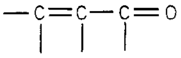
formed when 5 was refluxed for 1 h in benzene with an excess of $P(OMe)_3$; only 5 was recovered, and no exchange of PMe_3 by $P(OMe)_3$ was observed by treatment of 3 with an excess of $P(OMe)_3$. This suggests that during the reaction a vacant site must be created on the iron atom to allow the incorporation of the $P(OMe)_3$ group leading to 7 and this supports step iv.

This unique incoorporation of a



$$-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=O$$

fragment into a carbon–sulfur double bond is unprecedented. The use of this reaction in organic synthesis is under investigation.

Acknowledgment. Authors are grateful to Prof. M. S. Brookhart and M. F. Lappert for helpful discussions.

Registry No. 2, 71004-25-6; 3, 88968-59-6; 4, 88968-60-9; 5, 88968-61-0; 6, 88968-62-1; 7, 88968-63-2; 8 (isomer 1), 89016-43-3; 8 (isomer 2), 88968-65-4; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; $EtO_2CC{\equiv}CCO_2Et$, 762-21-0.

Supplementary Material Available: Tables of crystallographic data, interatomic distances and angles, final positional and thermal parameters, and structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

Competitive Redox-Catalyzed Migratory Carbonyl Insertion and β-Elimination in Iron Alkyl Complexes[1]

Robert S. Bly,* Gary S. Silverman,
M. Mahmun Hossain, and Ruta K. Bly

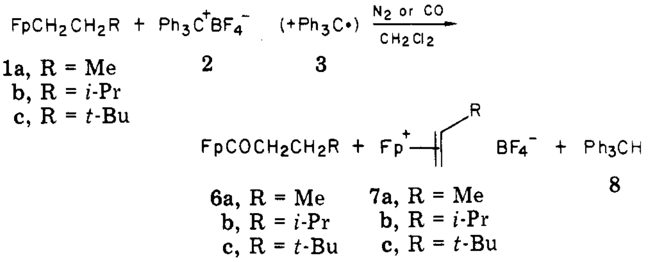
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

Received December 6, 1983

Summary: At reduced temperatures in the presence of carbon monoxide, migratory carbonyl insertion can compete with triphenylcarbenium-induced β-elimination in $(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2CH_2R$ (R = Me, *i*-Pr, *t*-Bu) complexes. The insertion is a catalytic, radical-chain process initiated by a one-electron transfer from Fe(II)–alkyl complex to cation. Added triphenylmethyl radical retards the rate of insertion but leaves the rate of elimination virtually unchanged.

Migratory carbonyl insertion accompanies β-elimination in the triphenylcarbenium-induced reactions of Fp norbornyls.[2] To examine the generality and mechanism of such competitive insertion and elimination we have studied the reaction of some conformationally mobile Fp alkyls (1)[3] with triphenylmethyl tetrafluoroborate (2).

Typically[4] (run 2, Table I), precooled, equiequivalent solutions of **1a**[5] and **2**[6] in carbon monoxide blanketed dichloromethane were mixed, and the mixture was stirred at −78 °C for 1 h and then at −20 °C overnight. Sequential concentration under vacuum, addition of diethyl ether at 0 °C, filtration, and washing with ether gave pale yellow crystals of (η^5-cyclopentadienyl)(η^2-propene)dicarbonyliron tetrafluoroborate (**7a**, 69%).[7] Chromatography of the concentrated, combined filtrate and washings at −10 °C on activity III alumina with 2% diethyl ether in pentane gave triphenylmethane (**8**, 71%) and (η^5-cyclopentadienyl)(η^1-butanoyl)dicarbonyliron (**6a**, 13%).[8c] In runs 8, 9, and 17 1 equiv of triphenylmethyl radical (**3**)[9] was mixed with **1** prior to the addition of **2**.



