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The Synthesis and Structure of (μ-η^2,η^3-Pentadienyl)(μ-alkanethiolato)pentacarbonyldiiron (Fe–Fe) Complexes. An Unusual Bonding Mode for the Pentadienyl Group

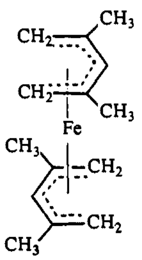
Dietmar Seyferth,* Lea L. Anderson, Fernando Villafañe, and William M. Davis

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received November 7, 1991*

Abstract: The reaction of 5-bromopenta-1,3-diene with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ (R = *t*-Bu, Et, Ph) complexes gave products of type $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-}RS)Fe_2(CO)_5$ as well as the respective $(\mu\text{-}RS)_2Fe_2(CO)_6$. Similar reactions with 1-bromohexa-2,4-diene resulted in formation of $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCHCH_3)(\mu\text{-}RS)Fe_2(CO)_5$, which suggests that the reaction of the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anions with the halides is an S_N2' process. The structure of $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-}PhS)Fe_2(CO)_5$ has been determined by X-ray diffraction. This compound crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with $a = 9.763$ (6) Å, $b = 11.132$ (4) Å, $c = 9.346$ (4) Å, $\alpha = 111.71$ (3)°, $\beta = 111.57$ (4)°, $\gamma = 92.03$ (5)°, $V = 860.2$ (8) Å, and $Z = 2$. Refinement has converged at $R = 0.035$ and $R_w = 0.040$ on the basis of 217 parameters varied and 1799 unique observations.

Introduction

The pentadienyl ligand is known to coordinate to transition metal atoms in a number of ways. The most common pentadienyl complexes are those in which this ligand is bonded to the metal in an η^5 or η^3 fashion. Examples of neutral complexes in which the former type of bonding is operative include compounds **1**,[1] **2a**,[2] and **2b**.[3] Compounds **3**,[4] **4**,[5] **5**,[5] and **6**[6] are examples of the η^3 bonding mode. One compound which provides an example of the rare η^1 bonding mode, **7**, undergoes isomerization upon UV irradiation to η^5 and η^3 complexes (eq 1).[7] Compounds **1** and **2** are representatives of a large class of η^5-pentadienyl complexes in which the ligand has the "U" geometry. The "S" geometry also is possible, and **8**[8] and **9**[9] are examples. The pentadienyl group also may be η^1 bonded to the metal atom via the central carbon atom, as in **10**.[10] More exotic types of bonding are known. The reaction of σ,π-allylheptacarbonyldiiron (Fe–Fe) with simple acetylenes gives products in which the substituted pentadienyl



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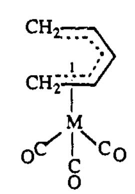
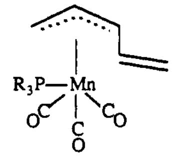


2 a, M = Mn
b, M = Re



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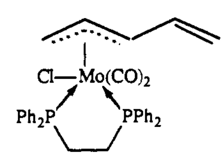

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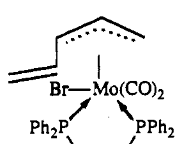

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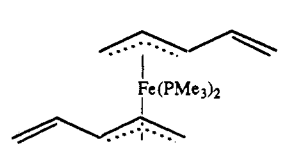

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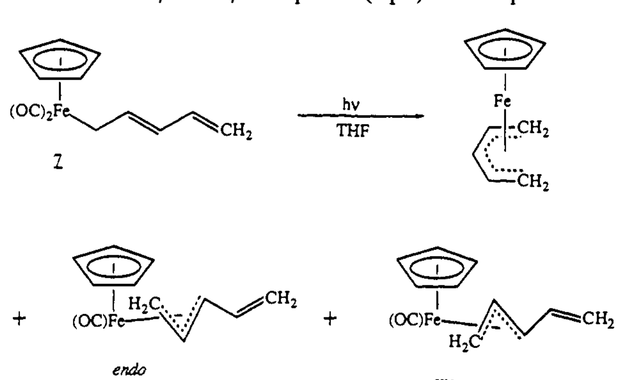

