524 *Organometallics* **1988,** *7,* 524–528

studies[13] have indicated it to be a half-sandwich with a η^5-cyclopentadienyl group. The calculated (observed) geometry of η^5-CpZnMe is given in Figure 1a; the agreement between calculation and experiment is satisfactory. The same is true for bis(pentamethylcyclopentadienyl)zinc, which has one η^5-bonded and one η^1-bonded (or σ-bonded) Cp ring;[14] AM1 predicts this structure to be the most stable, and the calculated (observed) geometry is given in Figure 1b. Again the agreement is satisfactory.

Use of MNDO in studies of reaction mechanisms and in biochemistry was restricted by its tendency to overestimate interatomic repulsions at separations greater than ca. 1.5 times the corresponding covalent distance.[2] MNDO consequently fails to reproduce hydrogen bonds adequately, and it leads to activation energies that are too large for reactions where the transition states contain unusually long bonds. Since these problems have been overcome in AM1 and since the AM1 results for zinc compounds are significantly better than those given by MNDO,[8] AM1 should prove a useful aid in studies of the chemistry and biochemistry of zinc.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Contract No. AF86-0022), and the Robert A. Welch Foundation (Grant No. F-126).

Registry No. η^5-CpZnMe, 67291-89-8; $ZnMe_2$, 544-97-8; $ZnEt_2$, 557-20-0; Zn n-Pr_2, 628-91-1; Zn n-Bu_2, 1119-90-0; ZnF_2, 7783-49-5; $ZnCl_2$, 7646-85-7; $ZnBr_2$, 7699-45-8; ZnI_2, 10139-47-6; ZnMeF, 102436-61-3; ZnMeCl, 5158-46-3; ZnMeBr, 18815-74-2; ZnMeI, 18815-73-1; ZnF, 20654-98-2; ZnCl, 18623-80-8; ZnBr, 13550-22-6; ZnI, 31246-29-4; ZnH, 13981-87-8; $ZnMe^+$, 47936-33-4; $ZnCl_2^+$, 102436-59-9; $ZnMe_2^+$, 102436-60-2; ZnO, 1314-13-2; η^1-ZnCpEt, 38282-37-0; η^5-ZnCpEt, 111689-06-6; η^1-ZnCpPh, 111616-47-8; η^5-ZnCpPh, 94980-39-9; Zn, 7440-66-6; Zn^+, 15176-26-8; Zn^{2+}, 23713-49-7; (η^1,η^5)bis(pentamethylcyclopentadienyl)zinc, 97286-54-9.

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[13] Haaland, A.; Samdal, S.; Seip, R. *J. Organomet. Chem.* **1978,** *153,* 187.

[14] Blom, R.; Haaland, A.; Weidlein, J. *J. Chem. Soc., Chem. Commun.* **1985,** 266.

Synthesis and Characterization of (μ-$R^1C{=}NPh$)(μ-RS)$Fe_2(CO)_6$ Complexes

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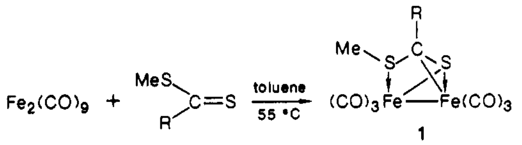
Received August 7, 1987

New μ-iminoacyl complexes of the type (μ-$R^1C{=}NPh$)(μ-RS)$Fe_2(CO)_6$ were prepared by the reactions of triiron dodecacarbonyl with thioimidates ($R^1C(SR){=}NPh$). The geometry of the bridging iminoacyl and thiolate ligands was determined primarily from IR and ^{13}C NMR spectral correlations to related acyl and thioacyl systems. In related work, reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2CO)_6]$ with N-phenylbenzimidoyl chloride was found to be an alternate and superior route to complexes of this class.

Introduction

The reactions of iron carbonyls with organic thiocarbonyl compounds have received considerable attention in the literature. These include the reactions of O-alkyl thioesters,[1,2] dithioesters,[3] O-alkyl S-alkyl dithiocarbonates,[4] trithiocarbonates,[5] O-alkyl thioformates,[2,4b] dithioformates,[2] thioketones,[6] thioureas,[7] and thioamides.[7] Diiron hexacarbonyl complexes are typically isolated in these instances with the organic thiocarbonyl substrate retaining its structural integrity and bonding to the diiron centers as a formal six-electron donor (e.g. eq 1).[3] In some cases, however, diiron hexacarbonyl complexes are isolated



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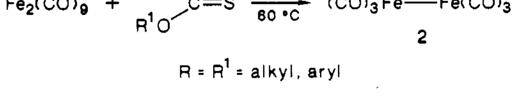
(1)

R = alkyl, aryl

where cleavage of an additional C–S bond has occurred with subsequent formation of bridging, three-electron thiolate and thioacyl ligands (e.g. eq 2).[4a] This type of



2

(2)

R = R^1 = alkyl, aryl

cleavage reaction also has been observed in the synthesis of other thiolate-bridged diiron hexacarbonyl complexes as well (eq 3–5).[8]

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[1] (a) Alper, H.; Foo, C. K. *Inorg. Chem.* **1975,** *14,* 2928. (b) Alper, H.; Chan, A. S. K. *J. Chem. Soc., Chem. Commun.* **1973,** 724.

