measurements are currently in progress.

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Protonation Sites in Thiolato Iron Carbonylates: Evidence for an Arrested Fe(RS–H) Oxidative Addition

Marcetta Y. Darensbourg,* Wen-Feng Liaw, and
Charles G. Riordan

Department of Chemistry, Texas A&M University
College Station, Texas 77843

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The recently synthesized series of iron thiolate complexes *trans*-$RSFe(CO)_3L^-$[1] and selenium analogues[2] contains particularly interesting functional groups, RSFe or RSeFe, in which both the chalcogen and the iron center are potential sites of reactivity with electrophiles. The Mulliken atomic charges derived from Fenske–Hall calculations[3] roughly quantify charge distribution in the complexes $MeSFe(CO)_4^-$ ($\delta_-(S) = -0.43$; $\delta_-(Fe) = -0.22$) and *trans*-$MeSFe(CO)_3PH_3^-$ ($\delta_-(S) = -0.45$; $\delta_-(Fe) = -0.29$). The sensitivity of charge distribution to substituents on sulfur[4] is noted in $PhSFe(CO)_4^-$, where the charges on S and Fe are almost equal ($\delta_-(S) = -0.28$ and $\delta_-(Fe) = -0.23$) and similar to that of H and Fe in $HFe(CO)_4^-$ ($\delta_-(H) = -0.22$; $\delta_-(Fe) = -0.26$).[5] The latter anion forms a dihydride on protonation, $H_2Fe(CO)_4$, and its P-donor substituted derivatives $H_2Fe(CO)_3PR_3$ are stabilized relative to the all-carbonyl derivative.[6] The thermodynamic dihydride product does not necessarily reflect the initial, presumably charge-controlled, collision complex. Nevertheless, the negative charge on Fe is available for transformation into an additional Fe–H bond as the electron-rich d^8 Fe(0) in trigonal bipyramidal (TBP) $HFe(CO)_4^-$ is converted into the d^6 Fe(II) in O_h $H_2Fe(CO)_4$. The similar stabilities of $HFe(CO)_3L^-$ and $REFe(CO)_3L^-$ (E = S, Se) raised the question of whether examples of iron hydrido thiolates $(RS)(H)Fe(CO)_3L$ might be prepared, or if all reactions with electrophiles should occur only at the more accessible, electron-rich sulfur site. The results presented below demonstrate *both possibilities* as well as evidence for a three-center η^2-Fe(RS–H) bond, arrested[7,8] along its way to an oxidative addition product.

The carbonyl stretching frequencies, ν(CO), for various $RSFe(CO)_3L^-$ in Table I reflect expected changes as the donor abilities of RS^- (MeS > PhS) and L ($PEt_3 > P(OEt)_3 >$ CO) are varied. In contrast to the anionic acyls $RC(O)Fe(CO)_4^-$, where metal site vs ligand (acyl oxygen) site reactivity depends on choice of alkylating agent,[10] reaction of all entries of Table I with either soft or hard alkylating agents resulted in formation of neutral, hexane-soluble thioether or selenoether derivatives, $(RER')Fe(CO)_4$.[1] Such reactions are characterized by moderate increases in ν(CO) values consistent with formation of the neutral Fe(0) carbonyls, eq 1. There was no indication of iron-site alkylation.

$$\underset{\substack{2016\ (w),\\ 1910\ (s)\ cm^{-1}}}{PhSFe(CO)_4^-} \xrightarrow{\text{MeI or } Me_3O^+} \underset{\substack{2054\ (m),\\ 1969\ (m),\\ 1946\ (s)\ cm^{-1}}}{(PhSMe)Fe(CO)_4} \quad (1)$$

$$2[PPN][PhSFe(CO)_4] + 2HBF_4 \xrightarrow{-78\ °C} H_2 + (\mu\text{-}PhS)_2Fe_2(CO)_6 + 2CO + 2[PPN][BF_4] \quad (2)$$