1a, R = Me
b, R = *i*-Pr
c, R = *t*-Bu

2

3

6a, R = Me
b, R = *i*-Pr
c, R = *t*-Bu

7a, R = Me
b, R = *i*-Pr
c, R = *t*-Bu

8

Our results reveal that migratory carbonyl insertion *can* compete with β-elimination even in simple, conformationally mobile Fp alkyls. Under carbon monoxide both **1a** and **1b** react with **2** to produce mixtures of the acyl and the π-complex, **6** and **7**, respectively (runs 2, 3, 13, 14); **1b** does so under nitrogen as well (run 10). When the β-hydrogen is hindered and/or cannot attain an antiperiplanar conformation relative to iron,[10] insertion may be the ex-

---

(1) Bly, R. S.; Bly, R. K.; Silverman, G. S. "Abstracts of Papers", 186th National Meeting of the American Chemical Society, Aug 28–Sept 2, 1983, Washington, DC; ORGN 33.

(2) Bly, R. S.; Silverman, G. S.; Bly, R. K. "Abstracts of Papers", 34th Southeast Regional Meeting of the American Chemical Society, Nov 3–5, 1982, Birmingham, AL; Abstr. No. 324.

(3) Fp = $(\eta^5\text{-}C_5H_5)(CO)_2Fe$; Fp′ = $(\eta^5\text{-}C_5H_5)(Ph_3P)(CO)Fe$.

(4) Dry, oxygen-free solvents and standard Schlenk techniques were employed throughout.

(5) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 68–69.

(6) Dauben, H. J.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442–1444.

(7) (a) Green, M. L. H.; Nagy, P. L. I. *J. Chem. Soc.* **1963**, 189–197. (b) Laycock, D. E.; Baird, M. C. *Inorg. Chim. Acta* **1980**, *42*, 263–266. (c) Cutler, A.; Ehntholt, D.; Giering, W. P., Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495–3507.