[2] (a) Womack, G. B. *Ph.D. Dissertation*, Massachusetts Institute of Technology, Cambridge, MA, 1984, pp 173–227. (b) Seyferth, D.; Womack, G. B. *Organometallics* **1984,** *3,* 1891.

[3] Benoit, A.; Le Marouille, J.-Y.; Mahé, C.; Patin, H. *J. Organomet. Chem.* **1981,** *218,* C67.

[4] (a) Patin, H.; Mignani, G.; Benoit, A.; Le Marouille, J.-Y.; Grandjean, D. *Inorg. Chem.* **1981,** *20,* 4351. (b) Patin, H.; Mignani, G.; Dabard, R.; Benoit, A. *J. Organomet. Chem.* **1979,** *168,* C21.

[5] Patin, H.; Mignani, G.; Mahé, C.; Le Marouille, J.-Y.; Southern, T.; Benoit, A.; Grandjean, D. *J. Organomet. Chem.* **1980,** *197,* 315.

[6] Alper, H.; Chan, A. S. K. *J. Am. Chem. Soc.* **1973,** *95,* 4905.

[7] Alper, H.; Chan, A. S. K. *Inorg. Chem.* **1974,** *13,* 225.

[8] (a) Hoke, J. B.; Seyferth, D., unpublished work. (b) King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961,** *83,* 3600. (c) Job, B. E.; McLean, R. A. N.; Thompson, D. T. *J. Chem. Soc., Chem. Commun.* **1966,** 895.

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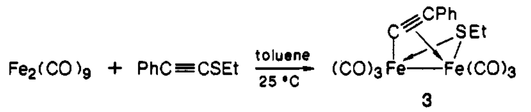
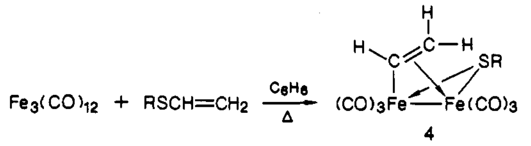
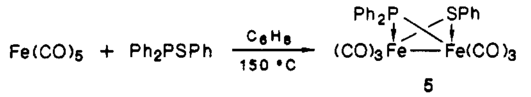
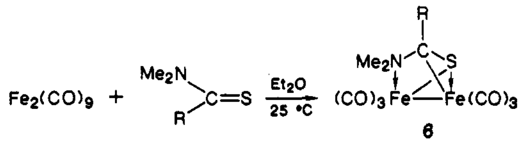

(3)


(4)

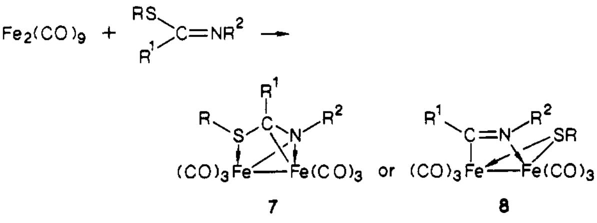
R = Me, Et, Vi, *i*-Pr


(5)

Alper has shown that reaction of diiron nonacarbonyl with *N,N*-dimethylthioamides generates, in very low yield, diiron hexacarbonyl species 6 in which the organic ligand has remained intact (eq 6).[7] In light of this result and our continuing interest in the synthesis of thiolate-bridged diiron hexacarbonyl complexes, we wondered if reaction of the isomeric thioimidates ($R^1C(SR){=}NR^2$) with diiron nonacarbonyl would produce related complexes of type 7 or ones of type 8 derived from cleavage of the C–S bond (eq 7). While mononuclear η^1- and η^2-iminoacyls[9–15] and trinuclear μ_2- and μ_3,η^2-iminoacyls[16–18] are well-known for the transition metals, binuclear μ_2-iminoacyl complexes of type 8 are not common in the literature. Mays has reported the synthesis of a (μ-formimidoyl)dirhenium complex, although supporting structural information was not given.[19] Evans has also reported the synthesis of a bis(formimidoyl)-bridged diyttrium complex although an X-ray crystal structure indicated that the bridge bonding was formally more σ,π in nature.[20] Isoelectronic μ-acyl complexes are well-known for the transition metals,[21] and in fact, a wide variety of thiolate- and acyl-bridged diiron hexacarbonyl complexes have been prepared.[22] Clearly, however, the analogous, dinuclear μ-iminoacyl complexes have little precedent.

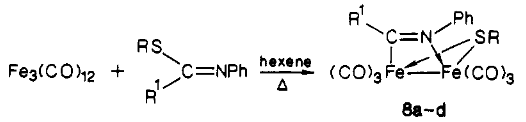

(6)

R = NMe₂, Me, Ph


(7)