Protonation of the phenyl thiolate complex at −78 °C formally oxidizes the iron(0) to iron(I), forming the well-known dimer,[11] with elimination of H_2, eq 2. When the protonation reaction was carried out with the more electron rich derivatives listed in Table I, thermally unstable intermediates could be detected by ν(CO) IR and ^{1}H NMR spectroscopy in the temperature range of −78 to −30 °C. The ν(CO) IR spectral shifts to higher energies of ca. 50 cm^{-1}, for protonation of **1**$^-$, are similar to those observed for the alkylation reaction, eq 1, and consistent with protonation at sulfur. The chemical shift of the complexed thiol, MeS–H = 2.4 ppm, is shifted ca. 0.6 ppm downfield from that of the free thiol.[12] Successive addition of Et_3N and HBF_4 permitted reformation of the thiolato anion and thiol derivatives without degradation at −78 °C, eq 3. Upon warming of the solution of $(RSH)Fe(CO)_4$ (R = Me, Et), decomposition yielding hydrogen and thiolato-bridged dimers analogously to eq 2 occurred with no intermediates observed.

In contrast, **2H** and **3H** showed no resonances attributable to a metal-bound thiol, but rather upfield doublets in the −7 to −8-ppm "hydride" region with splittings similar to the J_{H-P} values earlier observed for $HFe(CO)_3P(OEt)_3^-$ and $H_2Fe(CO)_3P(OEt)_3$.[13,14] At similar temperatures,[9] the ν(CO) showed increases in the average ν(CO) values over that of the anion precursors of ca. 150 cm^{-1}, also consistent with the $HFe(CO)_3P(OEt)_3^-$ protonation, eq 4.[14]

$$\underset{R\,=\,Me,\ Et}{RSFe(CO)_4^-} \underset{NEt_3}{\overset{HBF_4}{\rightleftharpoons}} (HSR)Fe(CO)_4 \quad (3)$$

$$\underset{\mathbf{2^-}}{PhSFe(CO)_3P(OEt)_3^-} \xrightarrow{HBF_4} \underset{\mathbf{2H}}{(H)(PhS)Fe(CO)_3P(OEt)_3} \quad (4)$$

The observation of two hydride resonances in the ^{1}H NMR spectrum for the complex **2H** is interpreted as indicative of two isomeric forms, consistent with the difference in J_{H-P} values of the two species[15] and by comparison to analogous derivatives of $(H)(Ph_3Si)Fe(CO)_3PPh_3$.[16,17] These latter complexes also have average ν(CO) values near 2000 cm^{-1} and high-field hydride resonances at −9 to −10 ppm.

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[2] [PPN][*trans*-$MeSeFe(CO)_3(P\{OEt\}_3)$] was prepared by reaction of [PPN][$HFe(CO)_3(P\{OEt\}_3)$] with Me_2Se_2 analogous to the synthesis of [PPN][*trans*-$PhSFe(CO)_3(P\{OEt\}_3)$] described in ref 1.

[3] Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768. Bond distances and angles were taken from the crystal structure of [PPN][$PhSFe(CO)_4$][1] and from the following: Ash, C. E.; DeLord, T.; Simmons, D.; Darensbourg, M. Y. *Organometallics* **1986**, *5*, 17.

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[9] (a) These IR spectra were measured on samples extracted from −78 °C solutions into a precooled syringe and loaded into a precooled cell. The exact temperatures were not known. (b) Precise low-temperature measurements were carried out by using a NaCl IR cell mounted on a brass block cooled to −78 °C in dry ice, and the sample was injected into the cell by using a precooled syringe. The temperature was measured with a thermocouple during data collection.

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[12] The ^{1}H NMR resonance of MeS–H in acetone-d_6 is 1.78 ppm.

[13] ^{1}H NMR: −10.3 ppm (d, J_{H-P} = 61.5 Hz) in acetone-d_6 for $H_2Fe(CO)_3P(OEt)_3$.[6b]

[14] Ash, C. E.; Darensbourg, M. Y.; Hall, M. B. *J. Am. Chem. Soc.* **1987**, *109*, 4173.

