

(those at C-4 and C-7 actually being in physical contact) the annulated pyranoside **10** resides in the conformation which enjoys the anomeric effect. In keeping with this circumstance, the diol **10c** fails to give an acetonide⁸ after prolonged exposure to the conditions¹⁰ that succeed when applied to **1b**.

Hydrolysis of the glycoside of **10a** followed by oxidation and de-O-acetylation afforded *N*-acetyl-desalanylactinobolin (**1b**), identical with the sample prepared from the natural compound.²⁵

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Supplementary Material Available: Proton NMR spectra, melting points, and electronic absorption spectra of compounds **1b**, **4a**, **5**, **6b**, **7**, **8**, **9a**, and **10b** and the transformation intermediates leading from **10b** to **1b** (5 pages). Ordering information is given on any current masthead page.

(25) The details of these transformations will be published elsewhere.

H/D Exchange and Addition in the Reaction of $(\eta^4\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})^-$ with D_2 . An Anionic Model for Homogeneous Hydrogenation

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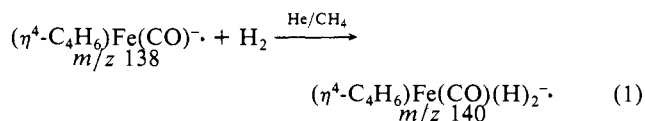
$\text{Fe}(\text{CO})_5$, $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), and various complexes of these transition metals are efficient homogeneous olefin hydrogenation catalysts at elevated temperature and high H_2 pressure.^{1,2a} Thermally active catalysts which effect hydrogenation at $\leq 25^\circ\text{C}$ and 1 atm of H_2 are produced by photolysis of these transition-metal carbonyls and several other $\text{L}_y\text{M}'(\text{CO})_x$ ($\text{M}' = \text{Fe}, \text{Cr}, \text{Mo}, \text{W}$) complexes.^{2,3} The proposed mechanism for such photocatalyzed olefin hydrogenations involves formation of the coordinatively unsaturated transition-metal complex as the active catalyst. This proposal is supported by numerous photochemical studies with these and related complexes dealing with the elementary reaction channels.³ We wish to report the generation and ion-molecule reactions of $(\eta^4\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})^-$ with H_2 and D_2 which corroborate certain steps in catalytic hydrogenation cycles and the coordination unsaturation of the catalytically active species.

Our studies are carried out in a previously described flowing afterglow (FA) apparatus⁴ at 298 K. Briefly, the ion of interest is generated in the upstream end of the flow tube in a fast flow of helium/ CH_4 (99/1) buffer gas ($P = 0.55$ torr, $\bar{v} = 80$ m/s). Following thermalization of these ions by collisions with the buffer gas (50 cm), H_2 or D_2 was added via an inlet port and the ion-molecule reaction occurs in the final 65 cm of the flow tube. The flow is sampled into a differentially pumped compartment (10^{-7} torr) containing a quadrupole mass spectrometer which monitors the ion composition of the flow. The bimolecular ion-molecule rate constants are determined under pseudo-first-order conditions,

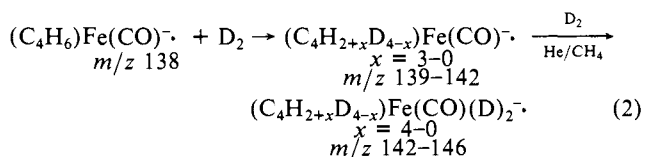
and the formation of product ions is observed directly.