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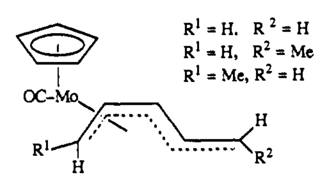

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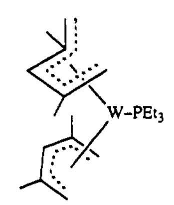

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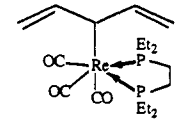

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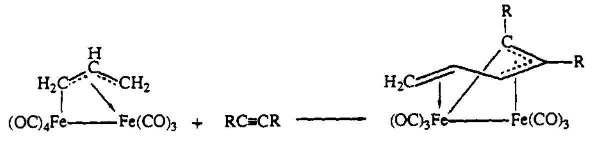
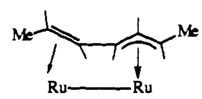
ligand is bonded to the iron atoms in η^1, η^2, and η^3 fashion, **11** (eq 2).[11] A related bonding mode of a 1,5-dimethylpentadienyl ligand was found in the cluster complexes $(\mu\text{-}1,5\text{-}Me_2C_5H_5)(\mu\text{-}H)(\mu_4\text{-}S)Ru_5(CO)_{12}$ and $(\mu\text{-}1,5\text{-}Me_2C_5H_5)(\mu\text{-}H)(\mu_4\text{-}S)Ru_6(CO)_{15}$ in which the organic ligand was bonded to two adjacent Ru atoms in an η^2,η^3 manner, **12**.[12] A hexacarbonyldiiron complex has been


(2)

R = H, Me

11



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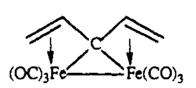
reported[13] in which the pentadienyl ligand is bonded as shown in **13**: the central carbon atom is a bridging carbene carbon, while the other four carbon atoms are olefinic and η^2-bonded to the two iron atoms. The pentadienyl ligand also may be of the η^1,η^2 type, as in **14**[14] and of the η^1,η^4 type, as in **15**.[15] Related to **11** in that the pentadienyl is at the same time η^1, η^2, and η^3 bonded to metal atoms is complex **16** (eq 3).[16] Finally, among these exotica, there is complex **17**.[17]



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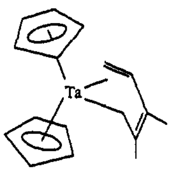

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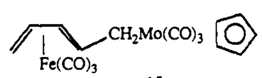

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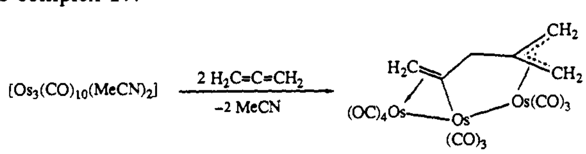
(3)

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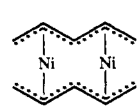
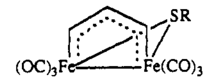


17

During the last eight years we have been investigating the rich chemistry of the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anions.[18] In earlier studies we found that they reacted with allyl chloride to give σ,π-allyl complexes.[18a] We wrote these (incorrectly) as **15**; the correct description is that shown as **18a,b**. In view of this finding, it was of interest to establish how the pentadienyl ligand, introduced by reaction of the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anions with 5-bromo-1,3-pentadiene, would be bonded to the $Fe_2(CO)_6$ unit. In any case, the pentadienyl ligand would have to be a three-electron donor, and one likely possibility seemed to be **19**.