(8) (a) **1b**: IR (CH_2Cl_2) 2001, 1945 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.74 (s, 5 H, Cp), 1.45 (m, 5 H, $-CH_2CH_2CH<$), 0.98 (d, J = 5.4 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 217.67 ($-C{\equiv}O$), 85.30 (Cp), 47.68 (>CH), 32.55 (>CH_2), 22.45 (CH_3), 1.15 ($FpCH_2-$). (b) **1c**: mp 33–34 °C; IR ($CDCl_3$) 2000, 1945 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.65 (s, 5 H, Cp), 1.05–1.55 (m, 4 H, $FpCH_2CH_2-$), 0.85 (s, 9 H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 217.63 ($-C{\equiv}O$), 85.32 (Cp), 52.40 (>C<), 32.98 (>CH_2), 29.17 (CH_3), −2.41 ($FpCH_2-$). Although **1c** has been prepared previously (Whitesides, G. M.; Boschetto, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 1529–1531. Jacobson, S. E.; Wojcicki, A. *Ibid.* **1973**, *95*, 6962–6970. Dizikes, L. J.; Wojcicki, A *Ibid.* **1977**, *99*, 5295–5303. Rogers, W. N.; Page, J. A.; Baird, M. C. *Inorg. Chem.* **1981**, *20*, 3521–3528), its spectral characteristics have not been elaborated. (c) **6a**: IR (CH_2Cl_2) 2012, 1957, 1639 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 4.85 (s, 5 H, Cp), 2.87 (t, J_{ab} = 7.2 Hz, 2 H, $FpCOCH_2{}^a$), 1.34 (~sextet, $J_{ba} \cong J_{bc} \sim 7.2$ Hz, 2 H, >$CH_2{}^b$), 0.77 (t, J_{cb} = 7.1 Hz, 3 H, $CH_3{}^c$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 259.52 (>C=O), 214.5 ($-C{\equiv}O$), 86.38 (Cp), 68.63 (FpCOC), 18.67 (>CH_2), 13.59 (CH_3); MS m/e 248$[M]^{+\cdot}$, 220$[M - CO]^{+\cdot}$, 192 $[M - 2CO]^{+\cdot}$, 205 $[M - C_3H_7]^{+\cdot}$, 177 $[M - COC_3H_7]^{+\cdot}$. Anal. Calcd for $C_{11}H_{12}FeO_3$: C, 53.26; H, 4.88. Found: C, 53.67; H, 4.98. (d) **6b**: IR (CH_2Cl_2) 2022, 1960, 1641 cm^{-1}, ^1H NMR ($CDCl_3$) δ 4.90 (s, 5 H, Cp), 2.86 (t, J = 7.2 Hz, 2 H, $FpCOCH_2-$), 1.40 (m, 3 H, $-CH_2CH<$), 0.90 (d, J = 5.4 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 256.38 (>C=O), 214.44 ($-C{\equiv}O$), 86.31 (Cp), 64.66 (FpCOC), 33.87 (>CH?), 27.5 (>CH_2 ?), 22.32 (CH_3); MS, m/e 276 $[M]^{+\cdot}$, 248 $[M - CO]^{+\cdot}$, 220 $[M - 2CO]^{+\cdot}$, 205 $[M - C_5H_{11}]^{+\cdot}$, 177 $[M - COC_5H_{11}]^{+\cdot}$, 121 $[M - (COC_5H_{11} + 2CO)]^{+\cdot}$. (e) **6c**: mp 47–49 °C; IR (CH_2Cl_2) 2022, 1960, 1647 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.94 (s, 5 H, Cp), 2.84 (t, J = 7.5 Hz, 2 H, $FpCOCH_2-$), 1.40 (t, J = 7.5 Hz, 2 H, >CH_2), 0.90 (s, 9 H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 256.78 (>C=O), 214.40 ($-C{\equiv}O$), 86.30 (Cp), 62.39 (FpCOC), 38.32 (>C< ?), 29.92 (>CH_2 ?), 29.14 (CH_3); MS m/e 290 $[M]^{+\cdot}$, 262 $[M - CO]^{+\cdot}$, 234 $[M - 2CO]^{+\cdot}$, 205 $[M - C_6H_{13}]^{+\cdot}$, 177 $[M - COC_6H_{13}]^{+\cdot}$, 121 $[M - (COC_6H_{13} + 2CO)]^{+\cdot}$. (f) **7b**: IR ($CH_2Cl_2$) 2081, 2041 cm^{-1}; ^1H NMR [$(CD_3)_2CO$] δ 5.9 (s, 5 H, Cp), 5.1–5.6 (m, 1 H, =CH—), 3.9 (d, J = 9 Hz, 1 H, *cis*-=CH_2), 3.5 (d, J = 15 Hz, *trans*-=CH_2), 1.4 (d, J = 5.4 Hz, 3 H, CH_3), 1.04 (d, J = 5.4 Hz, 3 H, CH_3); $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, 0 °C] δ 211.77 ($-C{\equiv}O$), 209.07 ($-C{\equiv}O$), 96.67 (=CH—), 90.18 (Cp), 51.06 (=CH_2), 34.8 (>CH), 24.98 (CH_3), 24.12 (CH_3).

(9) As an equilibrium mixture with the dimer prepared by treating triphenylchloromethane with excess zinc at room temperature (Isaacs, N. S. "Experiments in Physical Organic Chemistry"; Macmillan: New York, 1969, pp 216–217) and decanting the resultant clear supernatant solution.

(10) (a) Slack, D.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1974**, 701–702. (b) Laycock, D. E.; Hartgerink, J.; Baird, M. C. *J. Org. Chem.* **1980**, *45*, 291–299.

0276-7333/84/2303-0642$01.50/0

Table I. Isolated Product Yields from the Reaction of $(\eta^5\text{-}C_5H_5)(CO)_2Fe(\eta^1\text{-}R)$ (1) (R = alkyl) and $Ph_3C^+BF_4^-$ (2) in CH_2Cl_2[a]

