Reactions of Sulfur-Containing Molecules (CS_2, C_2H_4S) on the Aminocarbene Group of $[Fe_2(CO)_7\{\mu\text{-}RCCNEt_2\}]$ (R = Me, C_3H_5, $SiMe_3$)

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Received April 13, 1990

Reaction of CS_2 with diiron aminocarbene complexes $[Fe_2(CO)_7\{\mu\text{-}RCCNEt_2\}]$ (R = Me (1), C_3H_5 (2), $SiMe_3$ (3)) leads to C–S bond rupture and insertion of an S atom into the Fe=C (aminocarbene) bond to give binuclear complexes $[Fe_2(CO)_6\{RCCNEt_2\}S]$ (R = Me (4), C_3H_5 (5), $SiMe_3$ (6)). Similar insertion of sulfur is observed when C_2H_4S is reacted with 1–3. Complexes 4–6 were characterized by X-ray diffraction studies. They contain a sulfur-containing ligand that bridges both iron atoms. The Fe atoms are thus incorporated into two fused ferrathiete rings sharing the C_2S fragment. The following crystal data were obtained. Compound 3: monoclinic, $P2_1/n$, a = 9.975 (3) Å, b = 14.009 (2) Å, c = 15.802 (4) Å, β = 92.50 (2)°, R_w = 0.036 for 2840 reflections. Compound 4: triclinic, $P\bar{1}$, a = 9.627 (3) Å, b = 7.623 (2) Å, c = 12.594 (3) Å, α = 100.70 (2)°, β = 95.69 (2)°, γ = 104.81 (2)°, R_w = 0.0392 for 3566 reflections. Compound 5: triclinic, $P\bar{1}$, a = 7.553 (1) Å, b = 9.591 (3) Å, c = 14.444 (2) Å, α = 73.62 (2)°, β = 72.46 (2)°, γ = 75.99 (2)°, R_w = 0.0286 for 2195 reflections. Compound 6: monoclinic, $P2_1/n$, a = 16.219 (2) Å, b = 10.175 (1) Å, c = 13.558 (4) Å, β = 107.64 (3)°, R_w = 0.0416 for 2545 reflections.

Introduction

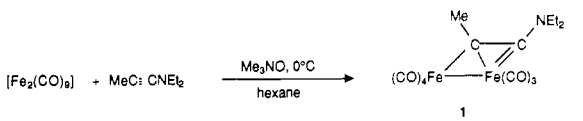
The chemistry of heterocumulenes such as RNCO, RNCS, COS, and CS_2 with transition-metal complexes is of current interest because these small molecules are structurally related to carbon dioxide and their metal complexes may be regarded as model compounds for CO_2 activation.[1]

We recently reported on reactions of the dinuclear aminocarbene complex $[Fe_2(CO)_7\{\mu\text{-}RCCNEt_2\}]$ (R = Me (1),[2] R = allyl (2)[3]) with heterocumulenes R′NCX (R′ = Me, Ph; X = O, S), which lead to binuclear complexes $[Fe_2(CO)_6\{\mu\text{-}C(R)C(NEt_2)C(X)N(R')\}]$ containing a ferrazole ring bound to the second iron atom. Carbon–carbon bond formation very likely results from a cycloaddition of the isocyanate C=N part with the Fe=C (aminocarbene) bond. These observations stimulated us to investigate the reaction of carbon disulfide.

The extensive organometallic chemistry of carbon disulfide with transition metals includes examples of the π-bound[4] and bridged[5] CS_2 ligand on a metal framework, examples of insertion of CS_2 into a M–X bond (X = H,[6] N,[1] C,[7] O,[8] P[9]), examples of cycloaddition to the triple bond of an acetylide iron complex,[10] and examples of coupling reactions.[11] Moreover, CS_2 has been observed to cleave, leading to the formation of thiocarbene,[12] trithiocarbonate,[13] or thiocarbonyl ligands.[14]

The reaction of 1, 2, and 3 (R = $SiMe_3$) with CS_2 does not give cycloaddition of the C=S bond with the Fe=C (aminocarbene) bond. Unexpectedly, one C=S bond of

Scheme I



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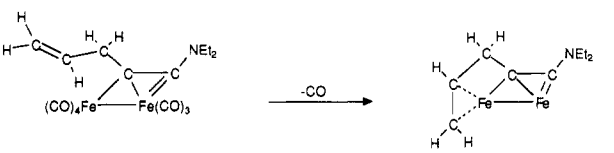
Scheme II



2 2′

Table I. Comparison of IR Spectra (ν(CO)) in Hexane for Complexes 1–3

R = Me (1)	R = C_3H_5 (2)	R = $SiMe_3$ (3)
2080 m	2090 m	2085 m
2030 s	2030 s	2030 s
1990 s	1985 s	1990 s
1960 sh	1960 sh	1960 sh
1950 m	1950 m	1950 m

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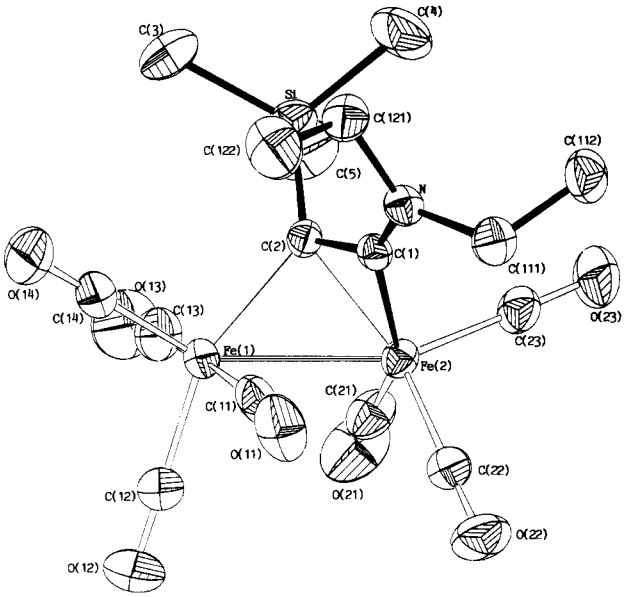


Figure 1. Structure of **3**.

CS_2 was broken, and this S atom was inserted into the aminocarbene bond, which yields a sulfur-containing ligand that bridges a $Fe_2(CO)_6$ unit: $[Fe_2(CO)_6\{\mu\text{-}RCC(NEt_2)S\}]$ (R = Me (**4**), C_3H_5 (**5**), $SiMe_3$ (**6**)). The syntheses and the X-ray structural characterizations of these three complexes are reported here. Similar complexes can be obtained by reaction of ethylene sulfide, which behaves as a sulfur donor.

Results and Discussion

Synthesis of 1, 2, and 3, $[Fe_2(CO)_7\{\mu\text{-}RCC(NEt_2)\}]$. The preparation of **1** is described elsewhere.[15] *N,N*-Diethylpropynyl-1-amine reacts with $[Fe_2(CO)_9]$ in hexane at 0 °C in the presence of Me_3NO to yield the aminocarbene diiron complex **1** (yield: 70%) (Scheme I).