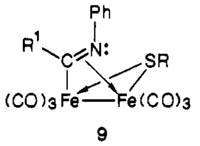
Results and Discussion

Reaction of $Fe_3(CO)_{12}$ with thioimidates, $R^1C(SR){=}NPh$ ($R = R^1$ = alkyl, aryl), in refluxing hexane produced diiron hexacarbonyl complexes in moderate yields which have been characterized as bridging iminoacyl derivatives of type 8 (eq 8). (Although reaction with $Fe_2(CO)_9$ proceeded analogously, superior yields were obtained with $Fe_3(CO)_{12}$.) While products of type 8 all gave consistent carbon/hydrogen combustion analyses, EI mass spectra, and ^1H NMR spectra, the coordination of the bridging ligands was determined primarily from the infrared and ^{13}C NMR spectra. The IR spectra of 8a–d all displayed a strong absorption in the range of 1555–1570 cm^{-1} assigned to $\nu_{C=N}$ of the μ-iminoacyl ligands. As expected for bridging ligands of this type (i.e., μ-acyl), this band is shifted somewhat to lower frequency (~60 cm^{-1}) when compared to the parent thioimidates ($\nu_{C=N}$ 1610–1632 cm^{-1}). In contrast, $\nu_{C=N}$ of isomers of type 7 (eq 7) should be shifted to much lower wavenumbers typical for a C–N single bond (ca. 1030–1230 cm^{-1}).[23] Similarly, if the bonding of the μ-iminoacyl ligands was σ,π in nature, then $\nu_{C=N}$ should be shifted considerably to lower frequency. Although one would expect an absorption indicative of a bond order between 1 or 2 for $(\mu\text{-}\sigma,\pi\text{-}R^1C{=}NPh)(\mu\text{-}RS)Fe_2(CO)_6$ (9), Evans surprisingly has reported $\nu_{C=N}$ to be around 1530 cm^{-1} for the related σ,π-bis(formimidoyl)-bridged yttrium


(8)

8a–d

a, R = Me, R¹ = Ph (43%)
b, R = Me, R¹ = Me (49%)
c, R = Me, R¹ = Et (52%)
d, R = Et, R¹ = Me (34%)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(9) (a) Adams, R. D.; Chodosh, D. F.; *J. Am. Chem. Soc.* **1977**, *99*, 6544. (b) Adams, R. D.; Chodosh, D. F.; Golembeski, N. M.; Weissman, E. C. *J. Organomet. Chem.* **1979**, *172*, 251. (c) Adams, R. D.; Chodosh, D. F. *Inorg. Chem.* **1978**, *17*, 41.

(10) (a) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J.; *J. Organomet. Chem.* **1978**, *157*, C27. (b) Clark, G. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Dalton Trans.* **1975**, 2556. (c) Christian, D. F.; Clark, H. C.; Stepaniak, R. F. *J. Organomet. Chem.* **1976**, *112*, 209. (d) Christian, D. F.; Clark, G. R.; Roper, W. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Chem. Commun.* **1972**, 458.

(11) (a) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1974**, *13*, 2145. (b) Yamamoto, Y.; Yamazaki, H. *J. Organomet. Chem.* **1970**, *24*, 717.

(12) Bassett, J.; Green, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1779.

(13) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 2088.

(14) Dormond, A.; Dahchour, A. *J. Organomet. Chem.* **1980**, *193*, 321.

(15) Alper, H.; Tanaka, M. *J. Organomet. Chem.* **1979**, *169*, C5.

(16) (a) Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7238. (b) Andrews, M. A.; Buskirk, G.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7245.

(17) (a) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579. (b) Yin, C. C.; Deeming, A. J. *J. Organomet. Chem.* **1977**, *133*, 123. (c) Dawoodi, Z.; Mays, M. J.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *219*, 103.

(18) Patin, H.; Mignani, G.; Mahé, C.; Le Marouille, J.-Y.; Benoit, A.; Grandjean, D.; Levesque, G. *J. Organomet. Chem.* **1981**, *208*, C39.

(19) Mays, M. J.; Prest, D. W.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 171.

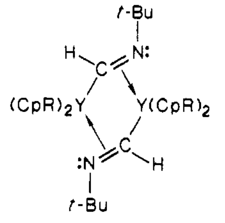
(20) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 1252.

(21) (a) Rosen, R. P.; Hoke, J. B.; Whittle, R. R.; Geoffroy, G. L.; Hutchinson, J. P.; Zubieta, J. A. *Organometallics* **1984**, *3*, 846. (b) McKennis, J. S.; Kyba, E. P. *Organometallics* **1983**, *2*, 1249. (c) Kyba, E. P., personal communication. (d) Yu, Y.-F.; Galluci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1983**, *105*, 4826. (e) Fischer, E. O.; Kiener, V.; Bunbury, D. St. P.; Frank, E.; Lindley, P. F.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1968**, 1378.

(22) (a) Reference 2a, pp 222–227, 274–277. (b) Archer, C. M. *Ph. D. Dissertation*, Massachusetts Institute of Technology, Cambridge, MA, 1986, pp 122–127, 207–214. (c) Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398. (d) Seyferth, D.; Archer, C. M. *Organometallics* **1986**, *5*, 2572.

(23) *Introduction to Organic Chemistry*, Streitwieser, A., Heathcock, C. H., Eds.; MacMillan: New York, 1976; p 1194.

complexes, $[(CpR)_2Y(\mu\text{-}\sigma,\pi\text{-}HC{=}N\text{-}t\text{-}Bu)]_2$ (10).[20] In



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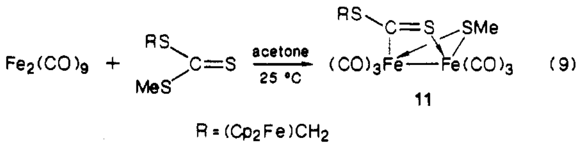
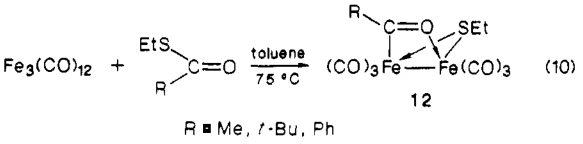
general, since the isomers 8 and 9 are structurally very similar, differentiation between the two based on spectroscopic data alone is very difficult without appropriate comparisons in the literature. The structure of $(\mu\text{-}R^1C{=}NR^2)(\mu\text{-}RS)Fe_2(CO)_6$ (8), however, seems more consistent with the observed infrared data.