run	FpR	mole ratio, 2/1	temp, time	% yield[b] 6	7	8
1[c]	**1a**	1.0	−78, 1; −20, 16		99[d]	97
2, 3	**1a**	1.0	−78, 1; −20, 16	13.5 ± 0.5	71 ± 3	68.5 ± 2.5
4–6	**1a**	0.33	−78, 1; −20, 16	15 ± 3	30.7 ± 1.1[e]	*f*
7	**1a**	3.0	−78, 1; −20, 16	11	78	81
8[c,g]	**1a**	1.0	−78, 1; −20, 16		95	94
9[g]	**1a**	1.0	−78, 1; −20, 16		95	*h*
10[c]	**1b**[i]	1.0	25, 22	11[j]	75[k]	76
11	**1b**	1.0	−78, 1; −20, 16	78[l]		14
12	**1b**	1.0	0, 9	85[l]		12
13, 14	**1b**	1.0	25, 1	74.5 ± 2.5	12[m]	11.5 ± 1.5
15, 16	**1b**	0.33	−78, 1; −20, 16	83 ± 2[l]		
17[g]	**1b**	1.0	25, 22	13	75	~86
18[c]	**1c**[n]	1.0	25, 48	48[o,p]		
19	**1c**	1.0	−78, 1; −20, 16	92		
20	**1c**	0.33	−78, 1; −20, 16	87		

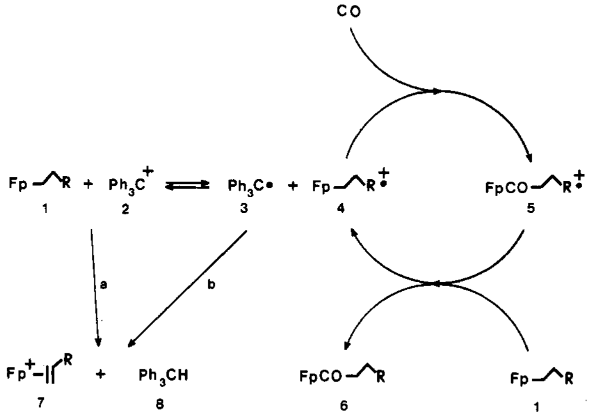
[a] Under excess CO at 1 atm unless otherwise indicated. Temp, °C; time, h. [b] Isolated yield based on 1 unless otherwise indicated. [c] Under 1 atm of N_2. [d] Green and Nagy[5] report an 86% yield in THF after 30 min at an unspecified temperature. [e] An average of 96% based on 2. [f] Also contains unreacted 1 from which it was not separated. [g] Also contains 1 mol equiv of 3. [h] Not determined. [i] Reference 8a. [j] Reference 8d. [k] Reference 8f. [l] A crystalline product of unknown structure is also present. [m] ^1H NMR integration of the reaction mixture gives 9%. [n] Reference 8b. [o] Also contains 22% unreacted 1c. Overall product balance is ⩾94% based on 1c: 22% recovered, 48% converted to **6c** and at least half of the remaining 30% decomposed to supply the CO necessary to form the 48% of **6c**. [p] Reference 8e.

clusive reaction (runs 18–20).

Competitive migratory carbonyl insertion is catalyzed by triphenylmethyl tetrafluoroborate (**2**). Stirred dichloromethane solutions of **1a** or **1b** and **6**, **7**, or **8**, either singly or in combination, are stable under carbon monoxide for extended periods at −20 °C, yet solutions containing but 0.33 mol of **2** per mol of **1b** or **1c** produce more than 0.8 mol of acyl complex **6** (runs 15, 16, 20). A similar mixture of **2** and **1a** yields 0.31 equiv of **7a** *and* 0.15 equiv of **6a** (runs 4–6).