A similar procedure was used to prepare complexes **2** and **3**. **2** was not isolated in a pure form because it transforms fairly rapidly and spontaneously at room temperature into another complex, **2'** (Scheme II). **2'** has not yet been fully characterized, but it is considered to result from **2** by the coordination of the allylic double bond.[16]

The infrared spectrum of **2** in hexane is very similar to spectra recorded for X-ray characterized complexes **1** and **3** (Table I) so that they may be considered to have the same structure. Moreover, its reaction with isocyanates and diazoalkanes is similar to the reactions involving **1** and **3**. This supports the proposed structure.[2,3]

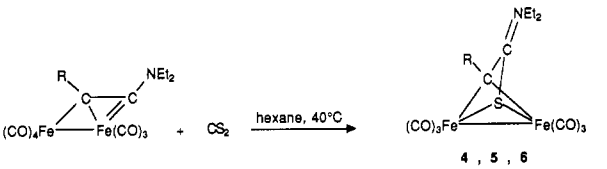
Complex **3** was obtained by the same reaction of the alkyne on $[Fe_2(CO)_9]$. Red crystals were grown from hexane. The structure of **3** was identified by X-ray diffraction (Figure 1). The *N,N*-diethyl[(trimethylsilyl)-ethynyl]amine is bound to the diiron carbonyl core in the same fashion as the *N,N*-diethylpropynyl-1-amine in **1**. The coordination of the initial C≡C triple bond is as follows. The $CSiMe_3$ moiety bridges both iron atoms as a carbene fragment, and the $CNEt_2$ moiety is bound to one iron atom as an aminocarbene. This particular bonding of aminoalkynes on two metal centers seems to be general. We have already described the same structure for **1** (i.e., $[Fe_2(CO)_7\{\mu\text{-}MeCCNEt_2\}]$)[17] and for $[Fe_2(CO)_7\{\mu\text{-}PhCCNEt_2\}]$.[3] A similar bonding mode was observed in $[Os_3(CO)_{10}\{MeC_2NMe_2\}]$ and in $[Os_3S(CO)_9\{MeC_2NMe_2\}_2]$ by Adams et al.;[18] Vrieze et al. recently reported it for the heterodinuclear complex $[FeRu(CO)_5(i\text{-}Pr\text{-}DAB)\{MeCCNEt_2\}]$ (R-DAB = RN=CHCH=NR).[19] The comparison of $FeMC_2N$ (M = Fe, Ru) cores is reported in Table II. The observed bond distances M–C(1), C(1)–N, and C(1)–C(2) and bond angles M–C(1)–N, M–C(1)–C(2), and N–C(1)–C(2) show that the geometry around the C(1) carbon atom is identical within experimental error for the three complexes.

Table II. Comparison of the M_2C_2N Core in Compounds 1, 3, and $[FeRu(CO)_5(i\text{-}Pr\text{-}DAB)(MeCCNEt_2)]$[a,19]

	1	3	$[FeRu(CO)_5$-$(i$-Pr-DAB)-$(MeC_2NEt_2)]$
M(1)–Fe(2)	2.617 (3)	2.6181 (5)	2.693 (1)
M(1)–C(2)	2.030 (8)	2.068 (2)	2.134 (7)
Fe(2)–C(1)	1.878 (8)	1.883 (2)	1.869 (7)
Fe (2)–C(2)	2.007 (9)	2.005 (2)	2.037 (7)
C(1)–N	1.327 (9)	1.300 (3)	1.297 (8)
C(1)–C(2)	1.369 (9)	1.376 (3)	1.407 (10)
M(2)–C(2)–Fe(1)	80.9 (3)	79.98 (9)	80.4 (4)
Fe(1)–C(1)–C(2)	74.5 (5)	74.1 (1)	62.6 (6)
Fe(1)–C(1)–N	147.7 (6)	146.9 (2)	149.1 (5)
N–C(1)–C(2)	137.8 (8)	138.7 (2)	135.0 (7)

[a] The numbering refers to Figure 1. Bond lengths are in angstroms and angles in degrees.

Scheme III



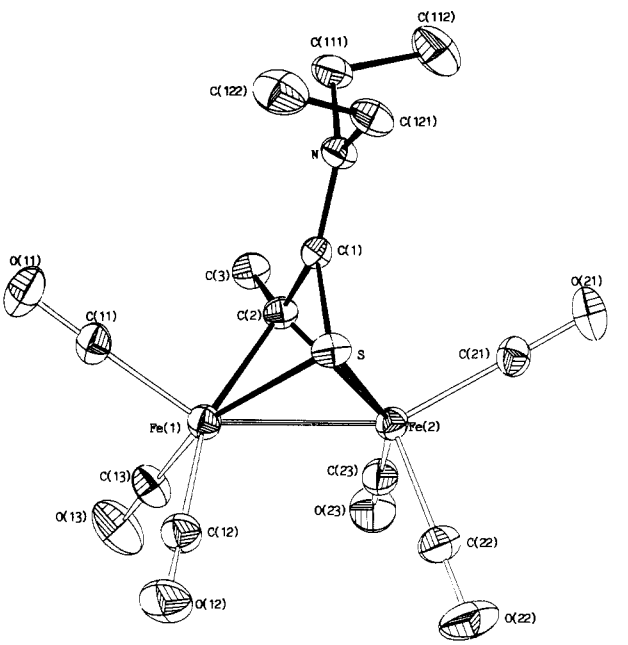


Figure 2. ORTEP drawing of **4**.

(15) Cabrera, E.; Daran, J. C.; Jeannin, Y. *Organometallics* **1988**, *7*, 2010.

(16) Cabrera, E.; Daran, J. C.; Jeannin, Y. *Organometallics* **1989**, *8*, 1811.

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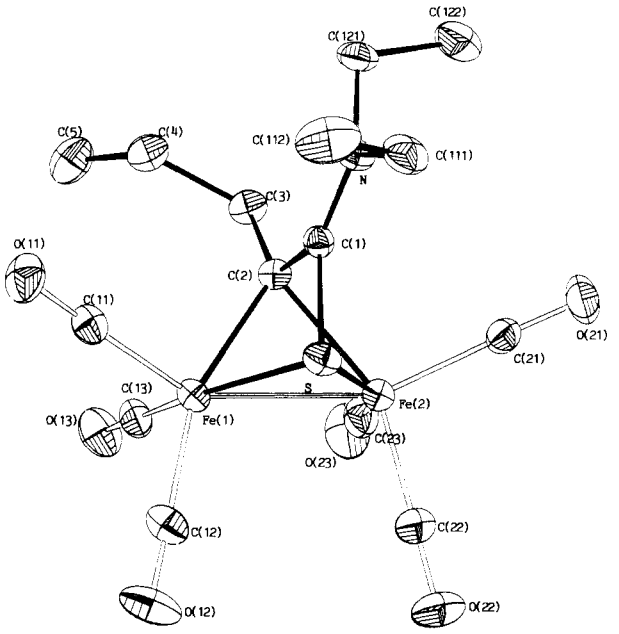


Figure 3. ORTEP drawing of **5**.

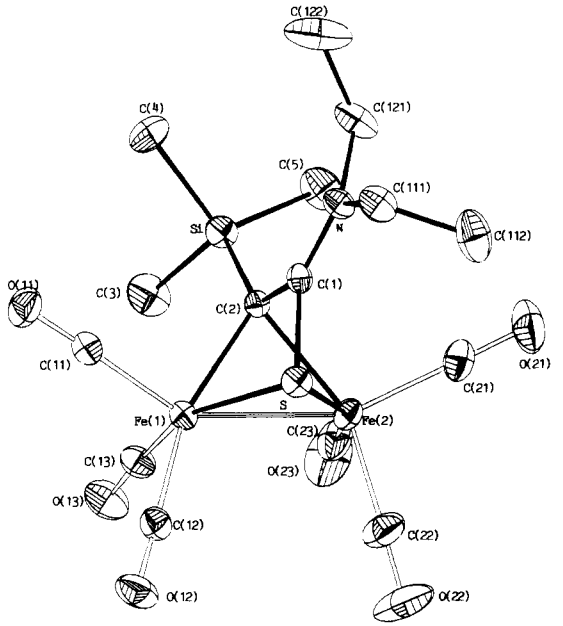


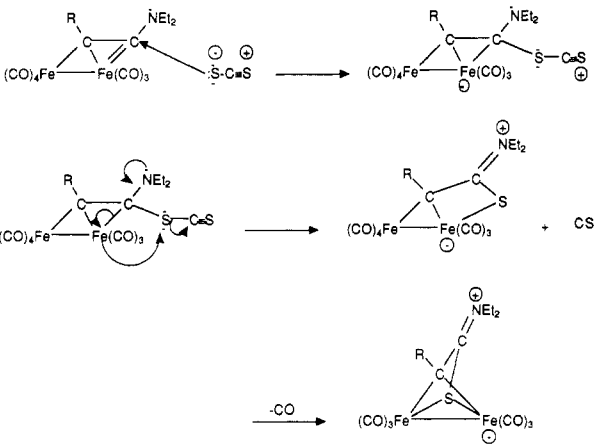
Figure 4. ORTEP drawing of **6**.

