Organometallics **1990**, *9*, 2248–2253

The Chemistry of (η^5-C_5H_5)Fe(CO)$_2$H Revisited

Thomas A. Shackleton, Stephen C. Mackie, Stuart B. Fergusson, Laura J. Johnston, and Michael C. Baird*

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Received December 14, 1989

The compound (η^5-C_5H_5)Fe(CO)$_2$H can, in spite of its reputation, be stabilized at ambient temperatures. The degradation commonly observed for this hydride appears to be a result of a chain process that is initiated by adventitious oxidant(s) but that can be inhibited by additives which render (η^5-C_5H_5)Fe(CO)$_2$H almost indefinitely stable; the mode(s) of action of the inhibitors apparently involves interception of the initiator and/or the chain-carrying intermediates. The hydride resonance of (η^5-C_5H_5)Fe(CO)$_2$H is unusually broad, the line width being both temperature- and concentration-dependent because of a rapid, reversible interaction of the hydride ligand of (η^5-C_5H_5)Fe(CO)$_2$H with a small amount of a paramagnetic iron species. The hydride (η^5-C_5H_5)Fe(CO)$_2$H also undergoes carbon monoxide substitution and hydride self-exchange reactions, the former via a chain process involving radical intermediates and the latter possibly via the dimeric intermediate [(η^3-C_5H_5)Fe(CO)$_2$(μ-H)]$_2$. The tertiary phosphine substituted product (η^5-C_5H_5)Fe(CO)(PMe$_2$Ph)H undergoes a thermal process in which the phosphine dissociates reversibly.

The compound (η^5-C_5H_5)Fe(CO)$_2$H was first reported in 1959[1] and thus was one of the first such metal hydrides prepared during the early renaissance period of organo-transition-metal chemistry.[2,3] Interestingly, (η^5-C_5H_5)-Fe(CO)$_2$H was initially reported to be quite unstable with respect to spontaneous decomposition to hydrogen and the dimer [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ (eq 1),[1] a conclusion that has

$$2(\eta^5\text{-}C_5H_5)Fe(CO)_2H \rightarrow [(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 + H_2 \quad (1)$$

gained considerable support over the intervening three decades.[4] Perhaps as a result, relatively few investigations have been devoted to the chemistry of this hydride, and it has been much less studied than have its many alkyl derivatives.[5]

As we have pointed out in a communication,[6] however, the extent of the degradation process represented by eq 1 varies erratically, and the process appears not to involve simple thermal decomposition of (η^5-C_5H_5)Fe(CO)$_2$H. While we were not previously able to suggest a mechanism for the conversion of (η^5-C_5H_5)Fe(CO)$_2$H to [(η^5-C_5H_5)-Fe(CO)$_2$]$_2$ and hydrogen, we have more recently shown, during an investigation of the hydrometalation and hydrogen-transfer reactions of (η^5-C_5H_5)Fe(CO)$_2$H with conjugated dienes, that solutions of (η^5-C_5H_5)Fe(CO)$_2$H are stabilized very effectively by traces of thiophenol.[7] Thus, the process of eq 1 clearly does not involve a simple thermal decomposition of the hydride, and an alternative explanation must be found.

This paper addresses the question of the kinetic stabilization of (η^5-C_5H_5)Fe(CO)$_2$H, as well as several other interesting facets of the chemistry of this hydride. For instance, we have noted during the course of our investigations that not only is the hydride resonance of (η^5-C_5H_5)Fe(CO)$_2$H unusually broad but also the line width is both temperature- and concentration-dependent; we discuss possible origins of this effect. We have earlier alluded to the possible role of radical species during CO substitution reactions of (η^5-C_5H_5)Fe(CO)$_2$H by tertiary phosphines,[6] and we now pursue this issue further. Finally, we discuss a hydride self-exchange reaction of (η^5-C_5H_5)-Fe(CO)$_2$H and a phosphine-exchange reaction of the substituted derivative (η^5-C_5H_5)Fe(CO)(PMe$_2$Ph)H.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen in dried, deoxygenated solvents. NMR spectra were run on Bruker HX-60, CXP-200, and AM-400 FT NMR spectrometers and IR spectra on a Bruker IFS-85 FT IR spectrometer. The compounds (η^5-C_5H_5)Fe(CO)$_2$H, (η^5-C_5H_5)Fe(CO)$_2$D, and (η^5-C_5H_4Me)Fe-(CO)$_2$H were prepared by a modification[7] of the procedure of Whitesides and Shelley;[4e] (η^5-C_5H_5)Fe(CO)(PMe$_2$Ph)H was made by the procedure of Kalck and Poilblanc.[8]

Results and Discussion

Synthesis and Properties of (η^5-C_5H_5)Fe(CO)$_2$H. As described previously,[6,7] (η^5-C_5H_5)Fe(CO)$_2$H is readily synthesized via acidification of the salt Na[(η^5-C_5H_5)Fe(CO)$_2$]. The hydride can be obtained as a pure yellow oil by distillation under reduced pressure or as bright yellow solutions in alkane solvents on chromatography through alumina. The IR spectrum in pentane solution exhibits two strong ν_{CO} bands at 2023 and 1967 cm^{-1} (2013, 1952 cm^{-1} in THF), while the NMR spectrum in benzene-d_6 at 20 °C exhibits η^5-C_5H_5 and hydride resonances at δ 4.17 (s) and δ −11.77 (br), respectively. Both chemical shifts are independent of temperature.