Both Lewis acids[11] and oxidants[12,13] are known to promote migratory carbonyl insertion. The former apparently coordinate at oxygen and increase the electrophilicity of a terminal carbonyl;[11] the latter oxidize the 18-electron, Fe(II)–alkyl to the more reactive, 17-electron, Fe(III)–alkyl cation radical.[14] LaCroce and Cutler have shown that Fp^+ acting as a Lewis acid can accelerate the conversion of $Fp\text{–}CH_3$ to $FpCOCH_3$,[15] while Magnuson, Giering, et al. found that either ferrocenium or silver cation in the presence of carbon monoxide can oxidize $Fp'CH_3$[3] and convert it to the corresponding acyl, $Fp'COCH_3$.[14c] Essentially stoichiometric amounts of Lewis acid are needed[11b–d] but only catalytic amounts of oxidant.[14c]

Scheme I



The migratory carbonyl insertions which we observe are redox rather than Lewis acid promoted. We find that while the addition of Fp^+ to a carbon monoxide blanketed solution of **1a** and **7a** in dichloromethane at room temperature causes insertion, none occurs in its absence.[16] Similarly, a mixture of **7b** and **1b** is stable under our reaction conditions. Apparently dissociation of the π-complexes, **7a** and **7b**, is not significant, and they themselves do not promote acyl formation under these conditions. Further, when **2** is added to a solution of **1a** in the presence of carbon monoxide at −40 °C the initially sharp proton resonances of the Fp alkyl broaden rapidly, then gradually sharpen in concert with those of the products as the reaction progresses. This is a strong indication of one or more transient radical intermediates.[17] Initial reversible one-electron transfer is also suggested by the fact that added **3** markedly inhibits acyl formation but does not otherwise alter the reaction course of **1a** or **1b** with **2** and carbon monoxide (see eq 2; compare runs 2 and 3 with 9, 13 and 14 with 17). In the absence of **1a**, solutions of **2** and **3** and/or **6a** are stable under our reaction conditions.

Combining our results with those of Giering[14] and others,[12,13,18] we suggest the mechanistic scenario in Scheme I for triphenylcarbenium-induced, competitive carbonyl insertion and β-elimination in Fp alkyls.

The redox insertion mechanism, Scheme I, raises the possibility of an alternate route for triphenylcarbenium-induced β-elimination. Normally such reactions involve

---

[11] (a) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766–4772. (b) Butts, S. B.; Richmond, T. G.; Shriver, D. F. *Inorg. Chem.* **1981**, *20*, 278–280. (c) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093–5100. (d) Richmond, T. G.; Basolo, F.; Shriver, D. F. *Inorg. Chem.* **1982**, *21*, 1272–1273.

[12] (a) Anderson, S. N.; Fong, C. W.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1973**, 163. (b) Nicholas, K. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1973**, *95*, 4449–4450. (c) Rogers, W.; Page, J. A.; Baird, M. C. *J. Organomet. Chem.* **1978**, *156*, C37–C42.

[13] (a) Hershberger, J. W.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1982**, 212–214. (b) Mikolová, D.; Vlček, A. A. *J. Organomet. Chem.* **1982**, *240*, 413–419. (c) Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61–73.

[14] (a) Magnuson, R. H.; Zulu, S.; T'sai, W.-M.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887–6888. (b) Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *Ibid.* **1982**, *104*, 5790–5791. (c) Magnuson, R. H.; Meirowitz, R.; Zulu, S. J.; Giering, W. P. *Organometallics* **1983**, *2*, 460–462.

[15] LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312–2314.

[16] We thank a referee for suggesting this experiment.

[17] Drago, R. S. "Physical Methods in Chemistry"; W. B. Saunders: New York, 1977, pp 444–449.

[18] (a) Sanders, A.; Giering, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 5247–5248; *J. Organomet. Chem.* **1976**, *104*, 49–65. (b) Treichel, P. M.; Wagner, K. P.; Mueh, H. J. *J. Organomet. Chem.* **1975**, *86*, C13–C16. (c) Daub, G. W. *Prog. Inorg. Chem.* **1977**, *22*, 409–423. (d) Rogers, W. N.; Page, J. A.; Baird, M. C. *Inorg. Chem.* **1981**, *20*, 3521–3528. (e) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648–4650. (f) Hayes, J. C.; Cooper, N. J. *Ibid.* **1982**, *104*, 5570–5572.

loss of an antiperiplanar hydrogen as hydride,[5,10] path a, but hydrogen *atom* abstraction by triphenylmethyl (**3**) from the intermediate cation radical, path b, is also conceivable.[19] The latter possibility is intriguing for it may be favored when β-hydrogen and metal cannot easily be antiperiplanar.

