green color. However, the absorbance at 16 200 cm^{-1} recovered only approximately half of its original intensity, presumably because of partial thermal decomposition.

Structure and Electronic Structures of $Cp'Fe(CO)_2$. Hofmann has carried out extended Hückel calculations on the 16-electron fragment $CpMn(CO)_2$,[21] showing via a Walsh diagram that this species should be "pyramidal" as in **A**, derived from the C_{3V} structure of $CpMn(CO)_3$, but with one CO removed. Placing electrons in the LUMO of $CpMn(CO)_2$, however, stabilizes the "planar" structure, **B**, in which the Cp centroid, the Mn, and the two CO ligands are coplanar. It is on this basis that Hofmann rationalizes the planar structure of the 18-electron compound $CpCo(CO)_2$. For the same reason, then, the 17-electron molecules $Cp'Fe(CO)_2$, with one electron in an orbital corresponding to the HOMO of $CpCo(CO)_2$, should assume a planar structure also. Furthermore, since the SOMO of $Cp'Fe(CO)_2$ is nondegenerate,[21] it also follows from Hofmann's analysis that 17-electron molecules of the type $Cp'Fe(CO)_2$ are not Jahn–Teller molecules, as is often the case for other 17-electron compounds.[1a,b]



A



B

As shown in Figures 3–5, the symmetric (A′) and antisymmetric (A″) CO stretching bands of $Cp''Fe(CO)_2$ are of comparable intensities, suggesting strongly that the OC–Fe–CO bond angle of this molecule is ~90°.[22] Furthermore, and perhaps rather surprising, the frequencies of the symmetric and antisymmetric CO stretching bands of $Cp''Fe(CO)_2$ (~1989, ~1921 cm^{-1}) are ~27 to ~35 cm^{-1} below those of $Cp^{\ddagger}Co(CO)_2$ (2016, 1956 cm^{-1} in CH_2Cl_2[23a]). Thus the degree of backbonding in the 17-electron iron compound appears to exceed that in the 18-electron cobalt compound, possibly because of the somewhat higher electronegativity of cobalt.[23a]

Several papers discussing similar 17-electron iron(I) compounds appeared as this research was being initiated or in progress. Thus Astruc *et al.* displaced the arene ligands from the compounds CpFe(arene) (arene = benzene, toluene) with PPh_3 to form the persistent 17-electron compound $CpFe(PPh_3)_2$.[24a] Giese and Thoma[24b,c] found that photochemically generated $CpFe(CO)_2$ adds to activated olefins to form new carbon-centered radicals, useful in C–C-forming reactions. In an analogous investigation of novel C–C bond forming reactions, Sen *et al.* found that $[CpFe(COD)]^-$ (COD = 1,5-cyclooctadiene) undergoes a one-electron oxidation with benzyl halide to form the neutral 17-electron species CpFe(COD),[24d] which then couples with the benzyl radical to form $CpFe(COD)CH_2Ph$ although CpFe(COD) has been briefly claimed to be reasonably persistent at room temperature.[25] Certainly the sterically hindered compounds $Cp^*Fe(C_2H_4)_2$ and $Cp^*Fe(COD)$, while substitutionally labile, are thermally very well behaved.[24d] Finally, the 17-electron $Cp^*Fe(dppe)$ (dppe = 1,2-bis(diphenylphosphino)ethane), prepared via reduction of $Cp^*Fe(dppe)(OSO_2CF_3)$, is sufficiently stable that an X-ray crystal structure has been reported.[24e] The crystal structure shows that the compound actually assumes a structure roughly intermediate between the "pyramidal" **A** and the "planar" **B**, a result presumably influenced by both steric and electronic factors.

$Cp^{\dagger}Fe(CO)LH$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3). Since hydrogen atom abstraction from $Cp^{\dagger}Fe(CO)_2H$ resulted in efficient dimer formation, it was anticipated that substitution of one of the carbonyl groups in $Cp^{\dagger}Fe(CO)_2H$ by phosphines and subsequent hydrogen atom abstraction would result in the formation of stabilized, substituted 17-electron compounds in which dimerization would be sterically impeded. To this end, several attempts were made to induce direct thermal substitution but to no avail. In addition, the bromo compound $Cp^{\dagger}Fe(CO)(PMe_3)Br$ was also prepared and unsuccessful attempts to substitute bromide by hydride were made.

The desired products were ultimately formed in useful yields via direct photochemical substitution of $Cp^{\dagger}Fe(CO)_2H$ with the phosphines. The products formed, $Cp^{\dagger}Fe(CO)LH$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3), were characterized by IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analyses. Some were also characterized by Raman spectroscopy. In all cases, the compounds exhibit CO bands in the IR spectra at 1915–1920 cm^{-1}, usually with a shoulder to lower frequencies. Since the compounds are chiral both at iron and in the $C_5(aryl)_5$ ligands (see above), they exist as diastereomers, thus explaining the apparent doubling of the CO bands. The ^1H NMR spectra all exhibit hydride resonances in the region δ −12 to −13.5, to somewhat higher field than for $Cp^{\dagger}Fe(CO)_2H$ (δ −10.35), and all with spin–spin coupling to ^{31}P (82–86 Hz). Unfortunately, these hydrides were found not to form $Cp^{\dagger}Fe(CO)L$ by reaction with the trityl radical, presumably for steric reasons, and they were therefore not studied further.

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[21] Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*. 536.

[22] For discussion of the relationship between bond angles and relative intensities, see: Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975; pp 36, 146.

[23] (a) Connelly, N. G.; Raven, S. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1613. (b) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215. This rationalization was suggested by a reviewer.

[24] (a) Ruiz, J.; Lacoste, M.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 5471. (b) Giese, B.; Thoma, G. *Helv. Chim. Acta* **1991**, *74*, 1135. (c) Giese, B.; Thoma, G. *Helv. Chim. Acta* **1991**, *74*, 1143. (d) Hill, D. H.; Parvez, M. A.; Sen, A. *J. Am. Chem. Soc.* **1994**, *116*, 2889. (e) Jonas, K.; Klusmann, P.; Goddard, R. *Z. Naturforsch.* **1995**, *50b*, 394. (f) Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1996**, *15*, 10.

[25] Jonas, K.; Schieferstein, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 549.