Stability of (η^5-C_5H_5)Fe(CO)$_2$H. In agreement with the observations of many who have worked with (η^5-C_5H_5)Fe(CO)$_2$H,[1,4] we find that samples of this yellow compound, whether as the neat compound or in solution in hydrocarbon solvents, routinely turn brown within minutes as the proportion of the intensely red dimer [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ increases. The two ν_{CO} bands of the hydride grow weaker, while the ν_{CO} bands of the dimer (2008, 1961, 1794 cm^{-1}) gain in intensity. Hydrogen gas was detected by GC, as expected on the basis of eq 1,

---

[1] Green, M. L. H.; Street, C. N.; Wilkinson, G. *Z. Naturforsch.* **1959**, *14B*, 738.

[2] For a brief historical overview, see: Yamamoto, A. *Organotransition Metal Chemistry*; Wiley-Interscience: New York, 1986.

[3] Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415.

[4] It would seem that most researchers working with (η^5-C_5H_5)Fe(CO)$_2$H have noted the ubiquitous presence of [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ and have presumed that the latter is formed via direct thermal decomposition of the former. See, for instance: (a) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58. (b) Clark, H. C.; Jacobs, W. J. *Inorg. Chem.* **1970**, *9*, 1229. (c) Harbourne, D. A.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 1765. (d) Brown, D. A.; Glass, W. K.; Ubeid, M. T. *Inorg. Chim. Acta* **1984**, *89*, L47. (e) Whitesides, T. H.; Shelley, J. *J. Organomet. Chem.* **1975**, *92*, 215.

[5] See, for instance: Johnson, M. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 4, p 331.

[6] Fergusson, S. B.; Sanderson, L. J.; Shackleton, T. A.; Baird, M. C. *Inorg. Chim. Acta* **1984**, *83*, L45.

[7] Shackleton, T. A.; Baird, M. C. *Organometallics* **1989**, *8*, 2225.

[8] Kalck, P.; Poilblanc, R. *C. R. Seances Acad. Sci., Ser. C* **1972**, *274*, 66.

0276-7333/90/2309-2248$02.50/0

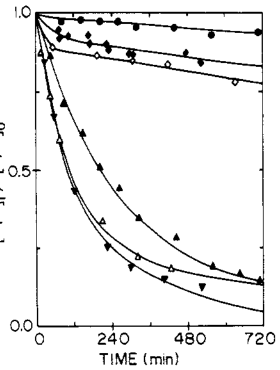


Figure 1. Plots of the relative concentrations of (η^5-C_5H_5)Fe(CO)$_2$H (FpH) versus time, showing the exponential decay of three samples containing no additives (▲, △, ▼) and containing thiophenol (●), diphenylphosphine (♦), and iodine (◇).

although we have not quantified this product.

However, the degradation process is not simply a result of a simple, spontaneous thermal decomposition of (η^5-C_5H_5)Fe(CO)$_2$H, as solutions in chloroform and ethanol exhibit enhanced stabilities while the rate and extent of the conversion of hydrocarbon solutions of (η^5-C_5H_5)Fe(CO)$_2$H to the dimer were found to vary significantly during the course of a large number of experiments. We have therefore carried out a kinetics investigation of the degradation process (22 °C, ~0.07 M (η^5-C_5H_5)Fe(CO)$_2$H in pentane) by monitoring changes in the ν_{CO} region of IR spectra of solutions of the hydride. Since radical species appear to be involved in reactions of many compounds containing the (η^5-C_5H_5)Fe(CO)$_2$ moiety[4e,7,9] while the formation of dimer could result from coupling of {(η^5-C_5H_5)Fe(CO)$_2$} radicals,[10] a number of runs were also performed in the presence of a variety of additives (~1 mol % relative to the (η^5-C_5H_5)Fe(CO)$_2$H) that might be expected to serve as radical scavengers or initiators.

The results for three control (no additive) experiments and experiments with thiophenol, diphenylphosphine, and iodine are shown in Figure 1, where significant variations in the control experiments and the effects of the additives are both obvious. Since first-order plots of the control experiments were reasonably linear, we present for purposes of comparison first-order rate constants for all the (η^5-C_5H_5)Fe(CO)$_2$H degradation rate experiments in Table I. The data illustrate the effects of 15 different additives and may be compared with a mean k_1 value of (4.1 ± 2.3) × 10^{-5} s^{-1} for 10 control samples run without additives.