In the ^{13}C NMR spectra of **8a–d**, the "carbene-like" iminoacyl carbons are observed at low field, $\delta_C \sim 233$. These values are shifted approximately 65 ppm downfield from the corresponding signals of the parent thioimidates. Patin has observed similar trends in the reactions of $Fe_2(CO)_9$ with *S*-alkyl xanthates (eq 2)[4] and ferrocenylmethyl trithiocarbonates (eq 9),[5] where products derived



from cleavage of a C–S bond (with subsequent formation of bridging thiolate and thioacyl ligands) were isolated. In these two cases, the thioacyl carbon resonances of the reaction products ($\delta_C \sim 293$ and 304) were shifted approximately 65 and 80 ppm downfield from the respective di- and trithiocarbonates. Similarly, Womack has obtained analogous results from the reaction of *S*-alkyl thioesters with triiron dodecacarbonyl (eq 10); the resulting μ-acyl

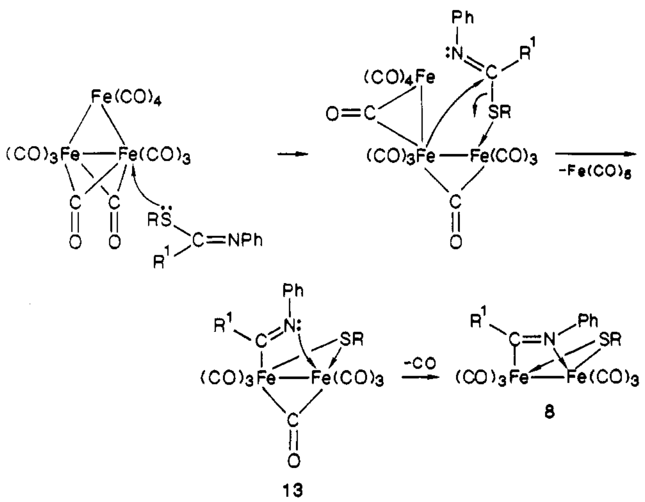


products showed a downfield shift of approximately 105 ppm ($\delta_C \sim 295$) for the respective acyl carbon atoms as compared to the parent thioesters ($\delta_C \sim 190$).[2]

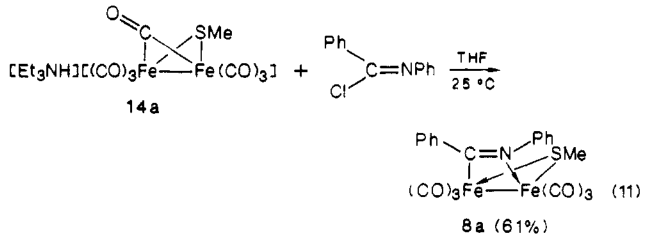
In contrast to these results, Patin has observed an opposite trend in the reactions of dithioesters with diiron nonacarbonyl. Diiron hexacarbonyl complexes were isolated where the original organic thiocarbonyl substrate had not been cleaved (eq 1).[3] In this instance, however, the thiocarbonyl resonances in the ^{13}C NMR spectra ($\delta_C \sim 75$) were shifted approximately 150 ppm *upfield* as compared to the free dithioesters. Womack has likewise noted this trend in the related reactions of dithioformates and *O*-alkyl thioesters with diiron nonacarbonyl.[2]

A possible mechanistic scheme accounting for the formation of the μ-iminoacyl products, 8, is proposed in Scheme I (see ref 5). The first step likely involves nucleophilic attack by sulfur at iron with concomitant cleavage of an Fe–Fe bond and migration of carbon monoxide to a new bridging position. Attack by the neighboring iron atom at the electrophilic thioimidate carbon then can lead to cleavage of the C–S bond, and, with loss of $Fe(CO)_5$, the terminal iminoacyl intermediate 13. Subsequent bridging by the nitrogen lone pair with loss of carbon monoxide then gives 8.

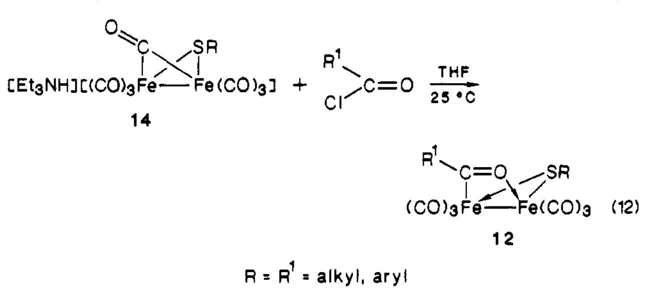
Scheme I



To provide further structural proof for the generation of μ-iminoacyl complexes of this type, we have synthesized **8a** alternately by the reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}MeS)Fe_2(CO)_6]$ (**14a**) with *N*-phenylbenzimidoyl chloride (eq 11). Reaction of anionic transition-metal reagents with