Synthesis of $[Fe_2(CO)_6\{\mu\text{-RCC(NEt}_2)S\}]$, R = Me (4), C_3H_5 (5), $SiMe_3$ (6). (i) Reaction of Carbon Disulfide with Complexes 1–3. Carbon disulfide in excess reacts with **1**, **2**, and **3** in hexane at 40 °C to yield as the major product $[Fe_2(CO)_6\{\mu\text{-RCC(NEt}_2)S\}]$ after 6 h (see Table VII). Complexes were separated by column chromatography. Air-stable red crystals of **4**, **5**, and **6** were grown from hexane (Scheme III).

These three complexes have been studied by X-ray diffraction. They have identical frameworks, differing only by the nature of the R substituents (Figures 2–4). The sulfur-containing ligand bridges both iron atoms that are incorporated in the two fused ferrathiete rings, which share three atoms, C(1)–C(2)–S. The rings reveal two interesting features of the reaction: the cleavage of one sulfur atom from carbon disulfide and its insertion into the Fe=C double bond.

This cleavage of a carbon disulfide C–S bond is not unique. A number of examples have been reported as

Scheme IV



follows. (a) A rhodium complex is formed containing a trithiocarbonate ligand that results from a metathesis reaction involving carbon disulfide and dithiocarbonate.[13a] (b) The thiocarbene-containing complex $[Cr(CO)_5\{C(SEt)Ph\}]$ is formed when a deprotonated aminocarbene complex $[Cr(CO)_5\{C(NH)Ph\}]^-$ is successfully treated with CS_2 and Et_3OBF_4.[12] (c) Thiocarbonyl complexes $[M(\eta\text{-}C_5H_4R)(CO)_2CS]$ of Cr, Mn, and Rh are obtained by reaction of $[M(\eta\text{-}C_5H_4R)(CO)_2(thf)]$ with CS_2/PPh_3 under ultraviolet (UV) conditions.[14] (d) Reactions of $[Co_2(CO)_8]$ and $[Os_3(CO)_{12}]$ with CS_2 have shown that the CS_2 molecule can be easily broken down and may rearrange on the cluster core to give carbide, sulfide, and various C_xS_y groups.[20]

In all the preceding examples of complexes, the cleavage is promoted either by temperature, UV, pressure, or addition of sulfur acceptors. In complexes **4–6**, the extraction of sulfur is straightforwardly obtained under mild conditions. On the other hand, some examples of sulfur insertion into a metal–carbene bond have already been reported; e.g., $[W(CO)_5\{C(p\text{-}C_6H_4R)(C_6H_5)\}]$ reacts on elemental sulfur or on sulfur cleaved from RNCS to give (aryl phenyl thioketone)pentacarbonyltungsten complexes $[W(CO)_5\{S{=}C(p\text{-}C_6H_4R)(C_6H_5)\}]$ by insertion of the sulfur atom into the metal carbene double bond,[21] and insertion of S into a Cr=C double bond is also observed if (dimethylthio)carbamoyl chloride reacts with $[Cr(CO)_5(thf)]$.[22] Complexes **4–6** seem to be the first examples of those two already described but separately observed types of reactions. It must be remembered that RNCS does not release sulfur when reacted with **1** but instead undergoes cycloaddition.[2] In order to check whether the sulfur insertion reaction may occur with another sulfur donor, ethylene sulfide was used.[23]

(ii) Reaction of C_2H_4S with Complexes 1–3. Ethylene sulfide in excess (30%) reacts with **1–3** in hexane at room temperature nearly quantitatively to yield compounds **4–6**, which were identified from their infrared spectra.

(iii) Proposed Mechanism for Sulfur Cleavage. To explain the formtion of these complexes, let us consider the canonical form $^+S{\equiv}CS^-$. The terminal carbene atom of the complex is positively charged[24] so that a nucleophilic

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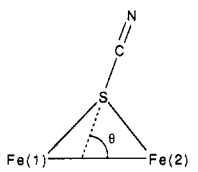
(23) (a) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* **1987**, *6*, 1717. (b) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1986**, *25*, 4514.

Table III. Interatomic Distances (Å) with Esd's in Parentheses

	4	5	6
Fe(1)-Fe(2)	2.4832 (4)	2.4861 (6)	2.4864 (6)
Fe(1)-S	2.2505 (6)	2.2472 (9)	2.2436 (9)
Fe(1)-C(2)	2.021 (2)	2.013 (3)	2.071 (3)
Fe(2)-S	2.2546 (6)	2.2518 (9)	2.2677 (9)
Fe(2)-C(2)	2.051 (2)	2.068 (3)	2.085 (3)
S(1)-C(1)	1.766 (2)	1.767 (3)	1.774 (3)
C(1)-N	1.331 (3)	1.329 (4)	1.331 (4)
C(1)-C(2)	1.414 (3)	1.413 (4)	1.421 (4)
C(2)-C(3)	1.507 (3)	1.511 (4)	
C(2)-Si			1.876 (3)
C(111)-C(112)	1.503 (5)	1.477 (7)	1.481 (7)
C(111)-N	1.463 (3)	1.484 (5)	1.480 (5)
C(121)-C(122)	1.493 (5)	1.502 (6)	1.494 (8)
C(121)-N	1.468 (3)	1.466 (4)	1.475 (5)
C(3)-C(4)		1.486 (5)	
C(4)-C(5)		1.300 (5)	
Si-C(3)			1.879 (5)
Si-C(4)			1.869 (5)
Si-C(5)			1.864 (4)
Fe(1)-C(1)	2.592 (2)	2.619 (3)	2.656 (3)
Fe(2)-C(1)	2.467 (2)	2.433 (3)	2.391 (3)

Chart I



attack of carbon disulfide may occur. A concerted move of electron pairs would then lead to a four-membered ring CCSFe with the simultaneous cleavage of the formal CS_2 carbon sulfur single bond. The coordination of the S atom to the second iron atom with CO elimination would give the expected complex (Scheme IV). No attempt was made to identify the presence of CS. A similar mechanism may be invoked for ethylene sulfide assuming the canonical form $^{-}SCH_2CH_2^{+}$.

(iv) Description of Structures. ORTEP drawings are shown in Figures 2–4. Important bond distances and angles are given in Tables III and IV.

A common feature is the eclipsed conformation of carbonyls. These molecules contain two $Fe(CO)_3$ moieities linked via a Fe–Fe single bond; they also are doubly bridged by the C(2) carbon atom and the sulfur atom of the ligand $RCC(NEt_2)S$. The ligand sits upright on a sawhorse formed by the two $Fe(CO)_3$ moieties. This sawhorse unsymmetrically supports the ligand as indicated by the C(11)–Fe(1)–Fe(2) and Fe(1)–Fe(2)–C(21) angles of 146.3 (1)° and 151.8 (1)°, respectively (mean values for the three complexes). This asymmetry is reflected by the position of the ligand: the C(2)–C(1)–N–C(111)–C(121)–S mean plane is not orthogonal to the Fe(1)–Fe(2) bond but is slightly bent toward Fe(2), resulting in the larger value observed for the Fe(1)–Fe(2)–C(21) angle when compared to C(11)–Fe(1)–Fe(2). To describe this bending, let us consider the angle θ between C(1)–N and Fe(1)–Fe(2) shown in Chart I.