The analogous thermal decomposition of HCo(CO)$_4$ to the dimer Co$_2$(CO)$_8$ is catalyzed by the latter,[11] but as the [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ that forms in the iron system has no effect on the rate of eq 1, a process involving catalysis by this product would appear not to be a factor. However, chain mechanisms for carbon monoxide substitution reactions of several metal hydrides appear to involve initial hydrogen atom abstraction by adventitious, as yet unidentified, radical initiators,[12] and we have considered possible degradation processes involving initial abstraction of a hydrogen atom from (η^5-C_5H_5)Fe(CO)$_2$H to give the 17-electron species {(η^5-C_5H_5)Fe(CO)$_2$}. No reasonable sequence of steps, compatible with the kinetics and the product distributions, presented itself.

Table I. Effects of Additives on the Rate of Degradation of (η^5-C_5H_5)Fe(CO)$_2$H at 22 °C in Benzene[a]

expt no.	additive[b]	k_1, 10^5 s^{-1} [f]
1	benzoyl peroxide[c]	0.09
2	thiophenol (in the dark)	0.12
3	thiophenol (under fluorescent lights)	0.13
4	benzoyl peroxide	0.19
5	diphenylphosphine (in the dark)	0.27
6	2,2-diphenyl-1-picrylhydrazyl	0.33
7	iodine	0.36
8	trimethylphosphine	0.48
9	glacial acetic acid	0.56
10	2,2′-azobis(isobutyronitrile) (AIBN)[c]	0.78
11	ethanol[d]	1.0
12	chloroform[e]	1.2
13	hydroquinone	2.9
14	quinone	2.9
15	9,10-dihydroanthracene	4.0
16	2,6-di-*tert*-butyl-4-methylphenol (BHT)	4.4
17	galvinoxyl	4.9

[a] About 7 × 10^{-2} M. [b] About 7 × 10^{-4} M. [c] Data collected following 5 min of thermal activation of a solution of (η^5-C_5H_5)Fe(CO)$_2$H and the additive in refluxing benzene. [d] In ethanol solution. [e] In chloroform solution. The iron-containing product is (η^5-C_5H_5)Fe(CO)$_2$Cl rather than [(η^5-C_5H_5)Fe(CO)$_2$]$_2$. [f] Error limit ±0.2.

Nor do simple acid–base processes appear to be a factor. Although (η^5-C_5H_5)Fe(CO)$_2$H exhibits a pK_a of 19.4 in acetonitrile and is deprotonated in that solvent by triethylamine,[13] we find that this hydride does not react with triethylamine in benzene-d_6. It is thus at best a very weak acid in the latter, nonpolar solvent, consistent perhaps with the known, very high nucleophilicity of its conjugate base, [(η^5-C_5H_5)Fe(CO)$_2$]$^-$.[14] Furthermore, as mentioned above, acetic acid acts as a stabilizer to (η^5-C_5H_5)Fe(CO)$_2$H. Thus, initiation of the degradation process via protonation or deprotonation of the hybride appears very unlikely, and we have perforce considered the possibility of electron-transfer-induced processes.

We outline below a chain mechanism for the degradation of (η^5-C_5H_5)Fe(CO)$_2$H (FpH) involving a series of steps initiated by an adventitious oxidant Ox, present in presumably very low initial concentration $[Ox]_{in}$ and hence unidentified:

$$\mathrm{FpH} + \mathrm{Ox} \xrightarrow{k_1} \mathrm{FpH}^+ \quad \text{initiation} \tag{2}$$

$$\mathrm{FpH}^+ + \mathrm{FpH} \xrightarrow{k_2} \mathrm{Fp}^+ + \mathrm{Fp} + \mathrm{H}_2 \quad \text{propagation} \tag{3}$$

$$\mathrm{Fp}^+ + \mathrm{FpH} \xrightarrow{k_3} \mathrm{FpH}^+ + \mathrm{Fp} \quad \text{propagation} \tag{4}$$

$$2\mathrm{Fp} \xrightarrow{k_4} \mathrm{Fp}_2 \tag{5}$$

$$\therefore \quad \frac{-d[\mathrm{FpH}]}{dt} = k_1[\mathrm{Ox}][\mathrm{FpH}] + k_2[\mathrm{FpH}^+][\mathrm{FpH}] + k_3[\mathrm{Fp}^+][\mathrm{FpH}] \tag{6}$$

Relevant data for eq 5 have been reported.[15] Making the steady-state approximation for Fp$^+$ and FpH$^+$, the chain-carrying species, and assuming, from (2), that $[\mathrm{FpH}^+] + [\mathrm{Fp}^+] = [\mathrm{Ox}]_{in}$

---

[9] See, for instance: (a) Fabian, B. D.; Labinger, J. A. *Organometallics* **1983**, *2*, 659. (b) Coville, N. J.; Albers, M. O.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1983**, 947. (c) Rosenblum, M.; Waterman, P. *J. Organomet. Chem.* **1981**, *206*, 197.

[10] Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217 and references therein.

[11] (a) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1969**, *20*, 205. (b) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1980**, *193*, 383. (c) Wegman, R. W.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 2494.

