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Gas-Phase Ion Chemistry of Two Isomeric $(C_4H_6)Fe(CO)_3$ Complexes

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The gas-phase ion chemistry of two isomeric $(C_4H_6)Fe(CO)_3$ complexes, where C_4H_6 = η^4-$(CH_2)_3C$ (trimethylenemethane) and η^4-$CH_2{=}CHCH{=}CH_2$ (1,3-butadiene), is described. Electron impact mass spectra of the two isomers collected at low (10^{-6} torr) and high (0.4 torr) pressure are compared and contrasted. Gas-phase ion/molecule reactions of the parent molecular negative ions of both complexes were examined in a flowing afterglow apparatus at 300 K. Oxidation reactions with O_2 and ligand substitution reactions with NO, SO_2, CO_2, and CS_2 showed marked differences between the two negative ions. The trimethylenemethane isomer consistently displayed a greater tendency to maintain the hydrocarbon ligand under conditions where the butadiene ligand was displaced. Reactions of both isomers with a series of reference acids exposed an approximately 5 kcal/mol greater proton affinity for the trimethylenemethane anion complex relative to the butadiene isomer. Proton abstraction and nucleophilic addition reactions between the 1,3-butadiene complex and a series of negative ions are also described.

Introduction

Contemporary studies of gas-phase organometallic ion chemistry have provided useful new thermodynamic information for transition-metal compounds as well as an instructive view of the reactivity of organometallic ions and molecules in the absence of solvation and ion-pairing effects.[1] Gas-phase experiments have also offered a unique opportunity to investigate the chemistry of reactive transition-metal species which have no precedent in solution such as bare atomic metal cations,[2] anions,[3] and other highly coordinatively unsaturated complexes.[4] Much of the current activity in this still infant field has focused on atomic transition metal cations and small cationic metal fragments produced by laser desorption,[5] electron impact,[6] surface ionization,[7] or collision-induced dissociation of selected metal-ion precursors.[8]

Recently, we have applied the flowing afterglow technique to the study of larger molecular transition-metal complexes in the gas phase, with particular emphasis on anionic species which are known or postulated to exist in solution.[9] We wish to present here our studies of the gas-phase ion chemistry of two isomeric $(C_4H_6)Fe(CO)_3$ complexes, (trimethylenemethane)tricarbonyliron (1, $(TMM)Fe(CO)_3$) and butadienetricarbonyliron (2, $(BUD)Fe(CO)_3$), which were carried out with the aim of assessing the influence of differing organic ligands on the

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(1) For reviews see: (a) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967. (b) Gregor, I. K.; Guilhaus, M. *Mass Spectrom. Rev.* **1984**, *3*, 39. (c) Simoes, J. A. M.; Beauchamp, J. L. *Chem. Rev.*, in press.

(2) (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445. (b) Hanratty, M. A.; Illies, A. J.; Bowers, M. T.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 7484. (c) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484. (d) Huang, S. K.; Allison, J. *Organometallics* **1983**, *1*, 883.

(3) (a) Mead, R. D.; Stevens, A. E.; Lineberger, W. C. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1984; Vol. 3, Chapter 22. (b) Sallans, L.; Lane, K.; Squires, R. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 6352. (c) Sallans, L.; Lane, K. R.; Squires, R. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 4379. (d) Weil, D. A.; Wilkins, C. L. *J. Am. Chem. Soc.* **1985**, *107*, 7316.

(4) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819. (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Phys.* **1984**, *106*, 3891. (c) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 5870. (d) McDonald, R. N.; Chowdhury, A. K.; Jones, M. T. *J. Am. Chem. Soc.* **1986**, *106*, 3105, and references cited therein. (e) Lane, K. R.; Squires, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 6403. (f) McElvany, S. W.; Allison, J. A. *Organometallics* **1986**, *5*, 416, 1219.

(5) (a) Cody, R. B.; Burnier, R. C.; Reents, W. D., Jr.; Carlin, T. J.; McCrery, D. A.; Lengel, R. K.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 37–43. (b) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (c) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1229, 1235, 1238.

(6) (a) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332. (b) Radecki, B. D.; Allison, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 946.

(7) (a) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (b) Elkind, J. L.; Armentrout, P. B. *J. Chem. Phys.* **1986**, *84*, 4862.

(8) (a) Carlin, T. J.; Sallans, L.; Cassady, C. J.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 632. (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 4623.

(9) (a) Lane, K. R.; Lee, R. E.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 5767. (b) Lane, K. R.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *107*, 5369. (c) Lane, K. R.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 4368. (d) Lane, K. R.; Sallans, L.; Squires, R. R. *Organometallics* **1985**, *3*, 408.

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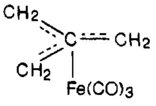
intrinsic (gas phase) properties and reactivity of simple organoiron complexes. We describe here a comparison of the gas-phase ion/molecule reactions of the parent molecular anions derived from these two isomers (1^-, 2^-) with series of neutral reagents, as well as a comparison of the reactions of 1 and 2 with a few negative ions. Estimates of the proton affinities of the two isomeric molecular anions are also presented, and the structural implications of these data are discussed.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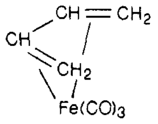
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Experimental Section

The majority of the experiments were carried out in a flowing afterglow (FA) apparatus, which we have described previously.[9] Briefly, the system is composed of a 100 cm × 7.3 cm i.d. flow reactor positioned between an electron impact ion source and a quadrupole mass spectrometer. A fast flow (ca. 90 m s^{-1}) of helium buffer gas maintained at relatively high pressure (0.2–1.0 torr) carries the ions generated in the source region through the reactor and rapidly cools them to a room temperature, thermal energy distribution. Neutral reactants are introduced into the flow tube through fixed or movable inlets located along the length of the reactor, and the steady-state ion composition is monitored by sampling ions of either charge through a small orifice (0.5 mm) into the quadrupole mass filter. Kinetic measurements and product distribution analyses were performed by using standard procedures.[10,11] Unless otherwise specified, the conditions used in all experiments were $P(\mathrm{He}) = 0.4$ torr, $F(\mathrm{He}) = 190$ STP $\mathrm{cm}^3\ \mathrm{s}^{-1}$, and $T = 296 \pm 2$ K.

Most of the reactant anions described in this work were generated via proton abstraction from the corresponding neutral acid by NH_2^- or OH^-. These precursor ions were generated by electron impact on NH_3 and an N_2O/CH_4 mixture, respectively. Hydride ion was generated by low-energy electron impact on reduced flow rates of NH_3 or CH_4 in the source region. Generally, SF_6 was added to the system just after the ion source to scavenge free electrons which might otherwise complicate the chemical or kinetic analyses.[9c,12] The experiments involving reactions of the neutral complexes were complicated by the relatively low volatility of the metal compounds. This not only precluded quantitative kinetics measurements due to the inability to reliably determine the required neutral flow rates but also made product identification difficult due to the excessive buildup of impurities in the system when the $(C_4H_6)Fe(CO)_3$ vapors were coaxed into the flow reactor with a heated inlet. Furthermore, the unavoidable presence of free electrons in the flow tube created occasional uncertainty as to the origins of the parent molecular ion signals which appeared in some of the mass spectra.