imidoyl chlorides has previously been shown to be a viable route to the synthesis of mononuclear iminoacyl complexes.[9b,15] Furthermore, anions of the general type $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ (14) have been shown to be versatile reagents for the synthesis of a wide variety of thiolate-bridged diiron complexes. Typically, reaction with an electrophile leads to net substitution of the bridging carbonyl ligand with a new bridging group.[22c,24] For example, reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ (14) with acid chlorides ($R^1C(O)Cl$, R^1 = alkyl, aryl) yields neutral bridging acyl complexes of type 12, $(\mu\text{-}R^1C{=}O)(\mu\text{-}RS)Fe_2(CO)_6$, in variable yields (eq 12).[22a-c] Subsequently,



reaction of **14a** with *N*-phenylbenzimidoyl chloride yielded the expected product, **8a**, in good yield. Analogously, $(\mu\text{-}PhC{=}NPh)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (**8e**) was prepared in 85% yield by the reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ (**14b**) with *N*-phenylbenzimidoyl chloride. Not surprisingly, in the ^{13}C NMR spectrum of **8e** the methyl resonance of the *tert*-butyl group (δ_C 34.18) is observed in

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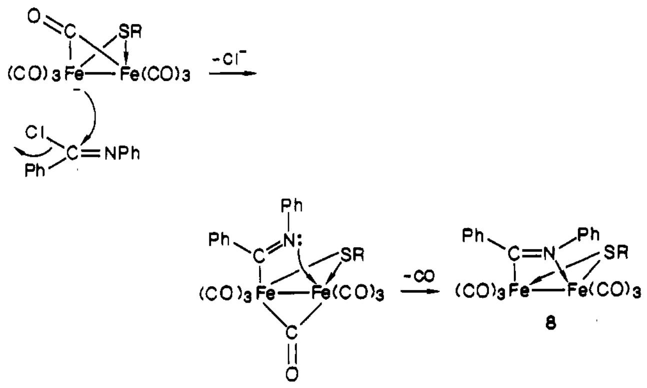
(24) (a) Reference 2a, pp 274–312. (b) Reference 22b, pp 120–138. (c) Hoke, J. B. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1987, Chapters 2 and 3.

Scheme II



the region typically found for thiolate-bridged diiron hexacarbonyl complexes.[24c]

Mechanistically, formation of the iminoacyl derivatives by this route can be envisioned as a simple S_N2 process with attack of an iron-centered anion at the imino carbon and concomitant elimination of chloride ion (Scheme II). Subsequent bridging of the dangling iminoacyl ligand by the nitrogen lone electron pair with loss of carbon monoxide then produces 8.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl. Hexane was distilled under nitrogen from lithium aluminum hydride. Triethylamine was distilled under nitrogen from calcium hydride. *tert*-Butyl mercaptan and methyl mercaptan (Matheson) were used without further purification. Triiron dodecacarbonyl ($Fe_3(CO)_{12}$)[25] and *N*-phenylbenzimidoyl chloride (PhC(Cl)=NPh)[26] were prepared by literature methods. The *N*-phenyl *S*-alkyl thioimidates all were prepared by a literature procedure.[27] and characterized fully by the standard analytical and spectroscopic techniques. Characterizing data are included below. All solvents and liquid reagents were purged with nitrogen prior to use. Solid thioimidates were recrystallized. *n*-Butyllithium (2.4 M in hexane) was purchased from Alfa and used as received.

The progress of all reactions was monitored by thin-layer chromatography (Baker Flex-Silica Gel 1B-F). Purification by filtration chromatography in which the reaction products were dissolved in a suitable solvent and chromatographed on a bed of Mallinckrodt 100 mesh silicic acid (ca. 200 mL) in a 350-mL glass-fritted filter funnel was used in most cases. Further purification by column chromatography was accomplished with a 350 × 25 mm column using Mallinckrodt 100-mesh silicic acid. All chromatography was completed without exclusion of atmospheric moisture or oxygen. Solid products were recrystallized from deoxygenated solvents at -20 °C.

Solution or neat infrared spectra (NaCl optics) were obtained by using a Perkin-Elmer Model 1430 double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a JEOL FX-90Q or a Bruker WM-250 NMR spectrometer operating at 90 or 250 MHz, respectively. Carbon-13 NMR spectra were obtained by using a Bruker WH-270 spectrometer operating at 67.9 MHz. Electron-impact mass spectra were obtained by using a Finnigan-3200 mass spectrometer operating at 70 eV. Masses were correlated by using the following isotopes: ^1H, ^{12}C, ^{14}N, ^{16}O, ^{32}S, and ^{56}Fe. Melting points were determined in air on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Characterizing Data for RC(SR′)=NPh Compounds. **EtC(SMe)=NPh**: bp 92.0–94.0 °C (4 Torr); ^1H NMR (CD_2Cl_2, 90 MHz) δ 1.12 (t, J = 7.57 Hz, 3 H, CH_2CH_3), 2.41 (m, 5 H, SCH_3 and CH_2CH_3), 7.59 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 12.55 (q, J = 128.5 Hz, CH_2CH_3), 12.64 (q, J = 141.1 Hz, SCH_3), 28.33 (t, J = 128.4 Hz, CH_2CH_3), 119.72 (d, J = 160.0 Hz, C_6H_5), 122.80 (d, J = 164.0 Hz, C_6H_5), 128.84 (d, J = 160.0 Hz, C_6H_5), 150.68 (s, ipso C_6H_5), 171.81 (s, C=N). Anal. Calcd for $C_{10}H_{13}NS$: C, 66.99; H, 7.31. Found: C, 66.98; H, 7.29.