[12] (a) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527. (b) Hoffman, N. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613.

[13] Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

[14] (a) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541. (b) Richardson, D. E.; Christ, C. S.; Sharpe, P.; Eyler, J. R. *Organometallics* **1987**, *6*, 1819.

[15] Pugh, J. R.; Meyers, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 8245.

$$\therefore \quad \frac{-d[FpH]}{dt} = k_1[FpH][Ox] + \frac{2k_2k_3[Ox]_{in}[FpH]}{k_2 + k_3} \qquad (7)$$

$$\therefore \quad \frac{-d[FpH]}{dt} = [FpH]\left(k_1[Ox] + \frac{2k_2k_3[Ox]_{in}}{k_2 + k_3}\right) \qquad (8)$$

where

$$k_{obs} = k_1[Ox]\frac{2k_2k_3[Ox]_{in}}{k_2 + k_3}$$

Thus, this mechanism is consistent with the first-order rate law observed for the degradation process in the absence of stabilizers. Furthermore, if the rate of eq 2 is sufficiently high and/or $[Ox]_{in}$ is sufficiently low that Ox is quickly and completely consumed, then $k_1[Ox]$ will quickly reduce to zero and the rate will depend on the initial concentration of Ox, thus rationalizing the large variation in k_1 observed for unstabilized solutions.

As a rationale for the chemistry of eq 3, we note that 17-electron complexes are generally very susceptible to nucleophilic attack[10] and, as mentioned above, that the anion $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ is very strongly nucleophilic.[14] Thus, it is reasonable to expect that $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ would act as a nucleophilic hydride toward the 17-electron, cationic species $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H]^+$ (eq 3). The postulated hydride-induced reductive elimination of hydrogen from the resulting diiron species (eq 3) would also appear to be reasonable,[16] as would the hydrogen atom transfer step of eq 4 if the iron–hydrogen bond strength of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H]^+$ is not significantly less than that of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$.[17] Finally, in support of the suggested mechanism, we find that addition of ~15 mol % of the one-electron oxidant ceric ammonium nitrate[20] to a solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ in ethanol results in the virtually instantaneous conversion of about 50% of the hydride to dimer before the degradation process slows to the rate observed in neat ethanol (see Table I and below).

While not postulated to be a chain-carrying species, the iron-centered radical $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$ is the likely precursor of the dimeric product $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.[10,15] Consistent with this hypothesis, we find that degradation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ in chloroform results in the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ rather than of dimer. As the chloro compound is the product anticipated from the exposure of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$ to chloroform,[10] we thus have confirmatory evidence for the role of the 17-electron species $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$. We do not suggest a termination step but note that, as with the analogous methyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Me]^+$,[20] a variety of decomposition pathways is presumably available.

As can be seen, the effects of the various types of additives are quite variable, there being no obvious correlation between anticipated chemical properties and efficacy for stabilizing the hydride $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$. Thus, some reagents (benzoyl peroxide, thiophenol, DPPH, diphenylphosphine, iodine, chloroform) that might be expected to affect radical processes do so to some extent, while others (hydroquinone, 9,10-dihydroanthracene, BHT, galvinoxyl) and fluorescent lighting do not. Several potential ligands (thiophenol, neat ethanol, diphenylphosphine, trimethylphosphine) exhibit a marked degree of effectiveness, as do several potential oxidants (benzoyl peroxide, iodine, acetic acid), although the latter group would also generate products that could act as ligands. Given the postulate of a chain initiator, the identity of which is not known, and two chain-carrying species, perhaps this diversity of behavior is not surprising. One of the postulated chain-carrying species, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H]^+$, is an iron-centered radical hydride that should be destroyed by oxidants, ligands, and radical sources. The other, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$, is a 16-electron complex that should coordinate almost any Lewis base. Thus, the effective additives comprise a very diverse group of reagents, and it is likely that some act to intercept one species in the chain reaction and some another. On the other hand, it is noteworthy that addition of a small amount of ceric ammonium nitrate to an ethanol solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ induces the instantaneous conversion of much of the hydride to dimer. Ceric ion is known to act as a one-electron oxidant to a wide variety of iron–alkyl compounds of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$,[20] and a reasonable interpretation of this observation is that $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H]^+$ is formed rapidly in sufficient quantity that several cycles of the chain process take place before the chain-carrying intermediates are intercepted by the ethanol. After this happens, the rate constant for degradation is essentially that which pertains in neat ethanol.