When the electron gun in the FA is operated at a low emission current ($\text{EC} < 50 \mu\text{A}$), $(\eta^4\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})_3$ attaches a thermalized electron giving the parent anion radical $(\eta^2\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})_3^-$ (m/z 194) exclusively; Krusic and San Filippo⁵ characterized the parent anion radical formed in the condensed phase as the 17-electron η^2 -diene complex. Increasing the EC to ~ 3 mA⁶ yields a mixture of m/z 194 and 166. Both m/z 194 and 166 react with NO giving $(\text{OC})_3\text{Fe}(\text{NO})^-$ and $(\text{OC})_2\text{Fe}(\text{NO})^-$, respectively, by exclusive displacement of the butadiene ligand. While the ion m/z 194 does not react with PF_3 , m/z 166 [$(\eta^4\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})_2^-$] readily adds PF_3 termolecularly forming the adduct, most likely $(\eta^2\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})_2(\text{PF}_3)^-$. Neither m/z 166 or 194 react with H_2 or D_2 ($k \leq 10^{-13}$ $\text{cm}^3/\text{molecule/s}$). Increasing the electron gun EC to ~ 12 mA produced a strong signal for m/z 138 along with signals for m/z 166 and 194.^{6,7} The anion m/z 138 (m/z 194 - 2CO) is considered to have the structure $(\eta^4\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})^-$.⁸ This 15-electron structure of m/z 138 is supported by the fact that m/z 138 rapidly adds PF_3 forming the adduct $(\eta^4\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})(\text{PF}_3)^-$ and undergoes ligand substitution with NO yielding $(\eta^4\text{-C}_4\text{H}_6)\text{Fe}(\text{NO})^-$ (major) and $(\text{OC})\text{Fe}(\text{NO})^-$ (minor).

Of special significance was the observation that anion radical m/z 138 adds H_2 termolecularly to form the adduct $(\eta^4\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})(\text{H})_2^-$ (eq 1) with an apparent bimolecular rate constant



of 1.4×10^{-11} $\text{cm}^3/\text{molecule/s}$. The reaction of m/z 138 with D_2 occurred at twice the apparent bimolecular rate for the reaction with H_2 and revealed that up to four H/D exchanges in the diene ligand took place sequentially and competitively with adduct formation (eq 2). The results of three data points in the kinetic/



product study of this reaction are given in Table I. Although the data for the 5% decay of m/z 138 with D_2 will have the largest errors, they show that the primary processes are competitive bimolecular H/D exchange and termolecular addition of D_2 . The data for the first two points establish that the contribution of $(\eta^4\text{-C}_4\text{H}_2\text{D}_4)\text{Fe}(\text{CO})^-$ to the m/z 142 signal is negligible since the m/z 141 ion is only just beginning to appear at 28% decay of m/z 138. At larger concentrations of added D_2 , the isotopmer of four H/D exchanges will contribute to the m/z 142 signal. No signals for adducts involving five (m/z 147) or six (m/z 148) H/D exchanges were observed when sufficient D_2 was added to eliminate the ion signals at m/z 139-141. The kinetic data suggest that a barrier exists in forming the excited adduct **2**,¹⁰ and the product data suggest that the rate of intramolecular H/D exchange in the diene ligand is relatively fast.

(5) Krusic, P. J.; San Filippo, J. *J. Am. Chem. Soc.* **1982**, *104*, 2645-2647.

(6) McDonald, R. N.; Chowdhury, A. K.; Schell, P. L. *J. Am. Chem. Soc.* **1984**, *106*, 6095-6096.

(7) Minor signals of unknown negative ions are observed at m/z 139, 140, and 141; the m/z 140 ion may be $(\text{OC})_3\text{Fe}^-$, which adds H_2 to give $(\text{O-C})_3\text{Fe}(\text{H})_2^-$.⁶ The presence of these minor ions does not affect the qualitative arguments given here.

(8) Blake, M. R.; Garnett, J. L.; Gregor, I. K.; Wild, S. B. *J. Chem. Soc., Chem. Commun.* **1979**, 496-497.

(9) $(\eta^4\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})(\text{H})_2^-$ reacts with SO_2 by exclusive loss of the butadiene ligand from the assumed association adduct forming $(\text{OC})\text{Fe}(\text{S-O}_2)(\text{H})_2^-$.

(10) For examples of the addition of H_2 to neutral transition-metal complexes involving barriers, with $\text{Ir}(\text{X})(\text{CO})(\text{PPh}_3)_2$, see: (a) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511-3514. Theoretical studies with $(\text{H}_3\text{P})_2\text{Pt}$: (b) Low, J. J.; Goddard, W. A. *Ibid.* **1984**, *106*, 6928-6937. Obara, S.; Kitaura, K.; Morokuma, K. *Ibid.* **1984**, *106*, 7482-7492.