MeC(SMe)=NPh: bp 89.0–91.0 °C (6 Torr); ^1H NMR (CD_2Cl_2, 90 MHz) δ 2.02 (s, 3 H, CCH_3), 2.43 (s, 3 H, SCH_3), 6.59–7.63 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 12.63 (q, J = 141.0 Hz, SCH_3), 20.94 (q, J = 129.7 Hz, CCH_3), 119.65 (d, J = 158.6 Hz, C_6H_5), 122.75 (d, J = 162.2 Hz, C_6H_5), 128.59 (d, J = 159.5 Hz, C_6H_5), 150.47 (s, ipso C_6H_5), 165.71 (s, C=N). Anal. Calcd for $C_9H_{11}NS$: C, 65.41; H, 6.72. Found: C, 65.57; H, 6.68.

PhC(SMe)=NPh: mp 62.5–63.5 °C; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.37 (s, 3 H, CH_3), 6.48–7.72 (m, 10 H, C_6H_5). Anal. Calcd for $C_{14}H_{13}NS$: C, 73.97; H, 5.76. Found: C, 73.86; H, 5.80.

MeC(SEt)=NPh. bp 85.0–110.0 °C (4 Torr); ^1H NMR (CD_2Cl_2, 90 MHz) δ 1.33 (t, J = 7.32 Hz, 3 H, SCH_2CH_3), 1.98 (s, 3 H, $N{=}CCH_3$), 3.03 (q, J = 7.32 Hz, 2 H, SCH_2CH_3), 6.69–7.41 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 13.92 (q, J = 128.0 Hz, CH_3), 21.44 (q, J = 129.7 Hz, CH_3), 24.00 (t, J = 140.4 Hz, SCH_2CH_3), 119.89 (d, J = 158.7 Hz, C_6H_5), 122.63 (d, J = 162.3 Hz, C_6H_5), 128.89 (d, J = 159.6 Hz, C_6H_5), 150.78 (s, ipso C_6H_5), 165.56 (s, C=N). Anal. Calcd for $C_{10}H_{13}NS$: C, 66.99; H, 7.31. Found: C, 66.91; H, 7.29.

Synthesis of (μ-PhC=NPh)(μ-MeS)$Fe_2(CO)_6$. A 300-mL, three-necked, round-bottomed flask equipped with a reflux condenser, glass stopper, stir bar, and rubber septum was charged with 1.12 g (2.22 mmol) of $Fe_3(CO)_{12}$ and 0.50 g (2.21 mmol) of *S*-methyl *N*-phenylbenzenecarboximidothioate and subsequently degassed by three evacuation/nitrogen-backfill cycles. The flask was then charged with 50 mL of hexane by syringe, and the resulting dark green solution was heated at reflux for 28 h. The solvent from the now red reaction mixture was removed in vacuo, and the red, oily residue that remained was purified by filtration chromatography. Pentane eluted a yellow band which gave 0.09 g (0.24 mmol, 22% based on S) of (μ-MeS)$_2Fe_2(CO)_6$, identified by its ^1H NMR spectrum.[28] Further elution with pentane yielded an orange band which gave 0.48 g (0.95 mmol, 43%) of (μ-PhC=NPh)(μ-MeS)$Fe_2(CO)_6$ (**8a**) as an air-stable, red solid: mp 162.0–165.0 °C after recrystallization from pentane; IR, terminal carbonyl region (pentane), 2075 (s), 2038 (vs), 1998 (vs), 1981 (m), 1971 (w) cm^{-1}; ^1H NMR (CD_2Cl_2, 90 MHz) δ 2.39 (s, 3 H, SCH_3), 6.52–7.53 (m, 10 H, C_6H_5); ^{13}C NMR (CD_2Cl_2, 67.9 MHz) δ 23.07 (q, J = 139.7 Hz, SCH_3), 121.51–130.46 (m, C_6H_5), 147.44 (s, ipso C_6H_5), 153.75 (s, ipso C_6H_5), 209.71, 210.56, and 214.09 (all s, FeCO), 233.02 (s, C=N). Anal. Calcd for $C_{20}H_{13}Fe_2NO_6S$: C, 47.37; H, 2.58. Found: C, 47.57; H, 2.75.

Similar experiments were carried out in order to synthesize the following.

(μ-MeC=NPh)(μ-MeS)$Fe_2(CO)_6$ (8b): 49% yeild; red solid; mp 98.0–100.0 °C (pentane); IR, terminal carbonyl region (pentane), 2069 (s), 2027 (s), 1995 (vs), 1977 (m), 1969 (s), 1942 (vw) cm^{-1}; ^1H NMR (CD_2Cl_2, 90 MHz) δ 2.03 (s, 3 H, $CH_3C{=}NPh$), 2.40 (s, 3 H, SCH_3), 6.42–7.52 (m, 5 H, C_6H_5); ^{13}C NMR (CD_2Cl_2, 67.9 MHz) δ 22.98 (q, J = 139.3 Hz, SCH_3), 34.83 (q, J = 128.5 Hz, $CH_3C{=}NPh$), 121.97 (d, J = 161.1 Hz, C_6H_5), 126.87 (d, J = 161.6 Hz, C_6H_5), 129.79 (d, J = 160.8 Hz, C_6H_5), 152.78 (s, ipso C_6H_5), 210.60 and 213.84 (both s, FeCO), 230.87 (s, C=N). Anal. Calcd for $C_{15}H_{11}Fe_2NO_6S$: C, 40.49; H, 2.49. Found: C, 40.64; H, 2.59.