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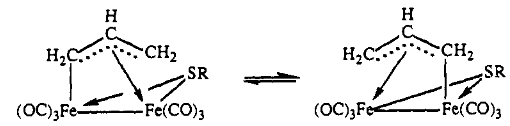
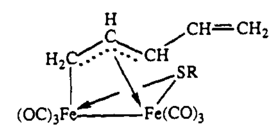


18a 18b



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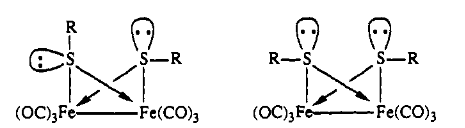
Results and Discussion

The reaction of the triethylammonium salts of the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anions (R = *t*-Bu, Et, Ph) (prepared by addition of triethylamine to $Fe_3(CO)_{12}$ and the respective thiol in THF at room temperature[18a]) with 5-bromopenta-1,3-diene, $CH_2{=}CHCH{=}CHCH_2Br$, occurred during 1–1.5 h at room temperature. A color change from dark brown-red to red was noted, and a white solid ($[Et_3NH]Br$) precipitated. In each reaction two products were formed: the pentadienyl product, $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-}RS)Fe_2(CO)_5$, **20a** (R = *t*-Bu), **b** (R = Et), and **c** (R = Ph), and the respective $(\mu\text{-}RS)_2Fe_2(CO)_6$ complex, **21**/**22** (Table I). The latter is an often encountered byproduct of reactions of the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anions and usually is formed as a mixture of the *a,e* and *e,e* isomers (**21** and **22**, respectively). In the present reactions such isomer mixtures also were formed, and the yield of **21**/**22** was greater than usually observed.



21, a,e 22, e,e

Elemental analysis and mass spectrometry established that a product of type $(C_5H_7)(\mu\text{-}RS)Fe_2(CO)_5$ had been formed. The fact that the product had an $Fe_2(CO)_5$ framework (rather than the usual $Fe_2(CO)_6$) indicated that the pentadienyl ligand was functioning as a five-electron donor, i.e., that both C=C bonds were involved in bonding to the two iron atoms. An unambiguous structure determination was provided by a single crystal X-ray diffraction study of **20c** (R = Ph). An ORTEP plot of the molecule is shown in Figure 1, an inspection of which shows the pentadienyl group to be bonded to the $Fe_2(CO)_5$ unit by η^2 (π-olefinic) and η^3 (π-allyl) type bonding (as in compounds of type 12), i.e., the ligand is solely π-bonded to the $Fe_2(CO)_5$ unit. Hence in the complexes **20** we have another example of an unusual mode of bonding of the pentadienyl group. In contrast to the formation of the ruthenium cluster complexes that contain a $\mu\text{-}\eta^2,\eta^3$-pentadienyl ligand, the present synthesis is straightforward and proceeds in high yield. It should be more generally applicable to the preparation of pentadienyl–metal complexes.

A closer inspection of Figure 1 and the bond distances is of interest. C(7) and C(8) are the olefinic carbon atoms which are coordinated to Fe(2) in an η^2 manner. The remaining carbon atoms of the C_5H_7 ligand comprise the allylic moiety which is

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Table I. Yields of $(\mu\text{-RS})_2Fe_2(CO)_6$, **21/22** and $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-RS})Fe_2(CO)_5$, **20**

R	21/22[a] (%)	20[b] (%)
t-Bu	43	53
Et	51	48
Ph	60	31

[a] Based on S. [b] Based on Fe.