[15] The ^{31}P NMR spectra in THF solution also showed two major products at 153.4 ppm (d, J_{H-P} = 67 Hz) and 171.4 ppm (d, J_{H-P} = 57 Hz) vs H_3PO_4.

[16] (a) Bellachioma, G.; Cardaci, G.; Colomer, E.; Corriu, R. J. P. *Inorg. Chem.* **1989**, *28*, 519. (b) Bellachioma, G.; Cardaci, G. *Inorg. Chem.* **1982**, *21*, 3232.

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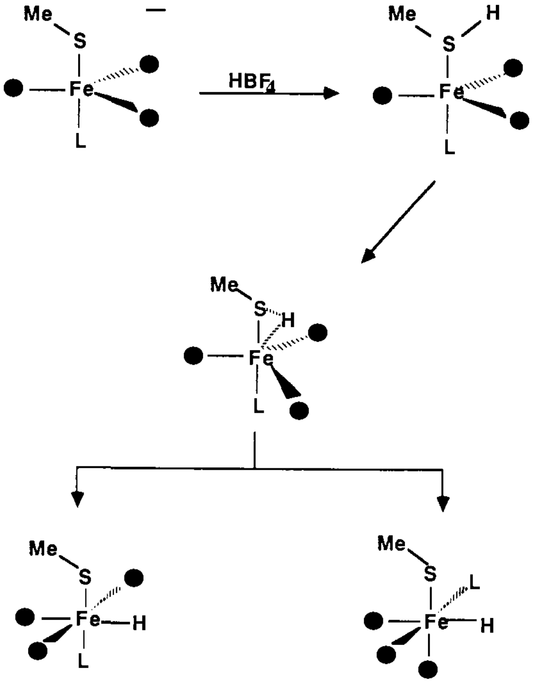
Table I. Spectral Parameters of *trans*-$REFe(CO)_3L^-$ and Protonated Derivatives

		anion				protonated derivatives		
entry		R	E	L	$\nu(CO)^a$		$\nu(CO)^e$	^1H NMR (ppm) (acetone-d_6)^j
1	**1**$^-$	Me	S	CO	2007 (w), 1899 (vs)^b	**1H**	2053 (m), 1966 (m), 1944 (s)^f	2.35
2	**2**$^-$	Ph	S	$P(OEt)_3$	1957 (vw), 1865 (vs)^c	**2H**	2076 (m) (2019 (sh), 2013 (s))^g	−7.22 (d, J_{H-P} = 67 Hz), −7.48 (d, J_{H-P} = 57 Hz)
3	**3**$^-$	Me	Se	$P(OEt)_3$	1950 (vw), 1851 (vs)^c	**3H**	2067 (m) (2006 (sh), 2001 (s))^f	−8.20 (d, J_{H-P} = 56.5 Hz)
4	**4**$^-$	Me	S	$P(OEt)_3$	1952 (vw), 1851 (vs)^c	**4H**	1997 (w) (1895 (s), 1890 (s))^f	−7.65 (d, J_{H-P} = 58.5 Hz)
5	**5**$^-$	Me	S	PEt_3	1934 (vw), 1838 (vs), 1821 (s)^d	**5H**	1870 (vs) (2050, 2000, 1980)^h	−7.88 (d, J_{H-P} = 40.7 Hz)
						5H	2050 (m) (2000 (s), 1980 (vs))^i	−7.70 (d, J_{H-P} = 42 Hz),^{k} −7.97 (d, J_{H-P} = 40 Hz)^k

[a] THF solution spectra of PPN^+ salts except entry **5**$^-$, which is $[Et_4N][MeSFe(CO)_3PEt_3]$. [b] Spectrum measured at 22 °C. [c] Ca. 0 °C. [d] Ca. −20 °C. [e] THF soluton spectra. [f] Temperature −30 °C, see ref 9a. [g] Temperature −50 °C, see ref 9b. [h] Temperature −57 °C; the species at 1870 cm^{-1} is ca. twice the intensity of the remaining bands. At 0 °C, the relative ratio is reversed. [i] Ca. 0 °C. [j] Varian XL, 400 MHz, spectra measured at −78 °C, except where noted. [k] Spectra measured at −20 °C.