These alternate paths cannot be distinguished kinetically.[20] Each predicts that added **3** will inhibit insertion as we observe but will have little effect on the rate of elimination. Comparison of the yields of the π-complex **7b** at different reaction times (runs 13, 14, 17) implies that this is true. To confirm that it is we have measured the rate of formation of triphenylmethane (**8**) from **1a** with and without added **3**.[16] Aliquots of the reacting mixtures were quenched at known times by shaking with mixtures of diethyl ether and aqueous ceric ammonium nitrate. The amount of extracted **8** was then determined gas chromatographically by comparison with an internal standard. At −45 ± 5 °C the rate of formation of **8** in the presence of added **3** is similar ($k = 1.9 \times 10^{-2}$ M^{-1} s^{-1}, $r^2 = 0.98$) to that in its absence ($k = 2.0 \times 10^{-2}$ M^{-1} s^{-1}, $r^2 = 0.99$).

In summary then we find that in the presence of excess carbon monoxide, redox-catalyzed migratory carbonyl insertion is competitive with triphenylcarbenium-induced β-elimination even in simple, conformationally mobile Fp alkyls. If carbon monoxide is supplied externally, redox-catalyzed insertion is more competitive the lower the temperature; if it must be produced internally by thermal decomposition of some of the σ-complex, higher temperatures are required and insertion is competitive only if elimination itself is relatively slow.

Acknowledgment. We thank Professors John Huggins and Dan Reger for many helpful discussions and suggestions and the NSF for partial support under its EPSCOR program.

Registry No. **1a**, 51177-83-4; **1b**, 89043-50-5; **1c**, 43157-76-2; **2**, 341-02-6; **3**, 2216-49-1; **6a**, 89043-51-6; **6b**, 89043-52-7; **6c**, 89043-53-8; **7a**, 37668-14-7; **7b**, 89043-54-9; **8**, 519-73-3; Fp$^+$, 69721-23-9; CO, 630-08-0.

---

(19) Cf.: Kashin, A. N.; Bumagin, N. A.; Beletskaya, I. P.; Reutov, O. A. *Dokl. Akad. Nauk SSSR* **1979**, *244*, 98–102.

(20) Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill, New York, 1981, pp 78–79.

The Series of Tricarbonyliron Hydride Anions $(OC)_3FeH_n^-$ (n = 1–3)

Richard N. McDonald,* A. Kasem Chowdhury, and Philip L. Schell

Department of Chemistry, Kansas State University
Manhattan, Kansas 66506

Received December 19, 1983

Summary: The primary ion products from the gas-phase reaction of $(OC)_4Fe^{-}\cdot$ with hydrogen atoms are $(OC)_3Fe^{-}\cdot$ and $(OC)_3FeH^-$. Both primary ions add H_2, giving the hydrides $(OC)_3FeH_2^{-}\cdot$ and $(OC)_3FeH_3^-$, respectively. With D_2, the primary ions form $(OC)_3FeD_2^{-}\cdot$ and $(OC)_3FeHD_2^-$ and $(OC)_3FeD_3^-$, respectively, the trideuteride arising by H/D exchange in $(OC)_3FeH^-$ ($\rightarrow (OC)_3FeD^-$).

The condensed-phase reaction of HO^- with $Fe(CO)_5$ yields the hydridoiron complex $(OC)_4FeH^-$ by the proposed mechanism in eq 1.[1]

$$HO^- + Fe(CO)_5 \xrightarrow{H_2O} \underset{\mathbf{1}}{(OC)_4Fe(CO_2H)^-} \xrightarrow{HO^-}$$
$$\underset{\mathbf{2}}{(OC)_4Fe(CO_2)^{2-}} \xrightarrow{-CO_2} (OC)_4Fe^{2-} \xrightarrow[-HO^-]{H_2O} (OC)_4FeH^- \quad (1)$$