Values observed for the three complexes **4**–**6** are reported in Table V. This points out that the angle slightly decreases when going from **4** to **5** and to **6**. Among the three complexes, **4** has the most symmetrical position of the ligand with respect to the $Fe(CO)_3$ moieties.

(24) The positive charge of the carben carbon atom was recently confirmed by an ESCA study on $[Fe_2(CO)_7\{PhC_2NEt_2\}]$: Folkesson, B.; Ragnar, L.; Crocq, V.; Jeannin, Y. To be published.

Table IV. Bond Angles (deg) with Esd's in Parentheses

	4	5	6
C(11)-Fe(1)-C(2)	104.9 (3)	104.9 (3)	104.9 (3)
C(2)-Fe(1)-S	70.65 (6)	70.72 (8)	71.10 (9)
C(11)-Fe(1)-S	102.40 (9)	100.7 (1)	105.0 (1)
C(11)-Fe(1)-C(2)	96.96 (9)	98.1 (1)	95.1 (1)
C(12)-Fe(1)-S	95.60 (9)	96.4 (1)	93.6 (1)
C(12)-Fe(1)-C(2)	160.4 (1)	159.0 (2)	161.5 (1)
C(12)-Fe(1)-C(11)	99.8 (1)	100.7 (2)	99.0 (2)
C(13)-Fe(1)-S	155.62 (9)	156.6 (1)	154.3 (1)
C(13)-Fe(1)-C(2)	94.0 (1)	92.6 (1)	101.3 (1)
C(13)-Fe(1)-C(11)	98.1 (1)	97.8 (2)	100.0 (2)
C(13)-Fe(1)-C(12)	93.7 (1)	94.2 (2)	88.0 (2)
C(2)-Fe(2)-S	70.07 (6)	69.70 (8)	70.35 (8)
C(21)-Fe(2)-S	102.76 (8)	104.2 (1)	106.4 (1)
C(21)-Fe(2)-C(2)	104.0 (1)	105.5 (1)	103.6 (2)
C(22)-Fe(2)-S	97.32 (9)	96.2 (1)	95.0 (2)
C(22)-Fe(2)-C(2)	155.0 (1)	153.6 (1)	155.4 (2)
C(22)-Fe(2)-C(21)	99.8 (1)	99.5 (2)	99.4 (2)
C(23)-Fe(2)-S	154.85 (8)	153.3 (1)	154.1 (1)
C(23)-Fe(2)-C(2)	90.35 (9)	90.7 (1)	92.9 (2)
C(23)-Fe(2)-C(21)	97.1 (1)	98.3 (2)	96.6 (2)
C(23)-Fe(2)-C(22)	94.3 (1)	94.1 (2)	92.9 (2)
Fe(2)-S-Fe(1)	66.90 (2)	67.09 (3)	66.89 (3)
C(1)-S-Fe(1)	79.39 (7)	80.5 (1)	81.9 (1)
Fe(2)-C(2)-Fe(1)	75.15 (7)	75.1 (1)	73.5 (1)
C(1)-S-Fe(2)	74.58 (6)	73.38 (9)	71.4 (1)
C(2)-C(1)-S	101.8 (1)	101.5 (2)	103.1 (2)
N-C(1)-S	122.1 (2)	121.6 (2)	120.1 (2)
N-C(1)-C(2)	136.2 (2)	136.8 (3)	136.8 (3)
C(1)-C(2)-Fe(1)	96.4 (1)	98.2 (2)	97.3 (2)
C(1)-C(2)-Fe(2)	88.8 (1)	86.5 (2)	83.7 (2)
C(3)-C(2)-Fe(1)	127.3 (2)	126.8 (2)	124.6 (2)
C(3)-C(2)-Fe(2)	127.6 (1)	127.4 (2)	129.8 (2)
C(3)-C(2)-C(1)	126.3 (2)	127.0 (3)	130.2 (2)
N-C(111)-C(112)	111.9 (3)	110.2 (4)	114.7 (4)
N-C(121)-C(122)	112.1 (3)	111.7 (3)	114.2 (4)
C(111)-N-C(1)	122.9 (2)	119.9 (3)	121.0 (3)
C(121)-N-C(1)	120.7 (2)	123.5 (3)	122.5 (3)
C(121)-N-C(111)	116.4 (2)	116.3 (3)	116.1 (3)
C(4)-C(3)-C(2)		113.5 (3)	
C(5)-C(4)-C(3)		124.7 (3)	
C(3)-Si-C(2)			113.4 (2)
C(4)-Si-C(3)			105.6 (3)
C(4)-Si-C(2)			109.1 (2)
C(5)-Si-C(2)			112.7 (2)
C(5)-Si-C(3)			104.6 (2)
C(5)-Si-C(4)			111.1 (3)

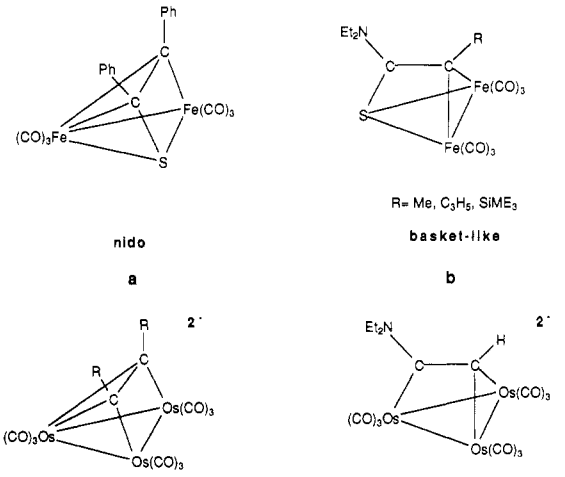
Table V. Comparison of the Fe_2C_2S Core for Complexes 4–6 with Schrauzer's Complex $[Fe_2(CO)_6Ph_2C_2S]$[a,25]

	4	5	6	$[Fe_2(CO)_6Ph_2C_2S]$
Fe(1)-Fe(2)	2.4832 (4)	2.4861 (6)	2.4864	2.533 (1)
Fe(1)-C(2)	2.021 (2)	2.013 (3)	2.071 (3)	1.969 (7)
Fe(2)-C(2)	2.051 (2)	2.068 (3)	2.085 (3)	2.089 (6)
Fe(1)-S	2.2505 (6)	2.2472 (9)	2.2436 (9)	2.256 (2)
Fe(2)-S	2.2546 (6)	2.2518 (9)	2.2677 (9)	2.243 (2)
θ	80.8	75.7	71.4	

[a] Bond lengths are in angstroms and angles in degrees.

The reason for the difference in the value of the angle θ may be either electronic or steric. There is no great change in the C(1)–N bond length, which remains close to a double bond, varying from 1.31 to 1.33 Å (mean values). Steric hindrance has then to be considered. The shortest H···H nonbonding contacts are observed in **6**, which has the smallest θ: H(21)···H(42) = 2.20 Å and H(21)···H(52) = 2.00 Å. These short contacts occurring between H(21) belong to a methylene group and H(42) and H(52) belong to two (trimethylsilyl)methyl groups. A normal H···H van der Waals contact between CH_2 and CH_3 groups usually is 2.30 Å. It then seems more likely that θ is influenced by steric hindrance since the more bulky group leads to the smallest θ value.