All reagents gases were obtained from commercial suppliers and were of the following purities: He, 99.995%; NH_3, 99.99%; N_2O, 99.0%; CH_4, 99.0%; CH_3CHCH_2, 99.0%; H_2S, 99.5%; CO_2, 99.5%; SO_2, 99.5%; NO, 99.5%; SF_6, 99.8%; O_2, 99.5%; CO, 99.5%. Liquid samples were also obtained commercially and were subjected to multiple freeze–pump–thaw cycles prior to use to remove dissolved gases. Butadienetricarbonyliron (2) was purchased from Alfa Products and used as supplied. (Trimethylenemethane)tricarbonyliron (1) was prepared from the reaction between 3-chloro-2-chloromethyl-1-propene and $Fe_2(CO)_9$ according to literature procedures.[13] Purification was achieved by vacuum distillation, and analysis of the IR and NMR spectra showed no significant impurities.

Table I. Fourier Transform Mass Spectra for Isomeric $(C_4H_6)Fe(CO)_3$ Complexes[a]

		complex/percentage	
m/z	ion	(TMM)Fe(CO)$_3$	(BUD)Fe(CO)$_3$
		Positive Ion	
194	$(C_4H_6)Fe(CO)_3^+$	19	7
166	$(C_4H_6)Fe(CO)_2^+$	12	26
138	$(C_4H_6)Fe(CO)^+$	5	10
112	$Fe(CO)_2^+$		7
110	$(C_4H_6)Fe^+$	21	17
84	$(C_2H_4)Fe^+/Fe(CO)^+$	5	14
82	$(C_2H_2)Fe^+$	27	
70	CH_2Fe^+	2	
56	Fe^+	9	19
		Negative Ion	
166	$(C_4H_6)Fe(CO)_2^-$	93	87
140	$Fe(CO)_3^-$		5
138	$(C_4H_6)Fe(CO)^-$	1	
84	$(C_2H_4)Fe^-/Fe(CO)^-$	4	
83	$(C_2H_3)Fe^-$		3
56	Fe^-	2	5

[a] Sample pressure ca. 1 × 10^{-6} torr, electron energy 70 eV, trapping time 200 μs.

Table II. Collision-Induced Dissociation Results for $(C_4H_6)Fe(CO)_2^-$ Ions Derived from 1 and 2

		source of $(C_4H_6)Fe(CO)_2^-$	
m/z	daughter ion	(TMM)Fe(CO)$_3$	(BUD)Fe(CO)$_3$
164	$(C_4H_4)Fe(CO)_2^-$		73
138	$(C_4H_6)Fe(CO)^-$	61	11
136	$(C_4H_4)Fe(CO)^-$		3
112	$Fe(CO)_2^-$		7
110	$(C_4H_6)Fe^-$	25	
84	$(C_2H_4)Fe^-/Fe(CO)^-$	9	3
82	$(C_2H_2)Fe^-$	4	
56	Fe^-	1	3

A few of the experiments utilized a Fourier transform mass spectrometer (FTMS) (prototype Nicolet FTMS-1000) for obtaining low-pressure electron impact (EI) mass spectra and collision-induced dissociation (CID) spectra for certain of the observed ions.[14] The system consists of a 2 in. cubic trapping cell and a 0.9-T electromagnet. Positive and negative ion mass spectra were recorded with a sample pressure of 1 × 10^{-6} torr and an electron energy of 70 eV with short trapping intervals prior to ion detection to minimize ion/molecule reactions. Collision-induced dissociation experiments were performed as described previously[14] using argon collision gas at ca. 5 × 10^{-6} torr. The CID pulse sequence begins with a quench pulse to remove all ions from the cell followed by electron impact ionization of the sample which is held at a static pressure of ca. 2 × 10^{-7} torr. The desired parent ion is isolated by double-resonance ejection of all other ions and then irradiated with an approximately 18-V CID pulse for 100 ms. A 100-ms time interval is then allowed for fragmentation of the translationally excited parent ion followed by the detection pulse and Fourier transformation to obtain the daughter ion mass spectrum.

Results and Discussion

I. Ion Formation and Structure. Positive ion EI mass spectra for 1 and 2 have been documented previously[15] and negative ion mass spectra for (BUD)Fe(CO)$_3$ and several other (η^4-diene)tricarbonyliron compounds have also been reported.[16,17] We have used an FTMS to

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(10) (a) Smith, D.; Adams, N. G. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1, Chapter 1. (b) Adams, N. G.; Smith, D. J. *J. Phys. B* **1976**, *9*, 1439.

(11) Anderson, D. R.; Bierbaum, V. M.; Depuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 4244.

(12) Streit, G. E.; Newton, T. W. *J. Chem. Phys.* **1980**, *73*, 3178.

(13) Ehrlich, K.; Emerson, G. F. *J. Am. Chem. Soc.* **1972**, *94*, 2464.

(14) (a) Cody, R. B.; Freiser, B. S. *Int. J. Mass. Spectrom. Ion Phys.* **1982**, *41*, 199–204. (b) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96–101.

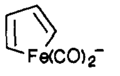
(15) (a) Emerson, G. F.; Ehrlich, K.; Giering, W. P.; Lauterbur, P. M. C. *J. Am. Chem. Soc.* **1966**, *88*, 3172. (b) Young, D. A. T.; Holmes, J. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1969**, *91*, 6968. (c) Butsugan, Y.; Yamashita, A.; Araki, S, *J. Organomet. Chem.* **1985**, *287*, 103.

(16) Blake, M. R.; Garnett, J. L.; Gregor, I. K.; Wild, S. B. *J. Organomet. Chem.* **1979**, *178*, C37.

collect both positive and negative ion mass spectra for each isomer as well as to perform CID experiments for a few of the more abundant EI fragment ions. The results are summarized in Table I and Table II. The fragmentation patterns exhibited in the EI mass spectra are in accord with those reported earlier,[15-17] except for minor differences in relative abundances owing to variations in instrumentation and experimental conditions.

Under low-pressure conditions (ca. 10^{-6} torr), 70-eV electron impact ionization of 1 and 2 results in significantly different fragmentations in the positive ion mode but only minor differences in the negative ion mode. Fragmentation reactions involving the organic ligand are observed in the case of $(TMM)Fe(CO)_3$ to give a pair of unusual ions, $FeCH_2^+$ and $FeC_2H_2^+$, while only consecutive elimination of neutral CO and butadiene ligands is observed for $(BUD)Fe(CO)_3$. Parent molecular anion formation is not observed with low-pressure EI on either isomer. Rather, the base peak is the $[M - CO]^-$ complex (m/z 166), formed by dissociative electron capture. This is the same type of behavior exhibited by $Fe(CO)_5$ and other mononuclear metal carbonyls.[18] Beyond loss of a single CO, very little fragmentation occurs.