Substitution Reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$. Information concerning the mechanism of carbon monoxide substitution reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ by tertiary phosphines has been obtained largely via monitoring product distributions under various conditions. Earlier workers have shown that $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ reacts readily with small tertiary phosphines such as PMe_3, $P(OMe)_3$, and PMe_2Ph at −20 °C to give the monosubstituted derivatives; in contrast, the relatively bulky PPh_3 reacts at a useful rate only at room temperature.[21] We have confirmed these observations, finding that the compounds $(\eta^5\text{-}C_5H_5)Fe(CO)LH$ (L = PMe_3, PMe_2Ph) are formed immediately at 0–15 °C, as evidenced by gas evolution, in tetrahydrofuran, chloroform, and benzene. The products were identified by comparison of IR and ^1H NMR data with literature values.[8] Interestingly, the PMe_2Ph substitution reaction in benzene was stopped by the addition of a small amount of acetic acid, while an attempted PPh_3 substitution reaction in chloroform yielded only $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)Cl$.[8]

The facile substitution reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ thus stand in stark contrast with those of the corresponding methyl compound $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$, which is generally inert to carbon monoxide substitution reactions except when induced photochemically.[9a] Although we have not carried out a kinetics study, the apparent inverse dependence on rates of substitution of the hydride with steric requirements of the incoming ligands also implies that the substitution process is associative in nature, and we look to mechanistic precedents in the work of Brown on the mechanisms of CO substitutions of the hydrides $(\eta^5\text{-}C_5H_5)M(CO)_3H$ (M = Mo, W) and $HRe(CO)_5$.[12] These

---

(16) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 339–343.

(17) The Fe–H bond dissociation energy of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ is reported to be 50 kcal/mol,[18] and one might anticipate little change on removing an essentially nonbonding electron on going from $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H]^+$. Presumably the increased charge on the metal would have an effect, and we note that the Co–H bond dissociation energy of the isoelectronic (with $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$) cation $[(\eta^5\text{-}C_5H_5)Co(CO)_2H]^+$ is 73 kcal/mol.[19]

(18) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711.

(19) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 190.

(20) (a) Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 5127 and references therein. (b) Golovin, M. N.; Meirowitz, R.; Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 2285 and references therein.

(21) (a) Merour, J. Y.; Cadiot, P. *C. R. Seances Acad. Sci., Ser. C* **1970**, *271*, 83. (b) Rosenblum, M.; Waterman, P. *J. Organomet. Chem.* **1981**, *206*, 197.

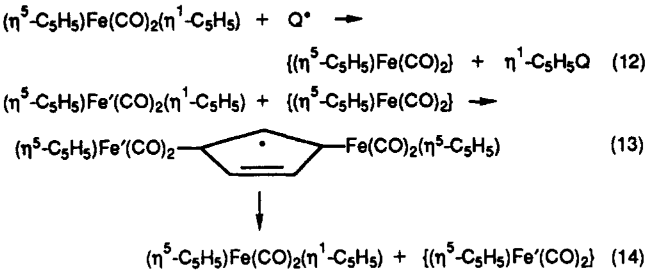
hydrides apparently undergo carbon monoxide substitution via radical chain processes exhibiting largely nonreproducible rates and initiated by as yet unidentified adventitious radical initiators Q, i.e.

$$HM(CO)_n + Q^\bullet \rightarrow QH + \{^\bullet M(CO)_n\} \quad (9)$$

$$\{^\bullet M(CO)_n\} + L \rightarrow \{^\bullet M(CO)_{n-1}L\} \quad (10)$$

$$\{^\bullet M(CO)_{n-1}L\} + HM(CO)_n \rightarrow \{HM(CO)_{n-1}L\} + \{^\bullet M(CO)_n\} \quad (11)$$

A similar radical process has been reported for carbon monoxide subsitution reactions of the compound $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$, which proceed much more rapidly than do comparable reactions of the methyl analogue,[9a] i.e.



The compound $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2CH{=}CH_2)$ also undergoes a very facile 1,3-migration, apparently involving a similar chain process.[21]

Thus, as mentioned above, there are ample precedents for the involvement of the radical $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$ in chain processes, and we suggest a scheme analogous to that of eq 9–11 for the substitution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ by tertiary phosphines:

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2H + Q^\bullet \rightarrow \{(\eta^5\text{-}C_5H_5)Fe(CO)_2\} + QH \quad (15)$$

$$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\} + L \rightarrow \{(\eta^5\text{-}C_5H_5)Fe(CO)L\} + CO \quad (16)$$

$$\{(\eta^5\text{-}C_5H_5)Fe(CO)L\} + (\eta^5\text{-}C_5H_5)Fe(CO)_2H \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)LH + \{(\eta^5\text{-}C_5H_5)Fe(CO)_2\} \quad (17)$$

As before,[12] the nature of the adventitious Q is not known, but substitution reactions (eq 16) of the iron-centered radical $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$ are known to be generally more facile than those of analogous electronically saturated compounds.[10] Furthermore, inasmuch as the hydrogen-transfer reaction of eq 17 is likely to be close to thermoneutral,[18] the overall mechanism is certainly reasonable. We note also that the slower reaction observed for the relatively bulky PPh_3, compared with those for the smaller PMe_3, $P(OMe)_3$, and PMe_2Ph, is consistent with the associative nature of eq 16.[10]

