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.

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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.

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[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

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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]

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

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

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

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-

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[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.

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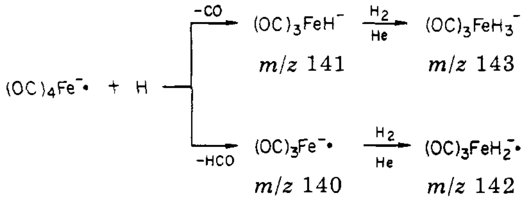
verted into their product ions *m/z* 142 and 143, respectively. Therefore, these latter two higher mass ions were determined to be formed by addition of molecular H_2 to the coordinatively unsaturated mononuclear species *m/z* 140 and 141. These results are summarized in eq 3–5.

$$\underset{m/z\ 168}{Fe(CO)_5 + e^- \rightarrow (OC)_4Fe^{-\cdot}} + CO \qquad (3)$$

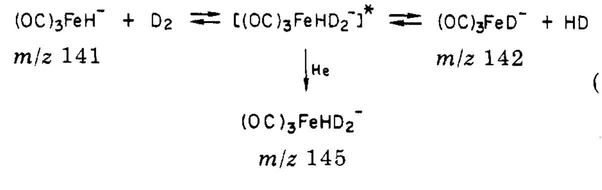


(4)

(5)

To further establish the sequence of reactions 4 and 5, the mixture of anions *m/z* 140–143 was allowed to react with D_2 which was added to the flow via an inlet located 30 cm downstream of the $H\cdot/H_2$ inlet. A new series of anions, *m/z* 142–146, were produced along with traces of *m/z* 140 and 141 ions concomitant with attenuation of the intensities of the signals for the ions *m/z* 142 (by ~30%) and 143 (by ~50%). The ion structures which we believe comprise this new series of ions are $(OC)_3FeH_2^{-\cdot}$ at *m/z* 142, $(OC)_3FeH_3^-$ at *m/z* 143, $(OC)_3FeD_2^{-\cdot}$ and $(OC)_3FeH_2D^-$ at *m/z* 144, $(OC)_3FeHD_2^-$ at *m/z* 145, and $(OC)_3FeD_3^-$ at *m/z* 146.

Formation of $(OC)_3FeD_3^-$ (*m/z* 146) is most interesting. Since no reaction was observed between $(OC)_3FeH_3^-$ or $(OC)_3FeH_2^{-\cdot}$ in their ground states and D_2, ion *m/z* 146 might be formed by either of two pathways: (a) if $(OC)_3FeD_2^{-\cdot}$ (*m/z* 144) were to fragment to $(OC)_3FeD^- + \cdot D$, $(OC)_3FeD^-$ would then add D_2 to give $(OC)_3FeD_3^-$ or (b) if H/D exchange occurred in $(OC)_3FeH^- + D_2 \rightarrow (OC)_3FeD^- + HD$ prior to formation of the stable adduct $(OC)_3FeHD_2^-$.[5] By increasing the electron-gun emission current, we observed that $(OC)_3Fe^{-\cdot}$ (*m/z* 140) was a minor product (~30%) of dissociative electron attachment with $Fe(CO)_5$; $(OC)_4Fe^{-\cdot}$ remained the major product ion.[6] Addition of D_2 to $(OC)_3Fe^{-\cdot}$ gave *only* $(OC)_3FeD_2^{-\cdot}$ (*m/z* 144) *without* formation of $(OC)_3FeD^{-\cdot}$ (*m/z* 142) over that expected for the ^{54}Fe isotope peak for *m/z* 144. This result eliminates pathway a as a source of $(OC)_3FeD_3^-$. Therefore, we conclude that $(OC)_3FeH^-$ undergoes H/D exchange (pathway b) according to eq 6 with fragmentation of vibrationally excited [*m/z* 145]* to $(OC)_3FeD^-$ competitive with collisional stabilization with the helium buffer gas. This H/D exchange is similar to related exchanges observed in the condensed phase between the neutral Cp_2TaH_3 and Cp_2NbH_3 complexes with D_2.[7] An important corollary of this conclusion is that the hydrogen and two deuteriums in *m/z* 145 are, or can readily become, chemically equivalent. Thus, it seems most reasonable that these three atoms are attached to iron in this complex as the trihydride, although the presence of a formyl ligand in the complex anion cannot be ruled out.



(6)

Assuming that $(OC)_4Fe^{-\cdot}$ produced in the gas phase has the C_{3v} structure of the matrix-isolated species,[8] addition of an H atom would reasonably yield the C_{3v} iron hydride $(OC)_4FeH^-$ (*m/z* 169) (eq 7). The large exothermicity (71 ± 21 kcal mol^{-1})[9] of this anion radical–radical combination reaction means that the chemically activated product anion $[(OC)_4FeH^-]^*$ would readily unimolecularly fragment with loss of a CO ligand producing the anion $(OC)_3FeH^-$ (*m/z* 141) or loss of HCO giving $(OC)_3Fe^{-\cdot}$ (*m/z* 140).

$$(OC)_4Fe^{-\cdot} + \cdot H \rightarrow (OC)_4FeH^- \qquad (7)$$

$$\Delta H^\circ = -71 \pm 21 \text{ kcal mol}^{-1} \text{ (ref 9)}$$

Alternatively, $[(OC)_3Fe(C(=O)H)^-]^*$ (**3**) might be the product of addition of an H atom to $(OC)_4Fe^{-\cdot}$. Although $\Delta H^\circ_f(\mathbf{3})$ cannot presently be estimated, decarbonylation of the formyl complex **3** would be a reasonable expectation with rearrangement of that product to $(OC)_3FeH^-$ by analogy with condensed phase results.[15] Each of the above possibilities strongly suggest that the anion *m/z* 141 contains the Fe–H bond.