Collision-induced dissociation experiments with either of the two $[M - CO]^-$ ions produces quite different results, as summarized in Table II. The $[M - CO]^-$ ion from $(BUD)Fe(CO)_3$ readily undergoes dehydrogenation to produce $(C_4H_4)Fe(CO)_2^-$ as the major daughter ion (73%), while that from $(TMM)Fe(CO)_3$ exhibits mainly sequential loss of CO. It is worthwhile to speculate about possible structures for the dehydrogenation product from $(BUD)Fe(CO)_2^-$ (i.e. **3**–**5**). Structure **3** could result from a (1,4) bis-insertion of the coordinatively unsaturated iron of the activated $[M - CO]^-$ ion into the ligand C–H bonds to produce an intermediate dihydride, $(\eta^2-C_4H_4)Fe(H)_2(CO)_2^-$, which subsequently eliminates a hydrogen molecule (eq 1). Insertion of transition metals into vinylic C–H bonds of organic ligands is precedented for coordinatively unsaturated neutral complexes in solution.[19] Moreover, several examples of neutral "ferroles" such as **6** and related complexes have been reported in which only the two terminal carbon atoms of a 1,3-diene chain are bonded to iron.[20] Subsequent rearrangement of **3** to either structure **4** or **5** (or both) may follow. However, the absence of $FeC_2H_2^-$ (m/z 82) in the CID spectrum makes structure **5** a less likely candidate. Also, while analogous (1,2)- and (2,3)-H_2 eliminations from the butadiene ligand to yield $(CH_2CHC{\equiv}CH)Fe(CO)_2^-$ and $(CH_2CCCH_2)Fe(CO)_2^-$ structures are also conceivable, they are considered unlikely due to the less favorable bonding to the $Fe(CO)_2$ fragment which would result.



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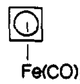

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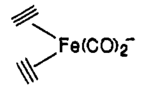

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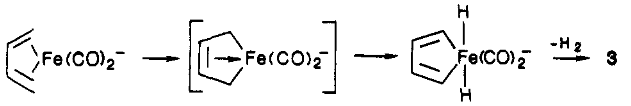

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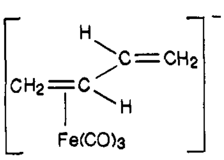
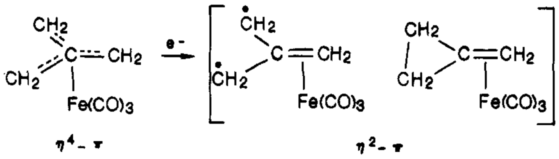
(1)

In a flowing afterglow, ionization is achieved at higher pressures (0.2–1.0 torr), so the electron energy distribution is significantly broader and fragmentation of primary ions is usually less evident. Accordingly, electron impact on each of the two complexes in the FA at 0.4 torr produces predominately the molecular anions $(C_4H_6)Fe(CO)_3^-$ (m/z 194) along with smaller amounts of $[M - CO]^-$ fragments. Gas-phase ion/molecule reactions of $[M - CO]^-$ and $[M - 2CO]^-$ ions from $(BUD)Fe(CO)_3$ formed in a flowing afterglow with an ion source operating with very high emission currents have been described recently by McDonald and co-workers.[21] Also, the solution chemistry of $(BUD)Fe(CO)_3^-$ (2^-) formed both under electrochemical conditions[22] and under dissolving alkali-metal conditions in ether[23] has been documented. The structure of the $(BUD)Fe(CO)_3^-$ ion observed in solution corresponds to the 17-electron $(\eta^2-C_4H_6)Fe(CO)_3^-$ complex illustrated below.[23] Here, slippage of the butadiene ligand from η^4-π to η^2-π occurs to accommodate the extra electron. This is qualitatively consistent with the fact that the lowest unoccupied molecular orbital of the neutral complex possesses considerable metal–olefin antibonding character. The corresponding molecular anion from $(TMM)Fe(CO)_3$ has not been observed in solution, nor are theoretical studies of this species currently available to guide in a structure assignment. Slippage of the TMM ligand from η^4-π to η^2-π accompanying addition of the extra electron would require hydrocarbon diradical character or formation of a methylenecyclopropane ligand (eq 2). Alternatively, bonding to this ligand in an η^3-π fashion may give rise to an 18-electron iron complex, while η^2-σ coordination as a metallocycle leads to a 17-electron structure:



2^-



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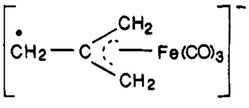
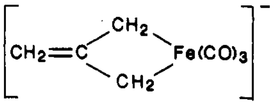


η^3-π



η^2-σ

As previously noted by McDonald and co-workers,[21] increasing the emission current at the ion source results in increased fragmentation of the $(BUD)Fe(CO)_3$ complex and production of two new metal ions at m/z 140 and m/z 138, which are assigned to $Fe(CO)_3^-$ and $(BUD)Fe(CO)^-$, respectively. Under these same conditions $(TMM)Fe(CO)_3$ gives fragment ions of the same nominal masses in addition to a metal ion which has expelled the last CO, i.e. $(C_4H_6)Fe^-$. At the highest emission current available with our source (10 mA), the fragment ion yields from $(TMM)Fe(CO)_3$ are $(TMM)Fe(CO)_3^-$ (74%), (TMM)Fe-

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(17) Blake, M. R.; Garnett, J. L.; Gregor, I. K. *J. Chem. Soc., Chem. Commun.* **1979**, 496.

(18) (a) Winters, R. E.; Kiser, R. N. *J. Chem. Phys.* **1966**, *44*, 1964. (b) George, P. M.; Beauchamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2959.

(19) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581.

(20) Hitchcock, P. B.; Mason, R. *Chem. Commun.* **1967**, 242.

(21) McDonald, R. N.; Schell, P. L.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 5578.

(22) Murr, N. E.; Payne, J. D. *J. Chem. Soc., Chem. Commun.* **1985**, *162*.

(23) Krusic, P. L.; Filippo, J. *J. Am. Chem. Soc.* **1982**, *104*, 2654.