However, the radical $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$ is also known to react with chlorinated solvents to form $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$,[10] and it is at first sight surprising that a substitution process involving this species could proceed in chloroform. To ascertain whether $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$ does react competitively with PMe_2Ph in chloroform, we carried out an experiment in which a chloroform solution of the dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was irradiated (Hanovia lamp) under nitrogen in the presence of a 5-fold excess of the ligand. The reaction was monitored by IR spectroscopy, and it was found that the sole products were $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ (minor) and $(\eta^5\text{-}C_5H_5)Fe(CO)(PMe_2Ph)Cl$ (major). In contrast, treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ with a 5-fold excess of PMe_2Ph in chloroform resulted in the almost exclusive formation of the ionic $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PMe_2Ph)]Cl$ (ν_{CO} = 2048, 2004 cm^{-1}),[22] and thus the $(\eta^5\text{-}C_5H_5)Fe(CO)(PMe_2Ph)Cl$ observed above is not formed simply via reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ with PMe_2Ph. Instead, since the photolysis of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ is known to result in homolytic cleavage of the dimer and formation of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$,[10] the product distribution in the photochemical experiment clearly demonstrates that the substitution of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$ with PMe_2Ph is indeed competitive with the chlorine abstraction reaction, i.e.

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 \xrightarrow{h\nu} 2\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\} \quad (18)$$

$$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\} + CHCl_3 \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)_2Cl + CHCl_2 \quad (19)$$

$$\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\} + PMe_2Ph \rightarrow \{(\eta^5\text{-}C_5H_5)Fe(CO)(PMe_2Ph)\} \quad (20)$$

$$\{(\eta^5\text{-}C_5H_5)Fe(CO)(PMe_2Ph)\} + CHCl_3 \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)(PMe_2Ph)Cl \quad (21)$$

Observation that an attempted substitution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ with PPh_3 in chloroform resulted in the formation not of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$ but only of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)Cl$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ is also compatible with this mechanism. Chlorine abstraction from the solvent by $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$ could certainly be more competitive than substitution in the case of the bulkier phosphine, and it is reasonable that the substituted radical $\{(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\}$ would also react preferentially with solvent rather than with the somewhat sterically hindered $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$.

Interestingly, substitution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ with PMe_2Ph does not proceed in the presence of acetic acid, probably because acetic acid reacts with the substituted radical of eq 16, thereby interrupting the chain mechanism, i.e.

$$\{(\eta^5\text{-}C_5H_5)Fe(CO)(PMe_2Ph)\} + H^+ \rightarrow [(\eta^5\text{-}C_5H_5)Fe(CO)(PMe_2Ph)]^+ + \tfrac{1}{2}H_2 \quad (22)$$

The substituted radical would be expected to be more susceptible to oxidation by protons than is $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$ because of the presence of the more electron-donating phosphine, and consistent with this hypothesis, H_2 was indeed found to be a product when a benzene solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, PMe_2Ph, and acetic acid as irradiated. Similarly, we find that $(\eta^5\text{-}C_5H_5)Fe(CO)(PMe_2Ph)H$ is decomposed by acetic acid under conditions in which the unsubstituted hydride $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ is stable.

^{1}H NMR Spectrum of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$. The ^{1}H NMR spectrum of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ in benzene-d_6 exhibits hydride and C_5H_5 resonances at δ 4.13 (s) and δ −11.7 (br s), respectively (δ 4.76, −12.0 in $CDCl_3$). The broadening observed for the hydride resonance has been little noted previously, but a series of preliminary experiments indicated that the line width, $\Delta\nu_{1/2}$, can vary between 4 Hz and an upper limit of about 60 Hz. Therefore, an attempt was made to ascertain the factors affecting this unusual behavior. Although results were somewhat erratic, $\Delta\nu_{1/2}$ for the hydride resonance was found to be both temperature- and concentration-dependent.

The temperature dependence is indicated in Table II and Figure 2, where it is seen that the hydride resonance is very broad at 20 °C in benzene-d_6, toluene-d_8, and $CDCl_3$ but as narrow as the TMS and C_5H_5 resonances at higher and lower temperatures; the hydride chemical shift is es-

---

[22] Angelici, R. J.; Formanek, T. *Inorg. Chim. Acta* **1983**, *76*, L9.

Table II. Effect of Temperature on $\Delta\nu_{1/2}$ of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$

in toluene-d_6		in $CDCl_3$	
temp, K	$\Delta\nu_{1/2}$, Hz	temp, K	$\Delta\nu_{1/2}$, Hz
343	6	313	10
323	16	293	18
293	25	263	11
263	15	218	6
243	9		

Table III. Effect of Temperature on $\Delta\nu_{1/2}$ of $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2H$ in Toluene-d_8

temp, K	$\Delta\nu_{1/2}$, Hz	temp, K	$\Delta\nu_{1/2}$, Hz
343	5.8	263	5.3
323	8.5	243	4.0
293	14.3		