Scheme I



Entries 4 and 5 of Table I are illustrative of attempts to more delicately balance electrophilic site competition. At −78 °C, the ^1H NMR spectrum of **5H** had only one resonance in the high-field region, −7.88 ppm, with J_{H-P} = 40.7 Hz. Although persistent at −78 °C, this resonance decayed on warming, with formation of two new doublets centered at −7.70 ppm (J_{H-P} = 42 Hz) and −7.97 ppm (J_{H-P} = 40 Hz). By −20 °C, the −7.88-ppm doublet was barely visible. On cooling to −78 °C again, the original spectrum did not reappear. The reasonable assumption that the species giving rise to the initial doublet was the kinetic product of a hydride that isomerized into more stable forms at higher temperatures was not corroborated by IR spectral studies. At the lowest temperature that can be achieved in our labs for IR spectral analysis, −57 °C, the predominate product resulting from protonation of $MeSFe(CO)_3(PEt_3)^-$ clearly matched that of an Fe(0) rather than Fe(II) product![18] On warming, the band at 1870 cm^{-1} disappeared, with concomitant formation of a spectrum similar to that observed for **2H** and **3H**, i.e., that of a hydrido thiolate derivative. The hydrido thiolate did not reconvert to the **5H** complex upon subsequent lowering of the temperature.

The scenario presented in Scheme I accounts for the spectral observations of the protonation of **5**$^-$ and invokes the first example of an S–H bond "arrested"[7,8] in its path toward oxidative addition. The high-field resonance for the η^2 (RS–H) proton is entirely consistent with what has been observed for three-center M, H, Si bonding in complexes such as $(\eta^6\text{-}C_6Me_6)(CO)_2\overline{Cr(H)Si}Ph_2H$ (Cr(Si–H) = −11.5 ppm)[19] and the agostic C–H interaction in $(CO)_3(\eta^3\text{-}C_6H_9)Mn$ (Mn(C–H) = −12.8 ppm).[20] That the analogous protonated derivatives of methyl selenate and phenyl thiolate are observed only in the iron(II) hydride form under the conditions of our studies may be explained by the smaller MeSe–H and PhS–H bond energies as compared to MeS–H (75 kcal/mol for MeSe–H and PhS–H vs 90 kcal/mol for MeS–H),[21] requiring a larger activation energy for conversion from the collision complex/kinetic product for the MeSH case. That for L = CO the thiol complex is the only observable low-temperature species represented in Scheme I attests to the extreme sensitivity of Fe to its ligands. It also raises the question of whether oxidative addition is imperative to account for the ultimate products of H_2 elimination and $(\mu\text{-}MeS)_2Fe_2(CO)_6$ formation. Attempts are being made to address this question.

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(18) A band at 2337 cm^{-1} (−57 °C) assigned to the metal-bound ν(MeS–H) disappears upon formation of the Fe(II) hydride (−20 °C). The ν(MeS–H) is 2550 cm^{-1} for the free thiol. The ν(Fe–H) stretch for the latter species could not be definitively assigned due to masking by the ν(CO) bands.

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Predominant Inversion of Configuration in an Intramolecular Carbene Addition to an Alkene

Kenneth B. Wiberg* and Antonio Chaves

Department of Chemistry, Yale University
New Haven, Connecticut 06511

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The reaction of the dibromide **1** with methyllithium was shown by Skattebøl to give the tricyclic hydrocarbon **2**.[1] The ^{13}C NMR spectrum showed that it has C2 symmetry[2] and indicated the bridgehead hydrogens to be trans. The detailed structure of **2** has recently become available via an X-ray crystallographic study.[3]

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