Table III. Reactions of $(BUD)Fe(CO)_3^-$ and $(TMM)Fe(CO)_3^-$ with Dioxygen

reactant ion	k^{II}_{obsd} [a]	efficiency [b]	primary products	%	terminal ions [c]
$(TMM)Fe(CO)_3^-$	$(5.7 \pm 0.9) \times 10^{-11}$	0.095	$(TMM)Fe(CO)O^-$	9	
			$(TMM)FeO_2^-$	66	$FeO_{2,3,4}^-$
			$(TMM)FeO^-$	23	
			FeO^-	2	
$(BUD)Fe(CO)_3^-$	$(8.7 \pm 0.3) \times 10^{-12}$	0.015	$(BUD)Fe(CO)_3O_2^-$	11	$FeO_{2,3,4}^-$
			$Fe(CO)_3O_2^-$	12	
			$Fe(CO)_2O_2^-$	37	
			$Fe(CO)_2O^-$	40	

[a] In units of cm^3 $molecule^{-1}$ s^{-1}, representing an average of at least four measurements at different flow rates of the neutral substrate. Sufficient quantities of SF_6 are added downstream from the ion source to scavenge free electrons that might effect the measurement. [b] Efficiency = $k_{obsd}/k_{Langevin}$: Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Chapter 3. [c] Secondary and tertiary product ions appearing in the mass spectra at high O_2 flow rates.

$(CO)_2^-$ (22%), $(TMM)Fe(CO)^-$ (1%), and $(TMM)Fe^-$ (3%). When the flow rates of the two neutral complexes into the flow reactor are increased, large signals at *m/z* 360 and *m/z* 388 appear in the mass spectra due to condensation reactions between the parent anion and excess precursor (eq 3). These products were not further characterized.

$$(C_4H_6)Fe(CO)_3^- + (C_4H_6)Fe(CO)_3 \begin{cases} \xrightarrow{He} [Fe_2(C_4H_6)_2(CO)_6]^- \\ \xrightarrow{-CO} [Fe_2(C_4H_6)_2(CO)_5]^- \end{cases} \quad (3)$$

II. Reactions of $(BUD)Fe(CO)_3^-$ and $(TMM)Fe(CO)_3^-$ with Small Molecules. In the following sections, the gas-phase ion/molecule reactions of $(BUD)Fe(CO)_3^-$ and $(TMM)Fe(CO)_3^-$ with the neutral reagents O_2, CO_2, CS_2, SO_2, and NO are described. For these studies the molecular anions 1^- and 2^- were generated in the flowing afterglow source region with an applied emission current of ca. 20 μA and sample partial pressures of less than 0.001 torr. Under these conditions the parent ions represented 80%–90% of the total ion composition in the flow reactor, with the remainder being the $[M - CO]^-$ complexes.[24]

Oxidation with Dioxygen. We have recently described the extensive metal oxidation reactions that take place when simple metal carbonyl negative ions react with O_2 in the gas phase.[25] Products could be identified in these reactions which show that expulsion of both CO and CO_2 neutral fragments may accompany addition of O_2 to $M(CO)_n^-$ ions. In analogous reactions with $[C_4H_6{\cdot}Fe(CO)_3]^-$ ions, the interesting possibility arises for oxidation of the organic ligand by O_2, in addition to oxidation of the metal and CO.

$(BUD)Fe(CO)_3^-$ and $(TMM)Fe(CO)_3^-$ each undergo a relatively slow reaction with O_2 to yield an interesting array of mononuclear metal oxide product ions.[26] Organic oxyanions, such as might have arisen from direct oxidation of the organic ligand and maintenance of the negative charge, are not observed. The measured rates and product distributions for these reactions are summarized in Table III. Figure 1 illustrates the product ion yields for these

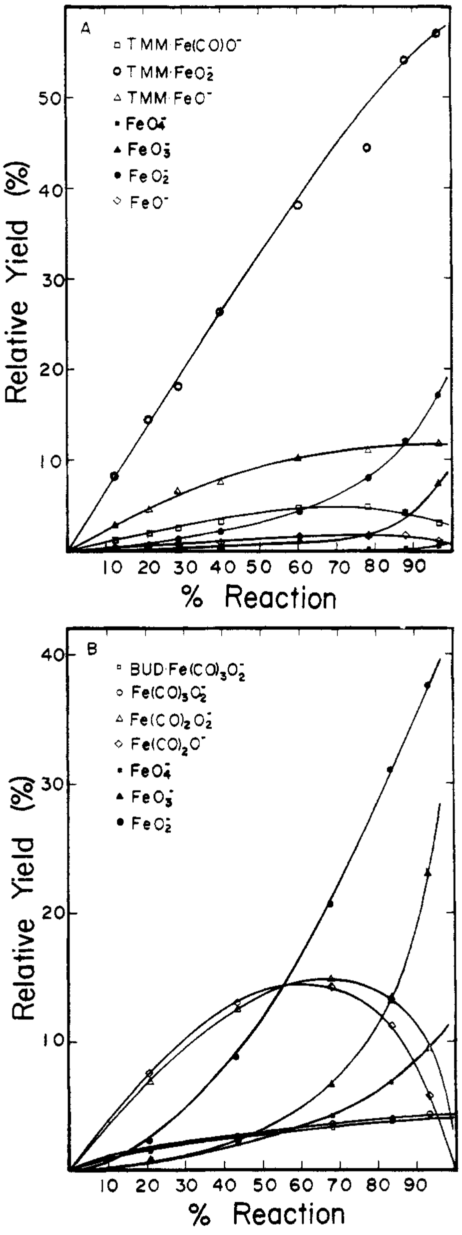

Figure 1. Product distribution plots for eactions of isomeric $(C_4H_6)Fe(CO)_3^-$ ions with dioxygen at 296 ± 2 K, *P*(He) = 0.40 torr; (A) $(TMM)Fe(CO)_3^-$ (TMM = trimethylenemethane); (B) $(BUD)Fe(CO)_3^-$ (BUD = 1,3-butadiene).

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[24] The $[M - CO]^-$ ion signals were carefully monitored during all ion/molecule reaction experiments involving the parent negative ions (M^-). These ions reacted with some reagents (e.g. $k \sim 5 \times 10^{-10}$ cm^3/s for SO_2) while with most others they were unreactive. The observed product ions reported in this paper are attributed to reactions of the parent ions based on their formation in far greater absolute yields than could be expected from the minor amounts of the $[M - CO]^-$ ions which were present initially. Moreover, in the case of oxidation with O_2, we have been able to confirm the origins of the observed product ions by carrying out this reaction in the collision chamber of a triple quadrupole system in which *only* the parent negative ions were present. It is worthwhile to note in this regard that the $[M - CO]^-$ ions most likely exist as 17-electron complexes in which the hydrocarbon ligand serves as a four-electron donor. Accordingly, they would not be expected to exhibit the enhanced reactivity which has been noted for more coordinatively unsaturated (< 17-electron) systems.[4,29]

[25] Lane, K. R.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2719.

[26] The actual bonding mode of the oxygen(s) in the observed products is not known. The structures shown are drawn by analogy with related compounds which have been examined spectroscopically in condensed phases. Cf. Almond, M. J.; Crayston, J. A.; Downs, A. J.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1986**, *25*, 19.