(1) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973.

(2) (a) Wrighton, M. S.; Ginley, D. S.; Schroeder, M. A.; Morse, D. L. *Pure Appl. Chem.* **1975**, *41*, 671-697. (b) Wrighton, M. S.; Graff, J. L.; Kazlauskas, R. J.; Mitchner, J. C.; Reichel, C. L. *Ibid.* **1982**, *54*, 161-176.

(3) Miller, M. E.; Grant, E. R. *J. Am. Chem. Soc.* **1984**, *106*, 4635-4636; **1985**, *107*, 3386-3387 and references therein.

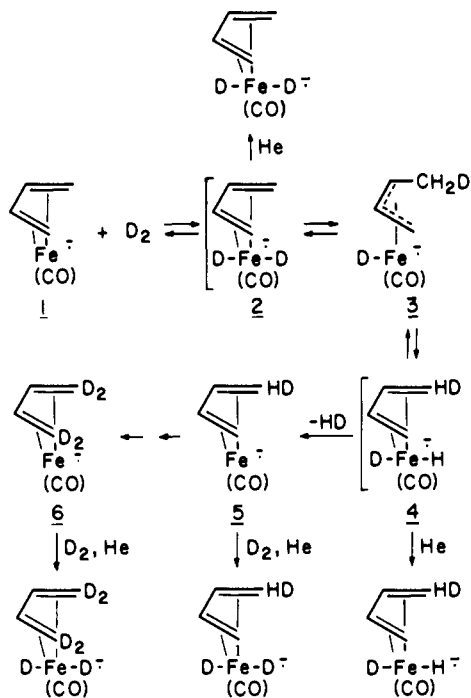
(4) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 2194-2203.

Table I. Data for Bimolecular H/D Exchange and Termolecular Addition of D₂ to (η⁴-C₄H₆)Fe(CO)⁻ (m/z 138)^a

% decay of m/z 138	% of product ion signals							
	(C ₄ H ₅ D)-Fe(CO) ⁻ m/z 139	(C ₄ H ₄ D ₂)-Fe(CO) ⁻ m/z 140	(C ₄ H ₃ D ₃)-Fe(CO) ⁻ m/z 141	(C ₄ H ₂ D ₄)-Fe(CO) ⁻ + (C ₄ H ₆)-Fe(CO)(D) ₂ ⁻ m/z 142	(C ₄ H ₅ D)-Fe(CO)(D) ₂ ⁻ m/z 143	(C ₄ H ₄ D ₂)-Fe(CO)(D) ₂ ⁻ m/z 144	(C ₄ H ₃ D ₃)-Fe(CO)(D) ₂ ⁻ m/z 145	(C ₄ H ₂ D ₄)-Fe(CO)(D) ₂ ⁻ m/z 146
5 ^{b,c}	22	28		20	15	15		
28 ^d	23	39	2	26	3	7		
90 ^e	7	16	11	28	8	16	8	6

^a These data are derived from the integrals of the ion signals for each mass. Small signals (2–3% of m/z 138) for unknown ions at m/z 139, 140 ((OC)₃Fe⁻?), and 141 in the starting negative ion spectrum and their possible reactions with D₂ impede a quantitative interpretation of the data. ^b The errors in this data set are the largest since the ion product signals are the smallest of the three points given. ^c 2.33 × 10¹¹ molecules/cm³ of D₂ added. ^d 1.83 × 10¹² molecules/cm³ of D₂ added. ^e 1.63 × 10¹³ molecules/cm³ of D₂ added.