Chart II



Although Fe–Fe, Fe–S, and Fe–C(2) distances are not identical within experimental errors (Table V), the Fe_2SC core may be regarded as unchanged in the three complexes. These distances compare well with those observed in the related $[Fe_2(CO)_6\{(C_6H_5)_2C_2S\}]$ compound prepared by Schrauzer.[25] However, in this last complex, C(2) is within bonding distance, 2.061 (6) Å, of Fe(2), and the four atoms, Fe(1), C(1), C(2), and S, lie approximately in a plane. The geometry of Schrauzer's complex may be described as "nido" square pyramidal (Chart IIa) with seven skeletal electron pairs.

In the three complexes **4–6**, Fe(2)–C(1) distances range from 2.467 to 2.393 Å and thus are nonbonding. These compounds can be viewed as basketlike cluster with the two iron atoms, the sulfur atom, and the R-bearing carbon atom forming the basket, and the other carbon atom providing the handle (Chart IIb). Although the electron count is the same, there is a structural change that may be related to the amine group, the only difference from Schrauzer's complex. The C(1)–N = 1.33 Å bond length (mean value) indicates a substantial double bond character: the carbon–nitrogen double bond in iminium salts lies within the range 1.28–1.38 Å. Moreover, C(2), C(1), S, N, C(111), and C(121) lie in a plane, with the largest deviation being less than 0.08 Å. The involvement of the nitrogen lone pair results in the rupture of the Fe(2)–C(1) bond. Weakening or breaking of metal–C(alkyne) bond when the substituent on C is an amino group seems to be general, as also observed by Adams et al.[18,9,26]

It is worth pointing out that a structure similar to that in Chart IIb is observed when S is replaced by the terminal nitrogen of $RR'CN_2$ ligands (R = R′ = Ph, H; R = H, R′ = COOEt).[3]

The description of the structure in Chart IIb allows an interesting comparison with the trinuclear cluster $[Os_3(CO)_9(\mu^3\text{-}HC_2NEt_2)(\mu\text{-}H)_2]$ described by Adams[26a] and Deeming[26b] in which the aminoalkyne was formed within the complex. The electronic structure of this nonclassical trimetallic alkyne cluster[27] complex indicates that the delocalization along C(1)–C(2)–N makes the acetylenic π orbital less available for bonding with the metallic triangle. This favors the basketlike structure (Chart IId). Moreover, the analogy between structures b and d shows the isolobal relationship between S and $Os(CO)_4$.

As a conclusion, this work shows that only the Fe=C (aminocarbene) bond is involved in the sulfur nucleophilic attack, whereas the bridging carbene remains untouched. The bridging group may play a stabilizing role, preventing the metal–metal bond rupture. Recently, Adams et al.[28] reported that hydrogenation of the ynamine ligand in $[Os_3(CO)_9\{\mu^3\text{-}MeC_2NMe_2\}(\mu^3\text{-}S)]$ yielded an ethyl(dimethylamino)carbene ligand attached to the $[Os_3(CO)_9(\mu^3\text{-}S)(\mu\text{-}H_2]$ framework. This hydrogenation involves the bridging carbon atom, which becomes a methylene group, while the terminal carbene remains a carbene. This provides evidence that the bridge may also be reactive, being selectively hydrogenated. It would be interesting to consider a similar reaction upon $[Fe_2(CO)_6\{RC_2(NEt_2)S\}]$ complexes, which has not yet been attempted.

Experimental Section

Reactions were carried out under dry nitrogen by using standard Schlenk or vacuum line techniques. Preparative column chromatography was performed by using 70–230-mesh Merck silica gel. For thin-layer analytical chromatography (TLC), sheets of aluminum silica gel $60F_{254}$ were used. Infrared absorption spectra were measured with a Perkin-Elmer 597 spectrometer. A Nermag R10-10 spectrometer was used for molecular mass determination. NMR spectra were recorded on a Brucker WM 200. Hexane and dichloromethane were purified by standard procedures and stored over molecular sieves. Literature procedure was used to prepare $MeC{\equiv}CNEt_2$, $C_3H_5C{\equiv}CNEt_2$, and $Me_3SiC{\equiv}CNEt_2$.[29]

Preparation of $[Fe_2(CO)_7\{C_3H_5C_2NEt_2\}]$ (2). An excess of *N,N*-diethylpent-4-en-1-ynyl-1-amine (0.244 g; 1.78 mmol) was added to a suspension of $[Fe_2(CO)_9]$ (0.500 g; 1.37 mmol) in 40 mL of *n*-hexane, and Me_3NO (0.135 g; 1.8 mmol) in 10 mL of dichloromethane was added dropwise. The reaction mixture was cooled to 0 °C and stirred for 4 h. The color rapidly changed from yellow to dark orange. Solvents were removed under reduced pressure, and the residue was chromatographed with *n*-hexane as eluant, giving three bands, yellow, dark orange, and red-orange. Evaporation of the solvent containing the yellow product followed by recrystallization from *n*-hexane at −20 °C afforded yellow crystals (0.150 g; 0.27 mmol; 21% yield) identified as the "ferrole" type complex $[Fe_2(CO)_6\{C_4(C_3H_5)_2(NEt_2)_2\}]$[16] from infrared and elemental analyses. Neither the dark-orange solution nor the red-orange solution could produce crystals. The dark-orange solution transformed into the red-orange solution in a few hours at room temperature. The dark-orange solution contained a complex identified as **2** $[Fe_2(CO)_7\{C_3H_5C_2NEt_2\}]$ by infrared and mass spectra. The red-orange solution afforded a complex **2′**, which was given the formula $[Fe_2(CO)_6\{C_3H_5C_2NEt_2\}]$ from mass spectrometry.

$[Fe_2(CO)_6\{C_4(C_3H_5)_2(NEt_2)_2\}]$ ("ferrole"): IR ν(CO) 1900 (m), 1965 (sh), 1975 (s), 2020 (s), 2060 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{30}O_6N_2Fe_2$: C, 52.01; H, 5.46; N, 5.05. Found: C, 52.43; H, 5.82; N, 5.14.

$[Fe_2(CO)_7\{C_3H_5C_2NEt_2\}]$ (**2**): IR, see Table I. MS *m/e* 445 (M^+).

$[Fe_2(CO)_6\{C_3H_5C_2NEt_2\}]$ (**2′**): IR ν(CO) 1960 (sh), 1970 (s), 2020 (s), 2070 (m) cm^{-1}. MS *m/e* 418 (M^+).