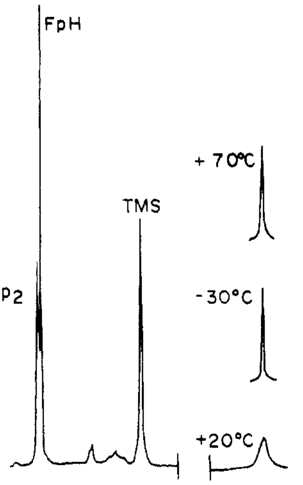


Figure 2. Variation of the line width of the hydride resonance of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ with temperature.

sentially invariant over the temperature range studied. The effect is completely reversible in both directions and is also observed for $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2H$ (Table III). A correlation between $\Delta\nu_{1/2}$ and the concentration of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ is indicated in Figure 3, where $\Delta\nu_{1/2}$ for a large number of unrelated experiments involving many batches of the hydride are shown. While the addition of acetic acid, triethylamine, AIBN (sample heated to 50 °C for 10 min prior to measurement), and styrene had no significant effect on $\Delta\nu_{1/2}$, addition of about 1 mol % of PMe_3 resulted in essentially complete narrowing of the hydride resonance. Substitution of CO in the latter case also occurred, of course, resulting in the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PMe_3)H$, and in the final solution, the two hydride resonances, the two $\eta^5\text{-}C_5H_5$ resonances, and the internal TMS resonances all exhibited comparable line widths. Interestingly, addition of thiophenol to a solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ partially reduced $\Delta\nu_{1/2}$, the residual broadening being temperature-dependent much as described above.

Hydride resonances of transition-metal hydrides may be broadened by spin–spin coupling and quadrupolar interactions with the metals, by exchange processes, and by paramagnetism.[23] Since the sole magnetic isotope of iron (iron-57, $I = {}^1/_2$) occurs in only 2.19% natural abundance, the first two possibilities are not factors here. Accordingly, since both the temperature and the concentration effects are consistent with some type of bimolecular exchange processes, we have considered the possible roles of both a self-exchange reaction and an exchange interaction with impurities, possibly paramagnetic. Interestingly, as will be shown below, self-exchange of the hydride ligand of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ does occur at a rate that is rapid on the NMR time scale. However, the effects of added thiophenol and trimethylphosphine on the hydride line width are inexplicable on the basis of self-exchange, and we rather favor an intermolecular exchange interaction with an as yet undefined species present in very low concentrations.

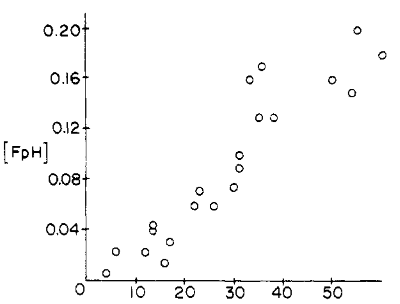


Figure 3. Variation of the line width of the hydride resonance of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ with concentration.

In an attempt to ascertain the identity of the exchange partner, a number of reagents were added to solutions of the hydride. The exchange process presumably does not involve acid–base exchange, as neither acetic acid nor triethylamine had an effect on $\Delta\nu_{1/2}$. Nor do radical species appear to be involved, since both the radical initiator AIBN and the radical scavenger styrene had no effect. The hydride resonance was sharpened, however, by the addition of a tertiary phosphine and a thiol, both of which can function as ligands and possibly as reducing agents to oxidized iron species. Hydride ligands readily bridge metal atoms,[24] and a rapid, reversible interaction of the hydride ligand of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ with a paramagnetic iron species, present in even very low concentration, would be consistent with our observations. Indeed, the exchange partner responsible for the line broadening may be a species involved in the degradation process, discussed above.

Hydride Self-Exchange in $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$. Equal amounts of $(\eta^5\text{-}C_5H_5)Fe(CO)_2D$ and $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2H$ were dissolved together in toluene-d_8, and a ^1H NMR spectrum was run at 294 K. Separate hydride resonances of approximately equal intensity at δ −11.77 and −11.65 ($\Delta\nu_{1/2}$ = 19 Hz for both) were assignable to $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ and $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2H$, respectively. When the sample was heated, the resonances broadened, coalesced at about 348 K, and sharpened further on continuing to 354 K; returning to 303 K confirmed the reversibility of the coalescence process. A small amount of thiophenol was then added to the sample, and the variable-temperature experiment was repeated; while changes in the hydride resonance line width were evident, the same coalescence temperature was observed.

The nature of the hydride self-exchange reaction is not at all clear. Presumably exchange involving a third species, i.e. those postulated above as participating in the thermal degradation or the hydride resonance broadening of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$, is not important, as the addition of thiophenol would be expected to affect the coalescence

---

[23] Schunn, R. A. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; p 206.

[24] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransitiom Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 83.

temperature. On the other hand, the exchange may involve bimolecular association of two (η^5-C_5H_5)Fe(CO)$_2$H molecules, perhaps via hydride bridging to sites resulting from η^3 coordination of the C_5H_5 ligands,[25] as in a dimeric intermediate such as [(η^3-C_5H_5)Fe(CO)$_2$(μ-H)]$_2$. While one might ask why a similar associative process does not appear to pertain to the simple ligand substitution reactions of (η^5-C_5H_5)Fe(CO)$_2$H discussed above, it may be that steric hindrance to the formation of species of the type (η^3-C_5H_5)Fe(CO)$_2$(PR_3)H renders the chain process discussed above more competitive. It does not seem possible to carry out kinetics studies which are sufficiently reproducible that concurrent chain and bimolecular mechanisms can be identified.

