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Synthesis and Chemical Properties of the 17-Electron Compounds (η^5-C_5Ph_4Ar)Fe(CO)$_2$ (Ar = Phenyl, *p*-Tolyl)

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Summary: Treatment of (η^5-C_5Ph_5)Fe(CO)$_2$H and (η^5-C_5Ph_4(p-tolyl))Fe(CO)$_2$H with the trityl radical, $Ph_3C^•$, results in hydride hydrogen atom abstraction and formation of the corresponding 17-electron pentaarylcyclopentadienyl compounds (η^5-C_5Ph_4Ar)Fe(CO)$_2$ (Ar = Ph, p-tolyl). The dicarbonyl radicals exist in solution in facile equilibrium with the corresponding 18-electron dimers [(η^5-C_5Ph_4Ar)Fe(CO)$_2$]$_2$ and were characterized by their IR spectra, which resemble the spectra of the analogous compounds (η^5-C_5H_5)Fe(CO)$_2$ and (η^5-C_5Me_5)Fe(CO)$_2$, and by their reactivities with organic halides and ^{13}CO, which are characteristic of 17-electron, metal-centered radicals.

There is currently considerable interest in the synthesis and characterization of 17-electron organotransition-metal compounds (metal-centered radicals).[1] Such species are often very reactive, taking part in a variety of redox, atom abstraction, and coupling reactions. However, they 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,[2] η^5-C_5H_5 by η^5-C_5Me_5[2h] and η^5-C_5Ph_5[3]).

The 17-electron species CpFe(CO)$_2$ and Cp*Fe(CO)$_2$ (Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5) have previously been formed by photolysis of the corresponding iron–iron-bonded dimers under various conditions and have been characterized by IR spectroscopy.[4] The carbonyl stretching frequencies of CpFe(CO)$_2$ occur at ~2000 and ~1938 cm^{-1}, depending on the medium and the temperature, and those of Cp*Fe(CO)$_2$ at 1984 and 1915 cm^{-1} (cyclohexane at 25 °C).

The iron-centered radicals are exceedingly reactive species, dimerizing at near-diffusion-controlled rates[4b,d,5a] and readily abstracting halogen atoms from organic halides,[5] i.e.

$$2\mathrm{CpFe(CO)_2} \rightarrow [\mathrm{CpFe(CO)_2}]_2 \qquad (1)$$

$$\mathrm{CpFe(CO)_2} + \mathrm{RX} \rightarrow \mathrm{CpFe(CO)_2X} + \mathrm{R^•} \qquad (2)$$

As a result, no stabilized derivatives of the type (η^5-C_5R_5)Fe(CO)L (R = H, alkyl, aryl; L = CO, tertiary phosphine) have as yet been reported.

As part of the development of new methodologies for the synthesis of novel 17-electron species, we[6] and others[7] have recently demonstrated the utility of persistent triarylmethyl radicals $Ar_3C^•$ to abstract hydrogen atoms from 18-electron transition-metal hydride complexes MHL_n and form the corresponding 17-electron compounds ML_n (eq 3). In the absence of suitable radical traps, the

$$\mathrm{MHL}_n + \mathrm{Ar_3C^•} \rightarrow \mathrm{ML}_n + \mathrm{Ar_3CH} \qquad (3)$$

species ML_n may couple and the organometallic products obtained are often the 18-electron diamagnetic dimers $[ML_n]_2$. On the other hand, in those cases where radical coupling is not feasible, the chemistry of eq 3 provides a convenient thermal route to new 17-electron compounds. Since a number of sterically hindered iron hydrides of the type (η^5-C_5R_5)Fe(CO)LH are available, it seemed possible that the corresponding iron-centered radicals (η^5-C_5R_5)Fe(CO)L might also be synthesized via abstraction of the hydridic hydrogen atom; we describe below a series of experiments in which hydrides of the type Cp′Fe(CO)LH are reacted with $Ph_3C^•$.