Preparation of $[Fe_2(CO)_7\{Me_3SiC_2NEt_2\}]$ (3). *N,N*-Diethyl[(trimethylsilyl)ethynyl]amine (0.600 g; 3.57 mmol) was added to a suspension of $[Fe_2(CO)_9]$ (1.000 g; 2.74 mmol) in 60 mL of *n*-hexane, and then Me_3NO (0.270 g; 3.57 mmol) in 20 mL of CH_2CL_2 was added dropwise. The resulting reddish solution obtained upon stirring for 4 h at room temperature was evaporated to dryness, and the residual solid was chromatographed with hexane as eluant, giving two bands, one yellow and one red. The

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Table VI. Synthetic Work Data

preparation	4, R = Me	5, R = C_3H_5	6, R = $SiMe_3$
amt of $[Fe_2(CO)_7\{RCCNEt_2\}]$, g	0.05 (0.12 mmol)	0.05 (0.11 mmol)	0.05 (0.10 mmol)
amt of CS_2, g	0.015 (0.2 mmol)	0.015 (0.2 mmol)	0.015 (0.2 mmol)
amt of complex, g	0.038 (0.09 mmol)	0.019 (0.04 mmol)	0.032 (0.07 mmol)
yield, %	75	36	67
amt of C_2H_4S, g	0.01 (0.17 mmol)	0.01 (0.17 mmol)	0.01 (0.17 mmol)
amt of complex, g	0.044 (0.10 mmol)	0.036 (0.08 mmol)	0.039 (0.08 mmol)
yield, %	83	72	80

Table VII. IR, ^1H NMR, and MS Data for Complexes 4–6

	4, R = Me	5, R = C_3H_5	6, R = $SiMe_3$
ν(CO), cm^{-1}	1945 (s), 1960 (vs)	1950 (s), 1975 (s)	1940 (sh), 1960 (vs)
	1970 (s), 1990 (s)	2000 (m), 2020 (s)	1970 (s), 1985 (s)
	2020 (s), 2070 (m)	2070 (s)	2030 (s), 2070 (m)
ν(C=N), cm^{-1}	1515 (m)	1530 (m)	1500 (m)
ν(CS), cm^{-1}	620 (m)	620 (m)	620 (m)
^1H NMR	1.2 (t, 6 H, $(CH_2CH_3)_2$)		0.34 (s, 9 H, $SiMe_3$)
(80 MHz, $CDCl_3$)	2.2 (s, 3 H, CH_3 bridge)		0.8 (t, 6 H, $(CH_2CH_3)_2$)
δ, ppm	3.3 (q, 4 H, $(CH_2CH_3)_2$)		3.1 (q, 4 H, $(CH_2CH_3)_2$)
MS, m/e (M^+)	423	449	481
Anal. Calcd for	$C_{13}H_{13}NO_6SFe_2$	$C_{15}H_{15}NO_6SFe_2$	$C_{15}H_{19}NO_6SSiFe_2$
calcd; found			
C	36.91; 36.83	40.12; 40.26	37.44; 37.31
H	3.10; 3.34	3.37; 3.51	3.98; 4.23
N	3.31; 3.36	3.12; 3.19	2.91; 3.00

Table VIII. Crystal Data

compd	3	4	5	6
formula	$C_{16}H_{19}O_7NSiFe_2$	$C_{13}H_{13}O_6NSFe_2$	$C_{15}H_{15}O_6NSFe_2$	$C_{15}H_{19}O_6NSSiFe_2$
fw	477.1	423.1	449.0	481.2
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	9.975 (3)	9.627 (3)	7.553 (1)	16.219 (2)
b, Å	14.009 (2)	7.623 (2)	9.591 (3)	10.175 (1)
c, Å	15.802 (4)	12.594 (3)	14.444 (2)	13.558 (4)
α, deg	90	100.70 (2)	73.62 (2)	90
β, deg	92.50 (2)	95.69 (2)	72.46 (2)	107.64 (3)
γ, deg	90	104.81 (2)	75.99 (2)	90
V, $Å^3$	2206	867	943	2132
Z	4	2	2	4
μ(Mo Kα), cm^{-1}	14.0	18.12	16.72	15.37
d_{calc}, g cm^{-3}	1.44	1.62	1.58	1.50
2θ range, deg	$3 < 2\theta < 50$	$3 < 2\theta < 60$	$3 < 2\theta < 50$	$4 < 2\theta < 50$
scan width, deg	1.1 + 0.34 tan θ	1.1 + 0.34 tan θ	0.9 + 0.34 tan θ	1.2 + 0.34 tan θ
scan speed, deg min^{-1}	2.1 < sp. < 5.5	1.1 < sp. < 5.5	2.4 < sp. < 5.5	5
diffractometer	Enraf-Nonium CAD4	Enraf-Nonium CAD4	Enraf-Nonium CAD4	Philips PW1100
no. of reflns collected	4206	5298	3437	3831
no. of unique reflns	3875	5051	3296	3428
merging R factor	0.01	0.016	0.015	0.012
reflns used ($I > 3\sigma(I)$)	2840	3566	2195	2545
abs correction	ψ scan[33]	Ψ scan[33]	difabs[34]	difabs[34]
R	0.0303	0.0313	0.0265	0.0385
R_w	0.0360	0.0392	0.0286	0.0416
coeff for Chebyshev series	9.1, −2.29, 7.14	7.74, −1.9, 6.14	1.90, −0.79, 1.18	2.29, 0.36, 1.96
no. of variables	304	248	273	236

evaporation of the solvent containing the yellow product followed by recrystallization from n-hexane at −20 °C afforded yellow crystals (0.260 g; 0.54 mmol; 20% yield) identified as $[Fe(CO)_3\{C_4(SiMe_3)_2(NEt_2)_2\}]$ from infrared and elemental analyses. The red solution afforded at −20 °C red crystals of **3** (0.730 g; 1.53 mmol; 56% yield).

$[Fe(CO)_3\{C_4(SiMe_3)_2(NEt_2)_2\}]$: IR (KBr pellets) ν(CO) 1930 (s), 2010 (s) cm^{-1}; ν(C=C) 1540 (m) cm^{-1}. Anal. Calcd for $C_{21}H_{38}O_3N_2Si_2Fe$: C, 52.71; H, 8.57; N, 5.85. Found: C, 53.01; H, 8.05; N, 5.02.

$[Fe_2(CO)_7\{Me_3SiC_2NEt_2\}]$ (**3**): IR, see Table I. MS m/e 478 (M^+). ^1H NMR (250 MHz, C_6D_6) δ 3.1 (m, 4 H, $(CH_2CH_3)_2$), 0.7 (t, 6 H, $(CH_2CH_3)_2$), 0.31 (s, 9 H, $Si(CH_3)_3$). ^{13}C NMR (250 MHz, C_6H_6, room temperature) δ 227.61 (s, CO), 212.71 (s, $CNEt_2$), 78.0 (s, $CSiMe_3$), 53.45 (s, CH_2CH_3), 40.73 (s, CH_2CH_3), 12.46 (s, CH_2CH_3), 11.40 (s, $CHCH_3$), 1.93 (s, $(CH_3)_3Si$).

Reactions of 1–3 with CS_2: Preparation of Complexes 4–6. The synthetic procedures were similar for the three complexes. Excess carbon disulfide was added to a n-hexane solution of compound **1**, **2**, or **3**. After stirring for 6 h at 40 °C, the solution was evaporated to dryness, and the residual solid was chromatographed, giving two red bands with n-hexane as eluant. The first red solution was attributed to unreacted starting diiron complexes. Evaporation of the second red solution followed by recrystallization from n-hexane at −20 °C afforded red crystals of **4**, **5**, and **6** (see Table VI).

The lower yield observed for complex **5** is related to the partial transformation of complex **2** into **2'** during reaction. IR, NMR, mass spectra, and elemental analyses are given in Table VII.

Reactions of 1–3 with Ethylene Sulfide. Ethylene sulfide in excess (10 μL, 0.17 mmol) was added to a solution of complex **1**, **2**, or **3** in n-hexane (40 mL) (Table VI). The mixture was stirred for 1 h at room temperature. Thin-layer chromatography showed only one reaction product. The solution was concentrated to ca. 5 mL and left at −20 °C. Red crystals of **4**, **5**, and **6** were obtained and identified by infrared spectra.