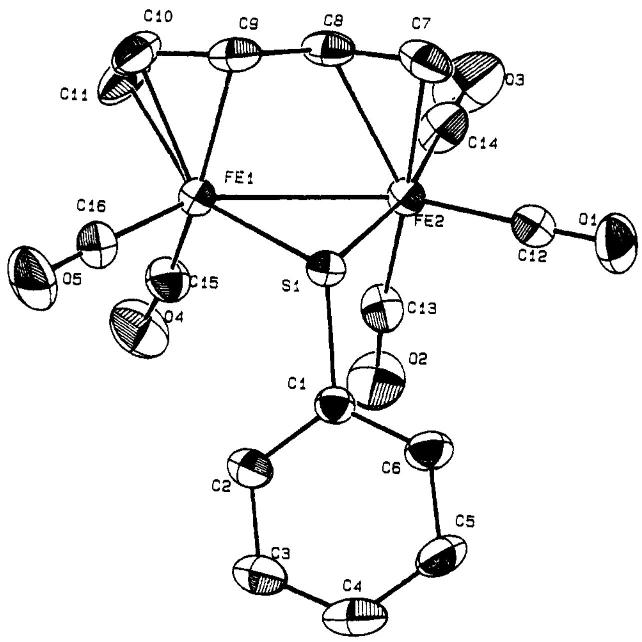
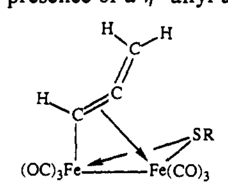
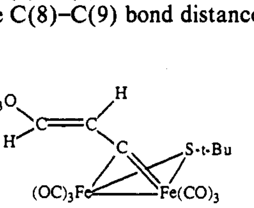


Figure 1. ORTEP plot of $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-PhS})Fe_2(CO)_5$, **20**. Important bond distances (Å) and angles are as follows: Fe(1)–Fe(2), 2.780 (2); Fe(1)–C(9), 2.088 (6); Fe(1)–C(10), 2.046 (6); Fe(1)–C(11), 2.128 (7); Fe(2)–C(7), 2.132 (6); Fe(2)–C(8), 2.281 (6); C(7)–C(8), 1.371 (8); C(8)–C(9), 1.448 (8); C(9)–C(10), 1.408 (9); C(10)–C(11), 1.39 (1); Fe(1)–S(1), 2.229 (3); Fe(2)–S(1), 2.263 (2); C(7)–C(8)–C(9) = 124.0 (6)°, C(8)–C(9)–C(10) = 120.2 (6)°, C(9)–C(10)–C(11) = 121.7 (6)°.

η^3-bonded to Fe(1). The Fe(1)–Fe(2) bond distance of 2.780 (2) Å is somewhat long for an Fe–Fe single bond in a neutral, doubly bridged $Fe_2(CO)_6$ complex (for instance, in **18** d(Fe–Fe) is 2.675 (1) Å[18a]). However, the Fe–Fe bond can, up to a point, adjust to the bite size of the organic bridge. Thus, in **23a** the Fe–Fe distance is 2.550 (1) Å,[18a] and in **23b** it is 2.5214 (6).[19] The Fe(1)–C(11), Fe(1)–C(10), and Fe(1)–C(9) distances establish the presence of a η^3-allyl unit. The C(8)–C(9) bond distance of



23a



23b

1.448 (8) Å is slightly shorter than a true C–C single bond, and this bond separates the η^3-allyl portion from the η^2-olefin portion of the ligand. The olefinic C–C bond, C(7)–C(8), at 1.371 (8) Å, is slightly elongated, compared to an uncomplexed C=C bond, as might have been expected. The benzenethiolate ligand does not bridge the two iron atoms symmetrically, with Fe(1)–S = 2.229 (3) and Fe(2)–S = 2.263 (2) Å. On the basis of these data the line drawing shown in Figure 2 is the best representation of complexes **20**.

The ^{1}H NMR spectra of **20a–c** are very complex. That of **20b** is shown in Figure 3 and tabulated in Table II. There are seven

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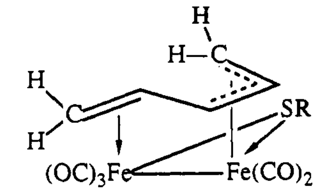
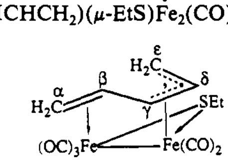


Figure 2. Line drawing of $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-RS})Fe_2(CO)_5$, **20**.