As expected,[4b,d,5a] treatment of CpFe(CO)$_2$H with excess $Ph_3C^•$ resulted in immediate formation of the deep red dimer [CpFe(CO)$_2$]$_2$. An attempt to stabilize a substituted monomeric species by treating CpFe(CO)(PPh$_3$)H with $Ph_3C^•$ also resulted in iron–iron bond formation via radical coupling, as the deep green Cp$_2$Fe$_2$(CO)$_3$(PPh$_3$) was formed (identified by IR and ^{1}H NMR spectroscopic comparisons with samples prepared as described previously[8]). The latter result resembles earlier observations with the

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analogous molybdenum hydride $CpMo(CO)_2(PPh_3)H$,[6a] which also forms a dimolybdenum compound containing a single PPh_3. In both systems, apparently, substituted radicals are formed but dimerize slowly or do not dimerize because of steric factors; however, partial decomposition and liberation of CO result in some formation of the carbonyl species $CpMo(CO)_3$ or $CpFe(CO)_2$, and these can couple preferentially with the corresponding substituted radicals to form the bimetallic compounds, which are isolated. That the iron-centered radical is formed in the hydrogen abstraction reaction of $CpFe(CO)(PPh_3)H$ with $Ph_3C^\bullet$ is shown by the observation solely of $CpFe(CO)(PPh_3)Cl$[9] (ν_{CO} 1951 cm^{-1} in benzene, 1958 cm^{-1} in CH_2Cl_2) when the reaction of $CpFe(CO)(PPh_3)H$ is carried out in the presence of excess trityl chloride. We note also that hydrogen atom abstraction from $CpFe(CO)(PPh_3)H$ with the 17-electron compound $Mn(CO)_5$ also yields $Cp_2Fe_2(CO)_3(PPh_3)$.[8d]

Since the metal-centered radicals $(\eta^5\text{-}C_5Ph_5)M(CO)_3$ (M = Cr, Mo) are much more stable with respect to dimerization than are $(\eta^5\text{-}C_5H_5)Cr(CO)_3$, $(\eta^5\text{-}C_5Me_5)Cr(CO)_3$, or $(\eta^5\text{-}C_5H_5)Mo(CO)_3$,[2h,3g,h] we next turned our attention to hydrogen abstraction reactions of the compound $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2H$.[10] As anticipated, treatment of a yellow benzene solution of $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2H$ with a yellow benzene solution of $Ph_3C^\bullet$ at 25 °C resulted in a rapid change of color to deep green, the color of the dimeric $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]_2$.[10,11] Monitoring the reaction by IR spectroscopy revealed that the carbonyl stretching bands of the hydride (ν_{CO} 2009, 1954 cm^{-1}) were replaced by strong terminal and bridging carbonyl stretching bands at 1956 and 1781 cm^{-1}, respectively, very close to the frequencies reported for $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]_2$ as a Nujol mull.[11a] Interestingly, however, the band at 1781 cm^{-1} was completely replaced within minutes by a band of comparable intensity at 1788 cm^{-1}, and it seemed possible initially that the dimer was undergoing *cis–trans* isomerization. However, for both $[CpFe(CO)_2]_2$ and $[Cp^*Fe(CO)_2]_2$, the differences between the terminal carbonyl stretching frequencies of the *cis*-bridged and those of the *trans*-bridged isomers are 40–50 cm^{-1}.[4b] Since there is little perceptible change in the absorption at ~1955 cm^{-1} during the reaction of $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2H$ with $Ph_3C^\bullet$, *cis–trans* isomerization seems an unlikely explanation for our observations. Instead, since the C_5Ph_5 groups are expected to be chiral by virtue of twisting of the phenyl groups,[12] it seems more likely that the bands at 1781 and 1788 cm^{-1} should be attributed to diastereomers in which the phenyl groups of pairs of C_5Ph_5 ligands in a molecule of the dimer have the same and the opposite chirality.[13a]

Of greater interest is the observation, in solution but not in the solid-state IR spectra, of very weak terminal carbonyl stretching bands at 1991 and 1922 cm^{-1}. These are very similar to the carbonyl stretching frequencies of $CpFe(CO)_2$ and $Cp^*Fe(CO)_2$, mentioned above, and are therefore possibly attributable to the monomer $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2$, in equilibrium with $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]_2$:[13b]

$$[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]_2 \rightleftarrows 2(\eta^5\text{-}C_5Ph_5)Fe(CO)_2 \quad (4)$$

Although rapid exchange with the thermodynamically more stable diamagnetic dimer rendered the system EPR inactive, tentative identification of the species in solution as an iron-centered radical was confirmed by its rapid reaction with methyl iodide in benzene to form the iodo (ν_{CO} 2029, 1989 cm^{-1}; compare $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2Br$, for which ν_{CO} is 2038, 1996 cm^{-1} in CH_2Cl_2[14]) and methyl (ν_{CO} 2002, 1948 cm^{-1}; compare 2002, 1946 cm^{-1} in CH_2Cl_2[11a]) analogues (eq 5), identified spectroscopically. Similar

$$\begin{aligned}&[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]_2 + MeI \rightarrow \\ &\qquad (\eta^5\text{-}C_5Ph_5)Fe(CO)_2Me + (\eta^5\text{-}C_5Ph_5)Fe(CO)_2I \quad (5)\end{aligned}$$

reactivity is exhibited by $CpCr(CO)_3$, which exists in solution to the extent of a few per cent of its diamagnetic dimer, with it is in equilibrium, but not, we find, by $[CpFe(CO)_2]_2$, which does not dissociate significantly in solution.[4,15]