Table IV. Ligand Substitution and Addition Reactions of $(C_4H_6)Fe(CO)_3^-$ Ions

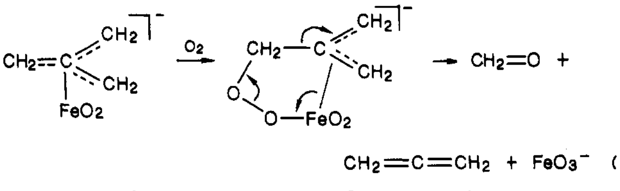
	$(TMM)Fe(CO)_3^-$				$(BUD)Fe(CO)_3^-$			
reactant	k_{obsd}^{II}	efficiency[a]	primary products	%	k_{obsd}^{II}	efficiency[a]	primary products	%
CO_2	0.024	0.0037	$(TMM)Fe(CO)_2(CO_2)^-$	100	<0.002	<0.0003[b]		
CS_2	0.187	0.019	$(TMM)Fe(CO)_2(CS_2)^-$	100	<0.002	<0.0002[b]		
SO_2	7.7	0.66	$(TMM)Fe(CO)_2(SO_2)^-$	55	5.1	0.44	$(BUD)Fe(CO)_2(SO_2)^-$	<1
			$Fe(CO)_3(SO_2)^-$	45			$Fe(CO)_3(SO_2)^-$	>99
NO	0.54	0.042	$(TMM)Fe(CO)_3(NO)^-$	68	0.20	0.01	$(BUD)Fe(CO)_3(NO)$	<1
			$(TMM)Fe(CO)_2(NO)^-$	21			$(BUD)Fe(CO)_2(NO)^-$	3
			$Fe(CO)_3(NO)$	11			$Fe(CO)_3(NO)^-$	>96
CO	*b*		$(Fe(CO)_4^-)$[c]		*b*		$(Fe(CO)_4^-)$[c]	

[a] Rate coefficients in units of 10^{-10} cm^3 molecule^{-1} s^{-1}. [b] Apparent rate below instrumental limit. [c] Trace product appearing in mass spectrum at high CO flow rates.

reactions in the form of plots of normalized ion abundance vs. percent conversion of the reactant ion.[11] $(TMM)Fe(CO)_3^-$ combines with dioxygen to yield $(TMM)FeO_2^-$ as the major primary product, corresponding the displacement of all three CO ligands in a single reactive encounter (eq 4). The other two significant primary products are

$$(TMM)Fe(CO)_3^- + O_2 \xrightarrow{66\%} (TMM)FeO_2^- + 3CO \qquad (4)$$

$(TMM)Fe(CO)O^-$ and $(TMM)FeO^-$, which correspond to displacement of one or two CO's and CO_2 (Figure 1A). Interestingly, $(BUD)Fe(CO)_3^-$ reacts some six times more slowly to yield an observable adduct $(BUD)Fe(CO)_3O_2^-$ and predominately iron carbonyl oxides in which the butadiene ligand is absent (Figure 1B). These latter ions are essentially the same as the primary products formed in reaction of O_2 with $Fe(CO)_4^-$.[25] Increasing the flow rate of O_2 results in further oxidation of the $(TMM)FeO_2^-$ ion to produce FeO_3^- and a smaller amount of FeO_4^-. It is instructive to consider the fate of the organic ligand in these secondary oxidation steps. While neutral products are not directly detected in our experiment, the formaldehyde and allene fragments shown in eq 5 represent the most mechanistically economical alternatives since hydrogen or carbon rearrangements are not required to produce them. The greater tendency to retain the C_4H_6 ligand in the primary product ions formed from $(TMM)Fe(CO)_3^-$ compared to $(BUD)Fe(CO)_3^-$ probably reflects the greater stability of 1,3-butadiene (ΔH_f = 26.3 kcal/mol)[27] compared to trimethylenemethane (ΔH_f = 58 kcal/mol)[28] (or methylenecyclopropane ΔH_f = 47.9 kcal/mol)[27] as a free ligand. That is, a larger barrier for oxidative displacement of the less stable TMM ligand is apparent. As will be shown later, this appears to be a general difference in the reactivity of these two ions under a variety of conditions.



(5)

Ligand Substitution and Addition. Ligand displacement and addition reactions of organometallic negative ions in the gas phase have been observed previously,[4d,4f,21,29] but not extensively documented. Table IV presents the measured rate coefficients and product distributions for reactions of the two $(C_4H_6)Fe(CO)_3^-$ ions with selected σ- and π-type ligand molecules. The $(BUD)Fe(CO)_3^-$ isomer is relatively unreactive compared to the TMM complex, exhibiting immeasurably slow reactions with CO_2 and CS_2 ($k_{obsd} \leq 2 \times 10^{-12}$ cm^3 s^{-1}). Under similar conditions the $(TMM)Fe(CO)_3^-$ isomer gives at least one ligand substitution with either neutral reactant wherein displacement of only CO occurs. The reaction of either isomer with CO is complicated by the unavoidable presence of reactive $[M - CO]^-$ ions in the system. That is, addition of large amounts of CO to the reactor through a downstream inlet produces no apparent decay in the $(C_4H_6)Fe(CO)_3^-$ signal intensity but does result in appearance of a product ion signal corresponding to $Fe(CO)_4^-$ (*m/z* 168). Here, the minor amount of $[M - CO]^-$ ion initially present (10%–20%) undergoes direct addition of CO to re-form the parent molecular anion, accounting for the absence of a significant decrease in the *m/z* 194 signal intensity (eq 6). Much slower displacement of the C_4H_6

$$\begin{tikzcd}
(C_4H_6)Fe(CO)_3 \arrow[r, "e^-"] & (C_4H_6)Fe(CO)_3^- \arrow[d, "CO"] & + & (C_4H_6)Fe(CO)_2^- \arrow[d, "CO"] & (6) \\
& Fe(CO)_4^- & & (C_4H_6)Fe(CO)_3^- \arrow[ll, "CO"'] &
\end{tikzcd}$$

ligand from the parent ion gives rise to $Fe(CO)_4^-$. It is noteworthy in this regard that Murr and Payne reported $Fe(CO)_4^-$ as the initially formed product of the reaction between 2^- and CO in solution; invoking a 19-electron $(\eta^2\text{-}C_4H_6)Fe(CO)_4^-$ complex as the probable intermediate.[22]

With the strong π-acceptor ligands NO and SO_2,[30] both isomers react, but exhibit marked differences in the distribution of product ions. For example, displacement of the hydrocarbon ligand is the nearly exclusive reaction channel for $(BUD)Fe(CO)_3^-$ with both NO and SO_2 but represents only a minor channel for $(TMM)Fe(CO)_3^-$. As in the dioxygen reactions, stronger binding of the TMM ligand to the metal compared to the BUD ligand is suggested by these results. We can make several conclusions regarding the displacement mechanisms and product ion structures based on the observed trends in the data shown in Table IV. First of all, it is necessary to emphasize that dissociative ligand substitution mechanisms such as are common in solution[30,31] are not likely for these gas-phase ion/molecule reactions since the latter are strictly bimolecular processes involving thermalized reactants with constant total energy. That is, a prior "unimolecular" ligand dissociation step from $(C_4H_6)Fe(CO)_3^-$ cannot occur once these ions are formed and thermalized in the up-

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[27] Pedley, J. B.; Rylance, J. *Sussex-N.P.L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex: Sussex, 1977.