Crystal Data for Complexes 3, 4, 5, and 6. For all compounds, preliminary unit cell dimensions and symmetry information were derived from precession photographs. Selected crystals were set up on an automatic diffractometer. Unit cell

Table IX. Fractional Atomic Coordinates, with Esd's in Parentheses, and Equivalent Isotropic Thermal Parameters U(eq) (Å^2)

$$U(\text{eq}) = [U_{11}U_{22}U_{33}]^{1/3}$$

atom	x/a	y/b	z/c	U(eq)
		Compound **3**		
Fe(1)	0.12150 (4)	0.62610 (3)	0.87010 (2)	0.0562
Fe(2)	0.11393 (3)	0.80509 (3)	0.91733 (2)	0.0500
C(1)	−0.0583 (2)	0.7751 (2)	0.8712 (1)	0.0451
C(2)	0.0306 (2)	0.7437 (2)	0.8131 (1)	0.0476
Si	0.0331 (1)	0.78412 (6)	0.70114 (5)	0.0672
C(8)	−0.0864 (6)	0.8839 (3)	0.6862 (3)	0.1106
C(9)	0.1994 (5)	0.8306 (4)	0.6738 (3)	0.1111
N	−0.1871 (2)	0.7828 (1)	0.8782 (1)	0.0541
C(3)	−0.2827 (3)	0.7382 (2)	0.8160 (2)	0.0720
C(4)	−0.3339 (5)	0.6448 (3)	0.8445 (4)	0.1110
C(5)	−0.2433 (3)	0.8335 (2)	0.9504 (2)	0.0699
C(6)	−0.2904 (4)	0.9316 (3)	0.9271 (3)	0.0880
C(7)	−0.0159 (5)	0.6838 (3)	0.6288 (2)	0.0953
C(11)	0.0114 (4)	0.6255 (2)	0.9570 (2)	0.0738
O(11)	−0.0581 (3)	0.6147 (2)	1.0119 (2)	0.0964
C(12)	0.0353 (4)	0.5304 (2)	0.8163 (2)	0.0786
O(12)	−0.0204 (3)	0.4688 (2)	0.7838 (2)	0.1131
C(13)	0.2512 (4)	0.6357 (3)	0.7944 (2)	0.0856
O(13)	0.3352 (3)	0.6345 (3)	0.7496 (2)	0.1276
C(14)	0.2456 (4)	0.5708 (3)	0.9391 (2)	0.0839
O(14)	0.3266 (3)	0.5361 (2)	0.9814 (2)	0.1184
C(21)	0.1098 (3)	0.8025 (2)	1.0306 (2)	0.0722
O(21)	0.1052 (3)	0.8009 (2)	1.1028 (1)	0.1026
C(22)	0.0938 (3)	0.9286 (2)	0.9063 (2)	0.0718
O(22)	0.0788 (4)	1.0092 (2)	0.8986 (2)	0.1071
C(23)	0.2905 (3)	0.8084 (3)	0.9028 (2)	0.0773
O(23)	0.4030 (3)	0.8132 (3)	0.8932 (2)	0.1106
		Compound **4**		
Fe(1)	−0.77815 (3)	0.05793 (4)	−0.23849 (2)	0.0473
Fe(2)	−0.82214 (3)	−0.27902 (4)	−0.31651 (2)	0.0447
S	−0.96933 (6)	−0.11118 (9)	−0.36614 (4)	0.0508
C(1)	−1.0277 (2)	−0.1805 (3)	−0.2479 (2)	0.0420
C(2)	−0.8938 (2)	−0.1565 (3)	−0.1817 (2)	0.0441
C(3)	−0.8741 (3)	−0.1890 (3)	−0.0674 (2)	0.0518
C(11)	−0.8479 (3)	0.2329 (3)	−0.1664 (2)	0.0559
C(12)	−0.6824 (3)	0.1856 (4)	−0.3293 (2)	0.0651
C(13)	−0.6184 (3)	0.0952 (4)	−0.1437 (2)	0.0630
C(21)	−0.9399 (3)	−0.5125 (3)	−0.3524 (2)	0.0547
C(22)	−0.7265 (3)	−0.2810 (4)	−0.4327 (2)	0.0654
C(23)	−0.6828 (2)	−0.3226 (4)	−0.2311 (2)	0.0552
C(111)	−1.2186 (3)	−0.3060 (4)	−0.1445 (2)	0.0597
C(112)	−1.2560 (4)	−0.5144 (5)	−0.1629 (3)	0.0874
C(121)	−1.2808 (3)	−0.2392 (4)	−0.3268 (2)	0.0635
C(122)	−1.3136 (4)	−0.0560 (6)	−0.3138 (4)	0.0884
N	−1.1679 (2)	−0.2394 (3)	−0.2394 (2)	0.0496
O(11)	−0.8938 (3)	0.3400 (3)	−0.1185 (2)	0.0795
O(12)	−0.6240 (3)	0.2678 (4)	−0.3859 (2)	0.0906
O(13)	−0.5161 (3)	0.1189 (4)	−0.0835 (2)	0.0900
O(21)	−1.0134 (3)	−0.6602 (3)	−0.3729 (2)	0.0757
O(22)	−0.6649 (3)	−0.2821 (5)	−0.5045 (2)	0.0967
O(23)	−0.5951 (2)	−0.3515 (3)	−0.1757 (2)	0.0752
		Compound **5**		
Fe(1)	0.22929 (6)	0.71643 (5)	0.83040 (3)	0.0441
Fe(2)	0.25394 (6)	0.79952 (5)	0.64832 (3)	0.0474
S	0.3939 (1)	0.89225 (9)	0.72946 (6)	0.0501
C(1)	0.1630 (4)	0.9944 (3)	0.7394 (2)	0.0419
C(2)	0.0559 (4)	0.8812 (3)	0.7632 (2)	0.0416
C(3)	−0.1559 (4)	0.8987 (3)	0.7854 (2)	0.0492
C(4)	−0.2540 (4)	0.9107 (4)	0.8895 (3)	0.0574
C(5)	−0.3663 (6)	0.8232 (5)	0.9518 (3)	0.0781
N	0.1298 (4)	1.1407 (3)	0.7225 (2)	0.0518
C(111)	0.2896 (6)	1.2227 (4)	0.6891 (3)	0.0751
C(121)	−0.0583 (5)	1.2302 (4)	0.7261 (3)	0.0583
C(112)	0.3427 (8)	1.2368 (6)	0.7760 (5)	0.1006
C(122)	−0.0997 (7)	1.2785 (5)	0.6253 (3)	0.0857
C(11)	0.1714 (5)	0.7696 (4)	0.9470 (2)	0.0568
O(11)	0.1328 (4)	0.8058 (3)	1.0198 (2)	0.0783
C(12)	0.4311 (5)	0.5719 (4)	0.8435 (3)	0.0637
O(12)	0.5555 (4)	0.4800 (3)	0.8521 (3)	0.0918
C(13)	0.0688 (5)	0.5925 (4)	0.8651 (2)	0.0553
O(13)	−0.0364 (4)	0.5140 (3)	0.8860 (2)	0.0739
C(21)	0.2381 (5)	0.9408 (4)	0.5371 (2)	0.0547
O(21)	0.2263 (4)	1.0277 (3)	0.4663 (2)	0.0780
C(22)	0.4599 (6)	0.6788 (4)	0.5984 (3)	0.0729
O(22)	0.5883 (5)	0.6001 (4)	0.5671 (3)	0.1062
C(23)	0.0964 (6)	0.6946 (4)	0.6432 (2)	0.0620
O(23)	−0.0070 (5)	0.6258 (3)	0.6420 (2)	0.0864
		Compound **6**		
Fe(1)	0.74802 (3)	0.11535 (4)	0.35887 (3)	0.0415
Fe(2)	0.65911 (3)	0.13871 (5)	0.47846 (4)	0.0480
S	0.66112 (5)	0.28807 (8)	0.35506 (6)	0.0465
C(1)	0.7439 (2)	0.3284 (3)	0.4705 (2)	0.0387
N	0.7516 (2)	0.4510 (3)	0.5064 (2)	0.0482
C(2)	0.7852 (2)	0.2056 (3)	0.5025 (2)	0.0387
Si	0.88666 (6)	0.1662 (1)	0.60926 (8)	0.0505
C(3)	0.9253 (3)	−0.0071 (5)	0.6044 (4)	0.0791
C(4)	0.9762 (3)	0.2736 (6)	0.5963 (4)	0.0787
C(5)	0.8729 (4)	0.1821 (6)	0.7403 (3)	0.0779
C(111)	0.6933 (3)	0.5563 (4)	0.4497 (3)	0.0616
C(112)	0.6110 (4)	0.5682 (6)	0.4750 (5)	0.0924
C(121)	0.8096 (3)	0.4864 (4)	0.6095 (3)	0.0674
C(122)	0.8715 (5)	0.5949 (5)	0.6086 (5)	0.1037
C(11)	0.8363 (2)	0.1799 (4)	0.3189 (3)	0.0532
O(11)	0.8926 (2)	0.2175 (3)	0.2934 (2)	0.0759
C(12)	0.6812 (3)	0.0517 (4)	0.2349 (3)	0.0570
O(12)	0.6408 (2)	0.0114 (3)	0.1572 (2)	0.0753
C(13)	0.7855 (3)	−0.0472 (3)	0.3921 (3)	0.0544
O(13)	0.8047 (2)	−0.1568 (3)	0.4041 (3)	0.0776
C(21)	0.6240 (3)	0.2259 (5)	0.5746 (4)	0.0677
O(21)	0.6030 (3)	0.2778 (4)	0.6374 (3)	0.1017
C(22)	0.5577 (3)	0.0656 (6)	0.4057 (4)	0.0775
O(22)	0.4958 (3)	0.0172 (6)	0.3603 (3)	0.1137
C(23)	0.6943 (3)	−0.0063 (4)	0.5528 (4)	0.0695
O(23)	0.7147 (3)	−0.0977 (4)	0.6014 (4)	0.0995

dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other pertinent information are summarized in Table VIII. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections were applied.

Computations were performed by using CRYSTALS[30] adapted on a MicroVax II. Atomic form factors for neutral Fe, C, N, O, S, Si, and H were taken from ref 31. Anomalous dispersion was taken into account. All structures were solved by interpretation of Patterson maps which indicated iron atom positions. All remaining non-hydrogen atoms were found by successive electron density map calculations. Hydrogen atoms were found on difference maps. Their atomic coordinates were refined with a variable overall isotropic thermal parameter. In compounds **5** and **6**, C–H distances and H–C–H angles were constrained to chemically reasonable values (C–H = 0.98 Å; H–C–H = 109°) by the method of Waser implemented in the CRYSTALS package. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Least-squares refinements with approximation to the normal matrix were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycle was $w = w'[1 - (\Delta F/6\sigma(F_o)^2]^2$ where $w' = 1/\sum_1{}^3\text{ArTr}(x)$ with three coefficients Ar for the Chebyshev polynomial $\text{ArTr}(x)$ where x was $F_c/F_c(\text{max})$.[32] Models reached

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convergence with $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(||F_o| - |F_c||)^2/\sum wF_o^2]^{1/2}$, having values listed in Table VIII. Criteria for a satisfactory complete analysis were the ratios of root-mean-square (rms) shift to standard deviation being less than 0.1 and no significant features in final difference maps. Atomic coordinates are given in Table IX.

Supplementary Material Available: Tables of anisotropic temperature factors, hydrogen coordinates, and bond distances and angles for CO ligands (10 pages); tables of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

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Preparation and Stoichiometric and Catalytic Reactivity of Hydrido Organometallic Ruthenium Complexes. X-ray Crystal Structure of $[RuH(\eta^5\text{-}C_8H_{11})_2]BF_4$

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Received April 12, 1990

Protonation of $Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})$ by $HBF_4{\cdot}Et_2O$ at −80 °C initially produces $[RuH(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})]BF_4$ (**1**). Complex **1** isomerizes in solution to $[RuH(\eta^5\text{-}C_8H_{11})_2]BF_4$ (**2**) through a mechanism that has been specifically studied by freezing the reaction through deprotonations. The X-ray crystal structure of **2** shows the complex to be a ruthenium(IV) hydride lacking any agostic interactions: space group $C_{2h}^6\text{-}C2/c$; a = 10.962 (1) Å, b = 9.922 (1) Å, c = 15.077 (1) Å, β = 98.71 (1)°; V = 1620.9 (5) Å^3; Z = 4. Complex **2** reacts with acetone to give an equilibrium mixture of **2** and $[Ru(\eta^5\text{-}C_8H_{11})(\eta^4\text{-}C_8H_{12})\text{-}(acetone)]BF_4$ (**3**), thus demonstrating the ease of hydrogen transfer in the system. The reaction of **1** with S (S = MeCN, H_2O) produces $[Ru(\eta^5\text{-}C_8H_{11})S_3]BF_4$ (**5** and **4**, respectively), while with C_5Me_5H the complex $[Ru(\eta^5\text{-}C_5Me_5)(C_8H_{12})]BF_4$ (**7**) is formed and shown by ^1H and ^{13}C NMR studies to adopt a ruthenium(II) structure with an agostic interaction. With cyclopentene, a similar complex is obtained for which the formula $[Ru(\eta^5\text{-}C_5H_5)(C_8H_{12})]BF_4$ (**9**) is proposed. **1** also reacts with $PMePh_2$ to yield $[Ru(\eta^5\text{-}C_8H_{11})(PMePh_2)_3]BF_4$ (**6**) and with C_6Me_6 to yield $[Ru(\eta^5\text{-}C_8H_{11})(\eta^6\text{-}C_6Me_6)]BF_4$ (**10**). Complex **1** or its derivatives are catalysts for 1-alkene isomerization, ethylene dimerization, and ring-opening polymerization of norbornene.

Introduction

Cationic organometallic derivatives and more specifically cationic allyl species of group 10 have shown high reactivity toward olefins and exhibit remarkable catalytic properties.[1] We have recently attempted the preparation of similar ruthenium complexes in order to compare their reactivities with those of group 10 metals and to develop new reactions.[2] In this regard, ruthenium complexes are increasingly studied in view of their potential catalytic applications.[3] For example, ruthenium hydride[4] compounds or derivatives of Ru(COD)(COT)[3] (COD is cyclooctadiene, COT is cyclooctatetraene) have been used for the linear codimerization of butadiene and acetylenes. However, the cationic complexes that we obtained, $[Ru(1\text{-}3{:}5\text{-}6\text{-}\eta\text{-}C_8H_{11})(\eta^6\text{-}C_8H_{10})]PF_6$ or $[Ru(1\text{-}3{:}5\text{-}6\text{-}\eta\text{-}C_8H_{11})(\eta^6\text{-}C_6H_6)]\text{-}PF_6$,[2] were electronically saturated and did not show high catalytic activity.

On the other hand, the protonation of low-valent olefinic organometallic complexes usually does not lead to hydride species but rather to unsaturated species that may show a strong C–H–M or agostic interaction.[5,6] A much greater reactivity was thus expected from these unsaturated or agostic species in which the three-center interaction can be easily broken. This property has been used for catalytic reactions such as the recent polymerization of ethylene using cobalt complexes.[4d] As part of our interest for hydrogen-transfer reactions related to the study of C–H activation,[7] we have examined the protonation of Ru(COD)(COT) and shown that the ruthenium complex can undergo numerous hydrogen-transfer reactions. The stoichiometric and catalytic reactivity of these species toward unsaturated hydrocarbons has been studied. However, problems of stability, in particular in the pres-

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0276-7333/91/2310-0455$02.50/0