At this point, since the very low solubility of $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]_2$[11] was hindering further progress, we opted to continue research with the sterically and electronically similar but more soluble *p*-tolyltetraphenylcyclopentadienyl system.[16] The IR spectrum (benzene) of $[(\eta^5\text{-}C_5Ph_4(p\text{-tolyl}))Fe(CO)_2]_2$[16] also exhibits pairs of carbonyl stretching bands for monomer (ν_{CO} 1989, 1922 cm^{-1}; absent in spectra of the solid) and dimer (ν_{CO} 1958, 1780 cm^{-1}), and it is found that the relative intensities are strongly concentration dependent. Thus, the intensities of the monomer bands are relatively high in dilute solutions (~0.002 M) but relatively low in more concentrated solutions (~0.013 M), consistent with a dissociative process analogous to that of eq 4. Assuming comparable extinction coefficients for the terminal carbonyl stretching bands of the monomer and the bridging carbonyl band of the dimer, as is found for the cyclopentadienyl analogue,[4d] the equilibrium constant for dimer dissociation is approximately 10^{-3} M.

As anticipated on the basis of the reactions of $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2$ with methyl iodide (see above) and of $CpCr(CO)_3$ with a variety of organic halides,[17] $(\eta^5\text{-}C_5Ph_4(p\text{-tolyl}))Fe(CO)_2$ reacts readily with methyl, allyl, and *tert*-butyl iodides to form $(\eta^5\text{-}C_5Ph_4(p\text{-tolyl}))Fe(CO)_2I$ and the

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[13] (a) While differences in the terminal carbonyl stretching bands of the diastereomers of $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]_2$ would still be anticipated, the band at 1956 cm^{-1} overlaps both a solvent absorption and one of the absorptions of the hydride, and any subtle variations during the reaction are obscured. (b) Carbonyl stretching frequencies of $\eta^5\text{-}C_5Ph_5$ compounds are expected to lie between those of the Cp and Cp* analogues.[3h]

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[16] The dimer $[(\eta^5\text{-}C_5Ph_4(p\text{-tolyl}))Fe(CO)_2]_2$ was prepared essentially the same as was $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]_2$. The known bromo compound $(\eta^5\text{-}C_5Ph_4(p\text{-tolyl}))Fe(CO)_2Br$[14] was reacted with $NaBH_4$[10] to form the corresponding hydride $(\eta^5\text{-}C_5Ph_4(p\text{-tolyl}))Fe(CO)_2H$, which was in turn treated with trityl radical.

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methyl (ν_{CO} 2000, 1947 cm^{-1}), η^1-allyl (ν_{CO} 1998, 1948 cm^{-1}), and hydrido (ν_{CO}, 2007, 1950 cm^{-1}) analogues, respectively, identified spectroscopically. Typical of halogen abstraction reactions from organic halides by metal-centered radicals,[17,18] the relative rates are allyl, *tert*-butyl ≫ methyl, lending support to our identification of the species exhibiting carbonyl stretching bands at 1989 and 1922 cm^{-1}.

Also typical of 17-electron species, which are generally very labile with respect to ligand substitution,[1] we find that a benzene solution of (η^5-C_5Ph_4(*p*-tolyl))Fe(CO)$_2$ reacts rapidly with enriched ^{13}CO (1 atm, room temperature) to yield fully exchanged monomer (ν_{CO} 1942, 1876 cm^{-1}) *and* dimer (ν_{CO} 1911, 1740 cm^{-1}) within minutes. For all four bands, the decreases in frequency associated with ^{13}CO substitution are very similar to those reported for [CpFe(CO)$_2$]$_2$[19] and are also as predicted theoretically.[20] We also find that [CpFe(CO)$_2$]$_2$ exchanges very little with ^{13}CO under these conditions,[21] again providing firm evidence for the identity of the iron-centered radical (η^5-C_5Ph_4(*p*-tolyl))Fe(CO)$_2$.

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(21) A more thorough investigation of this exchange reaction has been reported,[19] and it has been shown that exchange of [CpFe(CO)$_2$]$_2$ in the dark occurs *only* via the monomer.