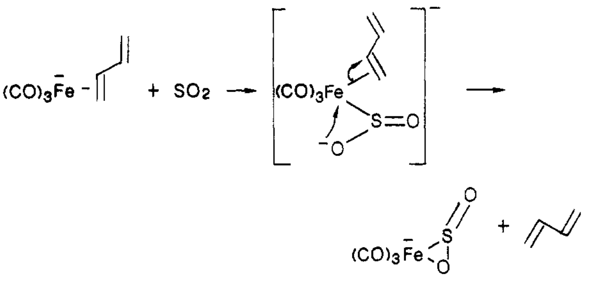
[28] Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. I, Chapter 5.

[29] (a) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808. (b) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1977**, *16*, 3135. (c) McDonald, R. N.; Schell, P. L.; McGhee, W. D. *Organometallics* **1984**, *3*, 182. (d) McDonald, R. N.; Chowdhury, A. K.; Schell, P. L. *J. Am. Chem. Soc.* **1984**, *106*, 6095.

[30] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry; A Comprehensive Text*, 4th ed.; Wiley: New York, 1980, Chapter 25.

[31] (a) Dobson, G. R. *Acc. Chem. Res.* **1976**, *9*, 300. (b) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, 1985.

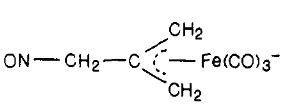
stream source end of the flow tube. In considering the several alternatives for the obligatory associative mechanism, we note that each of the reactive substrates, with the exception of CO, can bind to the electron-rich metal center in $(C_4H_6)Fe(CO)_3^-$ as a Lewis acid η^1-ligand with subsequent conversion to η^2. Equation 7 illustrates our view of the addition–elimination mechanism for $(BUD)Fe(CO)_3^-$ and SO_2 wherein initial attack by the nucleophilic metal yields a pyramidal η^1-SO_2 ligand.[32] Subsequent or



(7)

concerted internal displacement of the labile butadiene occurs to give the 17-electron η^2-SO_2 product. Associative interchange (I_a) or ligand slippage mechanisms are also conceivable;[22,31] however the trends exhibited in Table IV seem more consistent with a stepwise mechanism. For example, sulfur dioxide generally acts as a more potent electrophile than both CO_2 and CS_2 toward nucleophilic addition reactions involving negative ions in both the gas phase[33] and solution.[34] Wojcicki and co-workers have found this to be so with a variety of low-valent transition-metal complexes in solution, including $Na^+[(C_5H_5)Fe(CO)_2]^-$.[35] This is likely to be a thermodynamic effect since it is known from recent gas-phase equilibrium experiments that the negative ion binding energies of these Lewis acids generally increase in the order $CS_2 \leq CO_2 \ll SO_2$.[36] The order of reaction efficiencies with $(TMM)Fe(CO)_3^-$ listed in Table IV parallels this thermodynamic order. The fact that the $(BUD)Fe(CO)_3^-$ complex failed to react with either CO_2 or CS_2 while the $(TMM)Fe(CO)_3^-$ isomer reacted slowly by exclusive CO displacement further suggests that the initial addition step (analogous to that shown for SO_2 in eq 9) is *rate* determining, but the internal displacement step is *product* determining. That is, once the adduct forms, it decomposes by the ligand dissociation channel with the lowest barrier. For the $(TMM)Fe(CO)_3^-$ isomer, this corresponds to CO loss, but for $(BUD)Fe(CO)_3^-$, the η^2-butadiene is expelled. As the initial excess internal energy attending adduct formation increases across the series $CO_2 < CS_2 < SO_2$, loss of TMM eventually becomes accessible.

Similar mechanistic features can be used to describe the NO reactions. However, in this case initial binding occurs via a bent, one-electron-donor nitrosyl, with subsequent displacement of either C_4H_6 or CO from iron attending conversion to a linear, three-electron-donor nitrosyl.[30,37] The appearance of a stabilized NO adduct with $(TMM)Fe(CO)_3^-$ is especially interesting since it suggests that either a barrier exists for the bent/linear nitrosyl interconversion[37] or, alternatively, the NO may add to the TMM ligand to produce a structure like **7**. Anionic π-allyl

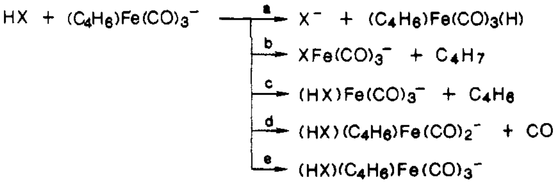


7

iron carbonyls related to **7** are well-known species in solution.[38] The almost exclusive displacement of butadiene in $(BUD)Fe(CO)_3^-$ by NO may suggest that addition to the metal is favored in this case.

III. Acid–Base Reactions. Molecular Anions. The reactions of $(BUD)Fe(CO)_3^-$ and $(TMM)Fe(CO)_3^-$ with a series of reference acids possessing known gas-phase acidities have been examined with the results summarized in Table V. Proton affinity estimates for the two ions may be derived from these results, provided the following caveat: the occurrence of proton transfer in one direction only can be monitored in these experiments since the corresponding neutral conjugate acids, $(C_4H_6)Fe(CO)_3(H)$, which would be required to study the reverse reactions (or proton transfer equilibria) are not available. If it can be shown independently that nonoccurrence of proton transfer is due only to reaction endothermicity and not extraordinary kinetic factors, then reliable bracketing of the metal ion proton affinity can be achieved.[39] With the present systems, several of the reference acids reacted to give other ionic products and, therefore, it must be noted that "nonoccurrence" of proton transfer could be due to faster competing channels rather than proton transfer endothermicity.