(μ-EtC=NPh)(μ-MeS)$Fe_2(CO)_6$ (8c): red solid; 52% yield; mp 92.5–97.0 °C (pentane); IR, terminal carbonyl region (pentane), 2070 (s), 2032 (vs), 1995 (vs), 1978 (m), 1970 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.88 (t, J = 7.63 Hz, 3 H, $CH_3CH_2C{=}NPh$), 1.96 (m, 1 H, $CH_3CH_2C{=}NPh$ diastereotopic CH_2), 2.14 (m, 1 H, $CH_3CH_2C{=}NPh$ diastereotopic CH_2), 2.32 (s, 3 H, SCH_3),

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(25) McFarlane, W.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 181.

(26) Vaughan, W. R.; Carlson, R. D. *J. Am. Chem. Soc.* **1962**, *84*, 769.

(27) Gosselin, P.; Masson, S.; Thuillier, A. *Tetrahedron Lett.* **1978**, 2715.

(28) (a) King, R. B. *J. Am. Chem. Soc.* **1962**, *84*, 2460. (b) Henderson, R. S. *Ph. D. Dissertation*, Massachusetts Institute of Technology, Cambridge, MA, 1981, pp 30–31. (c) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

(29) (a) Dahl, L. F.; Wei, C.-H. *Inorg. Chem.* **1963**, *2*, 328. (b) Reference 28b, p 35.

6.60–7.30 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 10.96 (q, *J* = 128.3 Hz, $CH_3CH_2C{=}NPh$), 22.71 (q, *J* = 139.2 Hz, SCH_3), 39.51 (t, *J* = 129.3 Hz, $CH_3CH_2C{=}NPh$), 121.24 (d, *J* = 161.0 Hz, C_6H_5), 126.42 (d, *J* = 161.7 Hz, C_6H_5), 129.44 (d, *J* = 161.0 Hz, C_6H_5), 152.83 (s, ipso C_6H_5), 210.04, 210.34, and 213.46 (all s, FeCO), 236.06 (s, C=N). Anal. Calcd for $C_{16}H_{13}Fe_2NO_6S$: C, 41.86; H, 2.85. Found: C, 41.76; H, 2.86.

(μ-MeC=NPh)(μ-EtS)$Fe_2(CO)_6$ (8d): red solid; 34% yield; mp 81.0–82.5 °C (pentane); IR, terminal carbonyl region (pentane), 2062 (s), 2045 (vw), 2020 (vs), 1990 (vs), 1972 (m), 1965 (m), 1940 (vw) cm^{-1}; ^1H NMR (CD_2Cl_2, 90 MHz) δ 1.50 (t, *J* = 7.32 Hz, 3 H, SCH_2CH_3), 1.96 (s, 3 H, $CH_3C{=}NPh$), 2.61 (q, *J* = 7.32 Hz, 2 H, SCH_2CH_3), 6.51–7.65 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 18.37 (q, *J* = 128.1 Hz, SCH_2CH_3), 33.88 (t, *J* = 140.0 Hz, SCH_2CH_3), 34.55 (q, *J* = 127.8 Hz, $CH_3C{=}NPh$), 121.52 (d, *J* = 160.4 Hz, C_6H_5), 126.43 (d, *J* = 162.0 Hz, C_6H_5), 129.25 (d, *J* = 161.8 Hz, C_6H_5), 152.29 (s, ipso C_6H_5), 209.94, 210.07, and 213.91 (all s, FeCO), 230.83 (s, C=N). Anal. Calcd for $C_{16}H_{13}Fe_2NO_6S$: C, 41.86; H, 2.85. Found: C, 41.83; H, 2.87.

Reaction of [Li][(μ-CO)(μ-MeS)$Fe_2(CO)_6$] with Ph(Cl)C=NPh. A 200-mL Schlenk flask equipped with a stir bar and rubber septum was charged with 1.51 g (3.00 mmol) of $Fe_3(CO)_{12}$, degassed by three evacuation/nitrogen-backfill cycles and then charged with 20 mL of THF by syringe. A cloudy solution of 3.00 mmol of lithium methanethiolate in 20 mL of THF (prepared in a separate flask at 0 °C by the reaction of an excess of methyl mercaptan with 3.00 mmol of *n*-butyllithium) was subsequently added by cannula. An immediate reaction ensued (with brisk gas evolution) and a gradual color change from dark green to brown-red was observed. The resulting [Li](μ-CO)(μ-MeS)$Fe_2(CO)_6$] reagent solution was stirred for 20 min at room temperature and subsequently used in situ without further purification.