The gas-phase reaction of HO^- with $Fe(CO)_5$ produced the M − 2CO adduct (*m/z* 157) which is consistent with the condensed-phase mechanism since the conversion of **1** → **2** is not possible under these conditions. In the gas phase, the vibrationally excited adduct **1*** apparently decarbonylates followed by rearrangement of HO from carbon to iron (deinsertion) and loss of a second CO ligand from the excited $[(OC)_4Fe(OH)^-]^*$ species (eq 2).[2] An alternate

$$HO^- + Fe(CO)_5 \xrightarrow[\text{phase}]{\text{gas}} [\mathbf{1}]^* \xrightarrow[\text{migration of HO}]{-CO,}$$
$$[(OC)_4Fe(OH)^-]^* \rightarrow \underset{m/z\ 157}{(OC)_3Fe(OH)^-} + CO \quad (2)$$

gas-phase route to $(OC)_4FeH^-$ could involve the reaction of $(OC)_4Fe^{-}\cdot$ with hydrogen atoms. We wish to report preliminary results of this reaction which yield $(OC)_3Fe^{-}\cdot$ and the novel series of tricarbonyliron hydride anions $(OC)_3FeH_n^-$ (n = 1–3) via primary and secondary ion–neutral reactions. $(OC)_4FeH^-$ can also be obtained as the major ion product of secondary ion–molecule reactions when CO is added to the flow before it reaches the H-atom/H_2 inlet.

Our studies were carried out in a flowing afterglow (FA) apparatus. $(OC)_4Fe^{-}\cdot$ was generated from $Fe(CO)_5$ by dissociative electron attachment in a fast flow of helium buffer gas at 298 K in the upstream end of the flow tube.[3] No reaction occurred between $(OC)_4Fe^{-}\cdot$ and H_2. A mixture of H atoms/H_2 was produced by passing H_2 through a glass tube in the cavity of a microwave discharge. This $H\cdot/H_2$ mixture was then added to the flow containing $(OC)_4Fe^{-}\cdot$ via a gas inlet located 30 cm downstream of the ion generation region. At low $H\cdot/H_2$ flows (<10% conversion of $(OC)_4Fe^{-}\cdot$), four product anions, *m/z* 140–143, were formed, while at high flows of $H\cdot/H_2$ only the anions *m/z* 142 and 143 were observed.[4] These results established that the ions *m/z* 140 and 141 were the primary products of the ion–neutral reaction of $(OC)_4Fe^{-}\cdot$ with H atoms. When H_2 was added to the flow containing the four ions *m/z* 140–143, the ions *m/z* 140 and 141 were con-

---

(1) Pearson, R. G.; Mauermann, H. *J. Am. Chem. Soc.* **1982**, *104*, 500–504.

(2) In the FA, the gas-phase reaction of CH_3O^- with $Fe(CO)_5$ yields the corresponding M − 2CO adduct considered to be $(OC)_3Fe(OCH_3)^-$, while the reaction with CF_3O^- gives the net adduct, the acylate anion $(OC)_4Fe(CO_2CF_3)^-$. These results agree with the suggestion of Foster and Beauchamp (Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 4924–4926; **1975**, *97*, 4808–4814) that strongly basic nucleophiles react with $Fe(CO)_5$ in the gas phase, giving the (M − 2CO) adducts. Collisional stabilization with the buffer gas in the FA allows us to observe the net adducts with weakly basic nucleophiles.

(3) (a) McDonald, R. N.; Schell, P. L.; McGhee, W. D. *Organometallics* **1984**, *3*, 182–184. (b) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 2194–2203. (c) Removal of all electrons and metastable He(2^3S) atoms was complete within 15 cm of the electron gun since no signal for $SF_6^{-}\cdot$ was observed when SF_6 was added at this point.

(4) The isotope ratios for ^{54}Fe for the ions *m/z* 140–143 clearly showed these ions to be mononuclear iron species, and the (M + 1) for *m/z* 143 was consistent with the structure $(OC)_3FeH_3^-$ for this ion.

0276-7333/84/2303-0644$01.50/0