The ionic products produced in reactions of either anion with Bronsted acids can all be identified as coming from one of the five pathways shown below (eq 8). Path a



$$\begin{aligned} \mathrm{HX} + (\mathrm{C_4H_6})\mathrm{Fe(CO)_3^-} &\xrightarrow{a} \mathrm{X^-} + (\mathrm{C_4H_6})\mathrm{Fe(CO)_3(H)} \\ &\xrightarrow{b} \mathrm{XFe(CO)_3^-} + \mathrm{C_4H_7} \\ &\xrightarrow{c} (\mathrm{HX})\mathrm{Fe(CO)_3^-} + \mathrm{C_4H_6} \\ &\xrightarrow{d} (\mathrm{HX})(\mathrm{C_4H_6})\mathrm{Fe(CO)_2^-} + \mathrm{CO} \\ &\xrightarrow{e} (\mathrm{HX})(\mathrm{C_4H_6})\mathrm{Fe(CO)_3^-} \end{aligned} \quad (8)$$

Table V. Protonation Reactions of $(C_4H_6)Fe(CO)_3^-$ Ions

		$(TMM)Fe(CO)_3^-$		$(BUD)Fe(CO)_3^-$	
acid (HX)	ΔH_{acid}[a] (HX)	proton transfer obsd	other products[b]	proton transfer obsd	other products[b]
CF_3CO_2H	322.7	yes		yes	
$CH_3C(Cl)HCO_2H$	336.4	yes		yes	d
HCO_2H[c]	345.2	yes	b, d	yes	d
$C_2H_5CO_2H$	347.3	yes	b, d	no	d
$(CF_3)_2CHOH$	348.4	yes		no	d, e
CH_3CO_2H	348.5	yes	b, d	no	c, d
C_6H_5OH	349.8	yes	b, d	no	c
CH_3COCF_3	350.3	no		no	
H_2S[d]	353.5	no	b, c, d	no	
C_2H_5SH	357.4	no	b, d, e	no	
CF_3CH_2OH	364.4	no	b, d, e	no	
CH_3COCH_3	368.8	no		no	

[a] In units of kcal/mol, ref 39. [b] Product channel from eq 8. [c] k(total) = 8.3×10^{-10} cm^3/s for $(TMM)Fe(CO)_3^-$ and 4.4×10^{-11} cm^3/s for $(BUD)Fe(CO)_3^-$. [d] k(total) = 3.3×10^{-10} cm^3/s for $(TMM)Fe(CO)_3^-$.

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(32) Ryan, R. R.; Kubas, G. T.; Moody, D. C.; Eller, P. G. *Struct. Bonding (Berlin)* **1981**, *46*, 47.

(33) DePuy, C. H. *Org. Mass Spectrom.* **1985**, *20*, 556.

(34) Pearson, R. G., Ed. *Hard and Soft Acids and Bases*; Dowden, Hutchinson and Ross: Stroudsburg, PA, 1973.

(35) Reich-Rohrwig, P.; Clark, A. C.; Down, R. L.; Wojciki, A. *J. Organomet. Chem.* **1978**, *145*, 57.

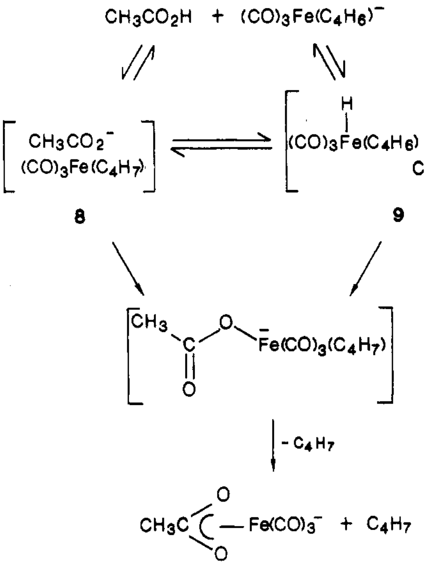
(36) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766.

(37) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; p 144.

(38) *Gmelin Handbook of Inorganic Chemistry, Organoiron Compounds*, part B5; Slawisch, A., Ed.; Springer-Verlag: Berlin, 1978.

(39) Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, Chapter 11.

Scheme I



corresponds to proton transfer (protonation site unspecified) and path b corresponds to proton transfer accompanied by hydrocarbon displacement by the conjugate base X^-. A plausible mechanism for this latter reaction is outlined in Scheme I using CH_3CO_2H as an example. Initial protonation can occur either at the metal or at the hydrocarbon ligand (vide infra). Facile interconversion of the resulting species (**8** and **9**) may be expected based on the documented facility with which olefin hydride complexes rearrange to metal alkyls in solution.[30,40] The C_4H_7 fragment could be bound to iron as an η^3-π-allyl ligand in either the BUD or TMM intermediate. The conjugate base anion of the attacking acid remains in the collision complex long enough to add to iron, necessitating a reduction in the bond order between the metal and the hydrocarbon ligand (slippage). In the case of acetic acid, intramolecular displacement of the hydrocarbon radical may then occur with the formation of a stabilized, 18-electron carboxylato complex.[41] This last step appears to be a common reaction which we have encountered previously in our studies of the gas-phase reactions of $XFe(CO)_3^-$ (X = H, OH, NH_2) ions with carboxylic acids.[42] Analogous mechanisms can be drawn for reaction 8b involving the alcohols shown in Table V. Pathways 8c and 8d correspond to substitution by the attacking acid of the hydrocarbon and CO ligands, respectively. Given the occurrence of the protolytic substitution channel 8b for many of the reactive systems, it is likely that paths 8c and 8d also procede via initial proton transfer. That is, the HX moiety of the products may not be intact as shown.

The observed thresholds for appearance of conjugate base anions from the series of reference acids differ for $(BUD)Fe(CO)_3^-$ and $(TMM)Fe(CO)_3^-$. The weakest acid for which proton abstraction by $(BUD)Fe(CO)_3^-$ is directly observed is HCO_2H (ΔH_{acid} = 345 ± 2 kcal/mol),[39] while for $(TMM)Fe(CO)_3^-$ it is C_6H_5OH (ΔH_{acid} = 350 ± 3).[39] The actual proton affinities of the two metal ions may actually be greater than these apparent thresholds since many of the weaker acids not showing proton transfer did yield other products. However, we can reasonably conclude that the $(TMM)Fe(CO)_3^-$ isomer possesses an approximately 4–5 kcal/mol greater proton affinity than $(BUD)Fe(CO)_3^-$. In attempts to determine whether protonation occurs on the hydrocarbon ligand in the two ions, we examined their reactions with the deuteriated acids CH_3OD, CH_3CO_2D, and EtSD, reasoning that reversible hydrocarbon protonation should manifest in observable H/D exchange.[43] However, no reaction at all was observed with CH_3OD, and no H/D exchange with either CH_3CO_2D or EtSD could be detected in either of the reactant $(C_4H_6)Fe(CO)_3^-$ ions nor any of the other metal ion products. EtSD can be shown independently to effect H/D exchange in cyclopentadienyl anion (PA = 355 ± 2 kcal/mol);[39] however it does so only very slowly. Therefore, the absence of H/D exchange with EtSD and the metal ions may not be definitive. The fact that the bracketed proton affinities for these two metal ions are some 25 kcal/mole *greater* than that which has been determined for $Fe(CO)_4^-$ (PA = 321 ± 5 kcal/mol)[44] argues for ligand protonation. Otherwise, an extraordinary substituent effect (CO vs. η^2-C_4H_6) on metal anion basicity would be necessary to account for our results. It is worthwhile to note in this regard that Murr and Payne recently found that the electrochemically generated $(BUD)Fe(CO)_3^-$ complex undergoes protonation with both water and phenol in tetrahydrofuran solution.[22] The initially formed product could be further reduced to yield (η^3-1-methylallyl)$Fe(CO)_3^-$. It was assumed (but not proven) that initial protonation occurs at the metal, with eventual hydrogen migration to the coordinated butadiene ligand. Reactions of dienyliron anions with other electrophiles such as alkyl and acyl halides in solution are generally believed to proceed by attack at the metal.[45] Suffice it to say here that the greater apparent basicity of $(TMM)Fe(CO)_3$ compared to $(BUD)Fe(CO)_3^-$, irrespective of protonation site, is consistent with the observed greater reactivity of the former ion in the oxidation and ligand substitution reactions described earlier. The origin of this difference is not immediately obvious and we are presently exploring the utility of MO calculations with the anionic complexes and their conjugate acids to help provide a rationale.