Our observation that up to four H/D exchanges in the diene ligand of (C₄H₆)Fe(CO)⁻ (**1**) occurred with D₂ strongly suggests that only the two terminal methylene groups are involved.¹¹ We interpret these results by reversible oxidative-addition of D₂ to **1** giving dideuteride **2** followed by rearrangement to the *cis*-CH₂D-π-allyl complex **3**;¹² **2**–**4** are excited adducts. Kinetic barriers must exist for one or both of these steps since the bimolecular rate constant for decay of **1** is much smaller than that of the collision limit ($k_{\text{col}} = 1.5 \times 10^{-9}$ cm³/molecule/s).¹³ Rotation of the C–CH₂D bond in **3** would place a hydrogen of the CH₂D group in proximity to Fe and rearrangement would yield **4**. Reductive-elimination of HD from **4** giving **5** would be irre-



versible due to the short ion–neutral reaction time (≤ 7 ms) and high dilution of product ions and neutrals ($\leq 10^8$ ions/cm³) in these experiments. Repetition of these steps in bimolecular ion–D₂ collisions would then produce the observed additional three H/D exchanged ions terminating at **6**. Competitive with these H/D

exchanges is termolecular formation of the five total adducts (m/z 142–146) which requires collisional stabilization with the He/CH₄ buffer gas to remove excess vibrational energy in the initially formed excited adducts.

If we assume that rearrangement of a deuterium in **2** could also occur to C₂ (or C₃) of the diene ligand, an excited, 15-electron (η³-CH₂=CHCHDCH₂)Fe(CO)(D)⁻ (**7**) complex would result. The absence of a fifth or sixth H/D exchange in the reaction of **1** with D₂ means that **7** cannot detach the π-bond of the η³-homoallyl ligand to effect rotation about the C₁–C₂ bond (required for H/D exchange) via the higher energy, 13-electron (η¹-1-but-3-enyl-d₁)Fe(CO)(D)⁻ intermediate. Thus, the deuterium at C₂ in **7** must return to Fe reforming **2**.

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Ultrasound-Induced Electrochemical Synthesis of the Anions Se₂²⁻, Se²⁻, Te₂²⁻, and Te²⁻

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Organoselenium and -tellurium compounds have become increasingly important as reagents and intermediates in organic synthesis.^{1–6} Furthermore, they are promising donor molecules for conductive and photoconductive organic materials.^{7–12} Re-

(11) Wrighton and Schroeder (Wrighton, M. S.; Schroeder, M. A. *J. Am. Chem. Soc.* 1973, 95, 5764–5765) observed that photolysis of a benzene solution of Cr(CO)₆, D₂, and a 1,3-diene that could achieve the *s-cis* configuration produced the *cis* olefin by 1,4-addition of D₂ to the diene.

(12) For examples of reversible hydride transfer between transition-metal centers and hydrocarbon ligands, in the condensed phase, see: Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* 1981, 506–507 and references therein. Transfer in the gas phase see: Jacobsen, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* 1985, 107, 72–80 and references therein.

(13) Su and Bowers (Su, T.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, Chapter 3) describe Langevin and average dipole orientation theories used to calculate k_{col} .

(1) Klayman, D. L.; Günther, W. H. H. "Organic Selenium Compounds: Their Chemistry and Biology"; Wiley: New York, 1973.

(2) Clive, D. L. *J. Tetrahedron* 1982, 34, 1049.

(3) Reich, H. J. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; Part C, Chapter 1.

(4) Reich, H. J. *Acc. Chem. Res.* 1979, 12, 22.

(5) Liotta, D. *Acc. Chem. Res.* 1984, 17, 28.

(6) "The Organic Chemistry of Tellurium"; Irgolic K. J., Ed.; Gordon and Breach: New York, 1974.

(7) Yamahira, A.; Nogami, T.; Mikawa, H. *J. Chem. Soc., Chem. Commun.* 1983, 904.

(8) Stark, J. C.; Reed, R.; Acampora, L. A.; Sandman, D. J.; Jansen, S.; Jones, M. T.; Foxman, B. M. *Organometallics* 1984, 3, 732.

(9) Endres, H.; Keller, H. J.; Queckbörner, J.; Schweitzer, D.; Veigel, J. *Acta Crystallogr., Sect. B* 1982, B38, 2855 and references therein.

(10) Chu, J. Y. C.; Günther, W. H. H. U. S. Patent 4030991, 1977.

(11) Kirk, C. W.; Nalewajek, D.; Blanchet, G. B.; Schaffer, H.; Moraes, F.; Boysel, R. M.; Wudl, F. *J. Am. Chem. Soc.* 1985, 107, 675 and references therein.