To the previously prepared [Li][(μ-CO)(μ-MeS)$Fe_2(CO)_6$] reagent solution (3.00 mmol) was added by cannula 0.65 g (3.01 mmol) of *N*-phenylbenzimidoyl chloride dissolved in a separate flask in 20 mL of THF. After the resulting reaction mixture had been stirred for 60 h at room temperature, the solvent was removed in vacuo to yield a brown-red tar which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.21 g (0.56 mmol, 37% based on S) of (μ-MeS)$_2Fe_2(CO)_6$ identified by its ^1H NMR spectrum.[28] Pentane eluted a second orange band which gave 0.94 g (1.84 mmol, 61%) of (μ-PhC=NPh)(μ-MeS)$Fe_2(CO)_6$ (8a) identified by comparison of its ^1H NMR spectrum to that of an authentic sample.

Synthesis of (μ-PhC=NPh)(μ-*t*-BuS)$Fe_2(CO)_6$. A 250-mL Schlenk flask equipped with a spin bar and rubber septum was charged with 1.51 g (3.00 mmol) of $Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-backfill cycles. The flask was then charged with 50 mL of THF, 0.42 mL (3.00 mmol) of triethylamine, and 0.34 mL (3.00 mmol) of *tert*-butyl mercaptan by syringe. The reaction mixture was stirred for 20 min at room temperature during which time slow gas evolution as well as a color change from dark green to brown-red were observed. The resulting [Et_3NH][(μ-CO)(μ-*t*-BuS)$Fe_2(CO)_6$] reagent solution subsequently was used in situ without further purification.

To the previously prepared [Et_3NH][(μ-CO)(μ-*t*-BuS)$Fe_2(CO)_6$] reagent solution (3.00 mmol) cooled to −78 °C was added by cannula 0.65 g (3.01 mmol) of *N*-phenylbenzimidoyl chloride dissolved in a separate flask in 20 mL of THF (also cooled to −78 °C). The reaction mixture was stirred for 15 min at −78 °C, warmed to room temperature, and then stirred for 40 h at room temperature. Subsequently, the solvent was removed in vacuo to yield a red, oily solid which was purified by filtration chromatography. Pentane eluted an orange band which was not collected. Pentane eluted a second orange band which gave 1.40 g (2.54 mmol, 85%) of (μ-PhC=NPh)(μ-*t*-BuS)$Fe_2(CO)_6$ (8e) as a red, air-stable solid: mp 124.0–126.0 °C after recrystallization from pentane: IR, terminal carbonyl region (pentane), 2068 (m), 2025 (vs), 1998 (vs), 1990 (vw), 1980 (vw) cm^{-1}; ^1H NMR (CD_2Cl_2, 90 MHz) δ 1.55 (s, 9 H, SC(CH_3)3), 6.55–7.22 (m, 10 H, C_6H_5); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 34.18 (q, *J* = 126.2 Hz, SC(CH_3)$_3$), 49.22 (s, SC(CH_3)$_3$), 120.84–129.92 (m, C_6H_5), 146.75 (s, ipso C_6H_5), 153.18 (s, ipso C_6H_5), 209.23, 210.96, and 213.75 (all s, FeCO), 232.88 (s, C=N). Anal. Calcd for $C_{23}H_{19}Fe_2NO_6S$: C, 50.30; H, 3.49. Found: C, 50.46; H, 3.61.

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Registry No. **8a**, 111905-37-4; **8b**, 111905-38-5; **8c**, 111905-39-6; **8d**, 111905-40-9; **8e**, 111905-41-0; $Fe_3(CO)_{1i}$, 17685-52-8; PhC(SMe)=NPh, 6780-43-4; MeC(SMe)=NPh, 58276-22-5; EtC(SMe)=NPh, 69079-30-7; MeC(SEt)=NPh, 87876-89-9; PhC(Cl)=NPh, 4903-36-0; methyl mercaptan, 74-93-1; *tert*-butyl mercaptan, 75-66-1.

Supplementary Material Available: IR and mass spectral data for new compounds (4 pages). Ordering information is given on any current masthead page.

Dimethylsilanone ($Me_2Si{=}O$) Generation by Retroene Decomposition of Allyloxysilanes

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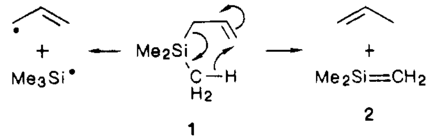
Gas-phase thermolysis of (allyloxy)dimethylsilane cleanly affords dimethylsilanone by retroene decomposition (log *A* = 12.6, E_a = 54.6 kcal/mol). However, substituting the ether-linked carbon with two methyl groups (3-(dimethylsiloxy)-3-methyl-1-butene) introduces a competition between C–O bond homolysis and retroene decomposition.

Introduction

The thermolysis of allylsilanes (e.g., **1**) has proved to be an attractive route to silenes (**2**) via retroene elimination of propene.[1] After more than a decade of controversy, it was finally established[2] that the unimolecular decomposition of allyltrimethylsilane (**1**) proceeds by two competitive processes—a concerted retroene reaction and Si–C bond homolysis.



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[1] For example: Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978** *100*, 1630; Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1978**, *100*, 5246; Barton, T. J.; Burns, G. T.; Arnold, E. V.; Clardy, J. *Tetrahedron Lett.* **1981**, *22*, 7; Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, *209*, C25; Barton, T. J.; Burns, G. T. *Organometallics* **1982**, *1*, 1455.

[2] Barton, T. J.; Burns, S. A.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Wood, I. T. *J. Am. Chem. Soc.* **1984**, *106*, 6367.

0276-7333/88/2307-0528$01.50/0