Neutral Complexes. The gas-phase reactions of both neutral complexes with a few simple organic and inorganic negative ions were briefly investigated in order to look for further differences the isomeric organic ligands may make in nucleophilic addition and proton transfer reactions.

In general, negative ions react with the two complexes by proton abstraction, electron transfer, and/or nucleophilic addition/fragmentation reactions similar to those that we have recently described for $Fe(CO)_5$.[9c] Proton abstraction occurred from both isomers with the strongly basic anions NH_2^- (PA = 403.6 kcal/mol),[39] H^- (PA = 400.4 kcal/mol),[39] and OH^- (PA = 390.7 kcal/mol),[39] yielding a $(C_4H_5)Fe(CO)_3^-$ product ion (*m/z* 193). Electron transfer and dissociative electron transfer could be shown to occur for both isomers with H^- (EA = 17.4 kcal/mol),[46] NH_2^- (EA = 17.2 kcal/mol),[46] and $CH_2CHCH_2^-$ (EA = 8.4 kcal/mol)[47] by noting the appearance of the $(C_4H_6)Fe(CO)_n^-$ (*n* = 2, 3) product ions when operating with low emission currents at the ion source and with added SF_6 in the flow reactor

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[40] Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.

[41] (a) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685. (b) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1974**, *22*, 129.

[42] Lane, K. R. Ph.D. Thesis, Purdue University, 1986.

[43] (a) Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650. (b) DePuy, C. H.; Bierbaum, V. M.; King, G. K.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2921. (c) Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185.

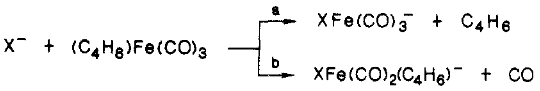
[44] Stevens, A. E.; Beauchamp, J. L., private communication.

[45] (a) Williams, G. M.; Rudisill, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 3357. (b) Timmers, F.; Brookhart, M. *Organometallics* **1985**, *4*, 1365.

[46] Janousek, B. K.; Brauman, J. I. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, Chapter 10.

[47] Oakes, J.; Ellison, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7734.

to act as a free electron scavenger. Hydride, amide, and hydroxide each reacted with (BUD)Fe(CO)$_3$ to form condensation product ions by displacement of both CO and the butadiene ligand (eq 9); however for the (TMM)Fe(CO)$_3$ isomer only path 9b for H^- could be identified unambiguously in the product ion mass spectrum. Allyl anion also reacted with (BUD)Fe(CO)$_3$ by displacement of the hydrocarbon ligand, in this case producing the (η^3-C_3H_5)Fe(CO)$_3^-$ complex[38] (eq 10). Problems associated with the low volatility of the organometallic complexes were especially acute with the (TMM)Fe(CO)$_3$ samples, and additional experiments were performed only with the (BUD)Fe(CO)$_3$ isomer. Proton abstraction from **2** was also observed with $CH_3C(O)CH_2^-$ (PA = 368.8 kcal/mol),[39] CH_2CN^- (PA = 372.1 kcal/mol),[39] $CH_2NO_2^-$ (PA = 358.7 kcal/mol),[39] and $C_6H_5O^-$ (PA = 349.8 kcal/mol),[39] but not with $CH_2CHCH_2^-$ (PA = 391.3 kcal/mol),[48] N_3^- (PA = 344.2 kcal/mol),[49] or Cl^- (PA = 333.4 kcal/mol).[39] From the occurrence of proton abstraction by phenoxide we can infer that $\Delta H_{\text{acid}}((\text{BUD})\text{Fe(CO)}_3) < 350$ kcal/mol. Interestingly, in attempts to refine this limit with protonation studies involving reference acids, we found that only CF_3CO_2H ($\Delta H_{\text{acid}} = 322.7$ kcal/mol)[39] would readily affect neutralization of the (C_4H_5)Fe(CO)$_3^-$ ion. This may indicate that rearrangement of the negative ion occurs to produce a weaker base than the initially formed conjugate anion.



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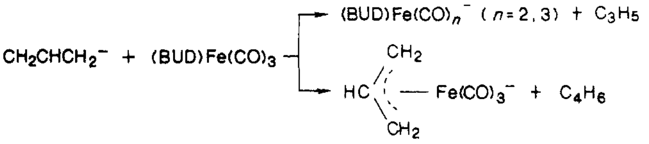

(10)

Conclusions

Significant differences in the mass spectra, collisional activation spectra, and gas-phase ion/molecule reactions are found for the tricarbonyliron complexes of 1,3-butadiene and trimethylenemethane. In general, the molecular anion of the TMM complex exhibits greater reactivity toward oxidation and ligand displacement reactions than does the BUD isomer and appears to possess stronger iron–hydrocarbon bonding. The gas-phase proton affinity of the (TMM)Fe(CO)$_3^-$ anion is found to be 4–5 kcal/mol greater than that for (BUD)Fe(CO)$_3^-$. Additional studies are planned to determine the site of protonation in the molecular anions, as well as to further characterize the negative ion/molecule reactions of the neutral complexes.

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Registry No. **1**, 12078-33-0; **2**, 12078-32-9; **2⁻**, 81277-11-4; (TMM)Fe(CO)$_3^-$, 107302-32-9.

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(48) Mackay, G. I.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Can. J. Chem.* **1978**, *56*, 131.

(49) Pellerite, M. J.; Jackson, R. L.; Brauman, J. I. *J. Phys. Chem.* **1981**, *85*, 1624.