Investigations of the gas-phase chemistry and thermochemical properties of $(OC)_3Fe^{-\cdot}$ and $(OC)_3FeH_n^-$ (n = 1–3) are under way, as are related studies with other transition-metal reactants $(OC)_XM^{-\cdot}$.

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Registry No. $(OC)_4Fe^{-\cdot}$, 51222-96-9; H, 12385-13-6; $(OC)_3FeH^-$, 89087-79-6; $(OC)_3FeH_3^-$, 89087-80-9; $(OC)_3Fe^{-\cdot}$, 53221-56-0; $(OC)_3FeH_2^{-\cdot}$, 89087-81-0; $(OC)_3FeD_2^{-\cdot}$, 89087-82-1; $(OC)_3FeH_2D^-$, 89087-83-2; $(OC)_3FeHD_2^-$, 89087-84-3; $(OC)_3FeD_3^-$, 89087-85-4.

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(5) The concentration of H atoms in the flow at the point of the D_2 inlet port must be small to zero in the presence of a large excess of $(OC)_4Fe^{-\cdot}$ under these low $H\cdot/H_2$ flow conditions. Since the rate constant for $H\cdot + D_2 \rightarrow HD + D\cdot$ is small ($k = 2.6 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 299 K: Westenberg, A. A.; de Haas, N. *J. Chem. Phys.* **1967**, *47*, 1393–1405), this cannot be a source of D atoms that would react with $(OC)_3Fe^{-\cdot}$ or $(OC)_4Fe^{-\cdot}$ giving $(OC)_3FeD^-$.

(6) (a) Compton, R. N.; Stockdale, J. A. D. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *22*, 47–55. (b) George, P. M.; Beauchamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2959–2964.

(7) (a) Barefield, E. K.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* **1970**, *92*, 5234–5235. (b) Tebbe, F. N.; Parshall, G. W. *Ibid.* **1971**, *93*, 3793–3795.

(8) Breeze, P. A.; Burdett, J. K.; Turner, J. J. *Inorg. Chem.* **1981**, *20*, 3369–3378.

(9) (a) Using $\Delta H_f^\circ(Fe(CO)_5) = -173.0 \pm 1.5$ kcal mol^{-1},[10] $\Delta H_f^\circ(CO) = -26.4 \pm 0.04$ kcal mol^{-1},[10] and $D^\circ((OC)_4Fe\text{–}CO) = 41 \pm 2$ kcal mol^{-1},[11] we calculate $\Delta H_f^\circ(Fe(CO)_4) = -105.6 \pm 3.5$ kcal mol^{-1}. (b) From EA(Fe(CO)$_4$) = 55.3 ± 6.9 kcal mol^{-1},[12] $\Delta H_f^\circ(OC)_4Fe^{-\cdot}) = -160.9 \pm 10.4$ kcal mol^{-1}. (c) Sweany[13] observed little or no activation energy for the reaction $H_2 + Fe(CO)_4 \rightarrow H_2Fe(CO)_4$, and Pearson and Mauermann[1] measured $E_a = 26 \pm 2$ kcal mol^{-1} for the reverse reaction. Assuming $D^\circ((OC)_4Fe\text{–}H_2) = 26 \pm 2$ kcal mol^{-1}, we calculate $\Delta H_f^\circ(H_2Fe(CO)_4) = -131.6 \pm 5.5$ kcal mol^{-1}. (d) From $\Delta H_{acid}^\circ(H_2Fe(CO)_4) = 319 \pm 5$ kcal mol^{-1},[14] $\Delta H_f^\circ(HFe(CO)_4^-) = -179.8 \pm 10.5$ kcal mol^{-1} was calculated.

(10) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

(11) (a) We thank Dr. Gregory P. Smith for this dissociation energy in a preprint of a paper submitted to *J. Am. Chem. Soc.* (with K. E. Lewis and D. M. Golden). (b) Smith and Laine (Smith, G. P.; Laine, R. M. *J. Phys. Chem.* **1981**, *85*, 1620–1622) originally reported $D^\circ((OC)_4Fe\text{-}CO) = 48 \pm 4$ kcal mol^{-1}.

(12) Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 5569–5573.

(13) Sweany, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 2410–2412.

(14) We thank Professor J. L. Beauchamp for a preprint (with A. E. Stevens) of the gas-phase acidity of $H_2Fe(CO)_4$.

(15) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; p 440.