Phosphine Exchange in (η^5-C_5H_5)Fe(CO)(PMe_2Ph)H. While working with this complex, we were intrigued by an earlier report[8] that the room-temperature ^{1}H NMR spectrum in benzene-d_6 exhibits only a single resonance for the two diastereotopic phosphine methyl groups. This observation is in contrast to observations for the analogous iodo and acetyl compounds,[26] and it seemed possible that the diastereotopic methyl groups of the hydride compound may exchange via either a dissociative process or an intramolecular rearrangement. While we eventually found that the room-temperature ^{1}H NMR spectrum of (η^5-C_5H_5)Fe(CO)(PMe_2Ph)H in CD_2Cl_2 is "normal", with two methyl resonances at δ 1.64 and 1.58 (J_{HP} = 8 Hz), this was not before we had investigated aspects of the NMR spectrum of this compound.

As reported previously,[8] the ^{1}H NMR spectrum of (η^5-C_5H_5)Fe(CO)(PMe_2Ph)H at 303 K in benzene-d_6 exhibits phenyl resonances at δ 7–7.5 (m), a C_5H_5 resonance at δ 4.22 (s), a methyl resonance at δ 1.32 (d, J_{HP} = 8 Hz), and a hydride resonance at δ −13.9 (d, J_{HP} = 80 Hz). The ^{13}C{^{1}H} NMR spectrum exhibits a carbonyl resonance at δ 220.9 (s), phenyl resonances in the region δ 128–142, a C_5H_5 resonance at δ 79.4 (s), and *two* methyl resonances at δ 22.1 (d, J_{CP} = 31 Hz) and δ 22.3 (d, J_{CP} = 32 Hz).

Variable-temperature studies of (η^5-C_5H_5)Fe(CO)(PMe_2Ph)H were carried out in benzene-d_6 over the range 303–348 K. When the temperature was raised the methyl and hydride doublets both coalesced to broad singlets in the temperature ranges 327–333 and 338–340 K, respectively. When the temperature was lowered to 300 K, the original spectrum was restored, demonstrating the reversibility of the coalescence phenomenon. The experiment was then repeated after the addition of slightly less than 1 equiv of free PMe_2Ph (methyl resonance at δ 1.09, J_{HP} = 3 Hz), with the finding that the two methyl doublets coalesced to a broad singlet at about 313 K and the hydride doublet coalesced at 334 K. Again, reversibility of the coalescence phenomena was confirmed by the reappearance of the original spectrum at lower temperature.

These observations are consistent with dissociative exchange of PMe_2Ph, similar to that reported recently for a series of ruthenium complexes of the type (η^5-C_5H_5)Ru(PMe_3)$_2$X,[27] i.e.

$$(\eta^5\text{-}C_5H_5)Fe(CO)(PMe_2Ph)H \rightleftarrows (\eta^5\text{-}C_5H_5)Fe(CO)H + PMe_2Ph \quad (23)$$

The fact that the ^{1}H NMR spectrum of (η^5-C_5H_5)Fe(CO)(PMe_2Ph)H in benzene solution exhibits only a single methyl resonance is thus attributed solely to chemical shift coincidence.

Acknowledgment. This research was made possible by financial support from the Natural Sciences and Engineering Research Council (operating grant to M.C.B., graduate fellowship to T.A.S.) and Queen's University (graduate fellowship to S.C.M.). We also thank D. Macartney and T. Ziegler for helpful discussions.

Registry No. (η^5-C_5H_5)Fe(CO)$_2$H, 35913-82-7; (η^5-C_5H_5)Fe(CO)(PMe_3)H, 35796-54-4; (η^5-C_5H_5)Fe(CO)(PMe_2Ph)H, 35796-56-6; (η^5-C_5H_5)Fe(CO)$_2$D, 93030-89-8; (η^5-C_5H_4Me)Fe(CO)$_2$H, 56483-17-1; benzoyl peroxide, 94-36-0; thiophenol, 108-98-5; diphenylphosphine, 829-85-6; 2,2-diphenyl-1-picrylhydrazyl, 1898-66-4; iodine, 7553-56-2; trimethylphosphine, 594-09-2; acetic acid, 64-19-7; 2,2'-azobis(isobutyronitrile), 78-67-1; ethanol, 64-17-5; chloroform, 67-66-3; hydroquinone, 123-31-9; quinone, 106-51-4; 9,10-dihydroanthracene, 613-31-0; 2,6-di-*tert*-butyl-4-methylphenol, 128-37-0; galvinoxyl, 2370-18-5.

---

[25] O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

[26] Brunner, H.; Schmidt, E. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 616.

[27] Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379.