Table II. Relevant ^{1}H and ^{13}C NMR Spectral Data for $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-EtS})Fe_2(CO)_5$, **20b**



δ (ppm)	^1J (Hz)	^2J (Hz)	assignment
^{1}H NMR Spectral Data (in $CDCl_3$ Solution)			
0.34 dd	13.04	2.78	*syn*-$CH_2CHCHCH{=}CH_2$ (*H*)
0.78 dd	10.54	2.09	*syn*-$C\mathit{H}_2CHCHCH{=}CH_2$
0.95 dt	13.01	7.60	$CH_2CHCHC\mathit{H}{=}CH_2$
1.92 d	6.95		*anti*-$C\mathit{H}_2CHCHCH{=}CH_2$
2.22 dd	7.34	2.40	*anti*-$CH_2CHCHCH{=}C\mathit{H}_2$
3.30 dd	7.68	5.02	$CH_2CHC\mathit{H}CH{=}CH_2$
5.96 m			$CH_2C\mathit{H}CHCH{=}CH_2$

δ (ppm)	J_{CH} (Hz)	assignment
^{13}C NMR Spectral Data (in $CDCl_3$ Solution)		
27.45 t	156.6	$CH_2CHCHCH{=}\mathit{C}H_2$
37.25 t	160.4	$\mathit{C}H_2CHCHCH{=}CH_2$
54.33 d	159.1	$CH_2CHCH\mathit{C}H{=}CH_2$
63.84 d	168.6	$CH_2CH\mathit{C}HCH{=}CH_2$
89.27 d	166.8	$CH_2\mathit{C}HCHCH{=}CH_2$

sets of resonances, each integrating for one proton, which corresponds to the seven protons of the pentadienyl ligand. The two sets of doublets of doublets at 0.34 and 2.22 ppm can be assigned to the terminal olefinic protons on C_α. Similarly, the doublets at 0.78 and 1.92 ppm can be attributed to the protons on C_ϵ, the terminal allylic carbon atom. The cause for the great difference in chemical shifts for these protons is related to the orientation of the protons with respect to the metal. The syn oriented protons, which point toward the iron atom, give rise to the upfield signals at 0.34 and 0.78 ppm due to shielding by the metal. The downfield signals at 2.22 and 1.92 ppm can be assigned as the protons with an anti orientation, or pointing away from the metal. The ^1J coupling constants also provide a clue as to which are the syn and the anti protons. Typically, protons with a syn orientation have larger ^1J coupling constants than do those with an anti orientation. This agrees with the assignments that have been made.

The remaining protons of the pentadienyl ligand can be assigned by examining the chemical shifts of the resonances and their splitting patterns. Upon close inspection of the ^{1}H NMR spectrum, it can be seen that the signal at 0.95 ppm is a doublet of triplets. This is more easily observed in the expanded region of the spectrum shown in Figure 4. This resonance is assigned to the internal olefinic proton on C_β. Coupling to the proton on the adjacent carbon atom, C_γ, would give rise to a doublet, and additional coupling to the protons on C_α would lead to a triplet such that the resonance appears as a doublet of triplets. Once again, by examining the splitting it can be determined that the doublet of doublets at 3.30 ppm can be attributed to the internal allylic proton on C_γ. The adjacent carbon atoms each possess one proton, so the splitting pattern observed is in agreement with what one would expect. Finally, the multiplet at 5.96 ppm is assigned to the central allylic proton on C_δ.

From the splitting patterns of the signals in the ^{13}C NMR spectrum of **20b** it was easily determined that the pentadienyl ligand had remained intact during the reaction and that no rearrangement had occurred. However, it was difficult to assign the peaks and to determine which proton signals from the ^{1}H

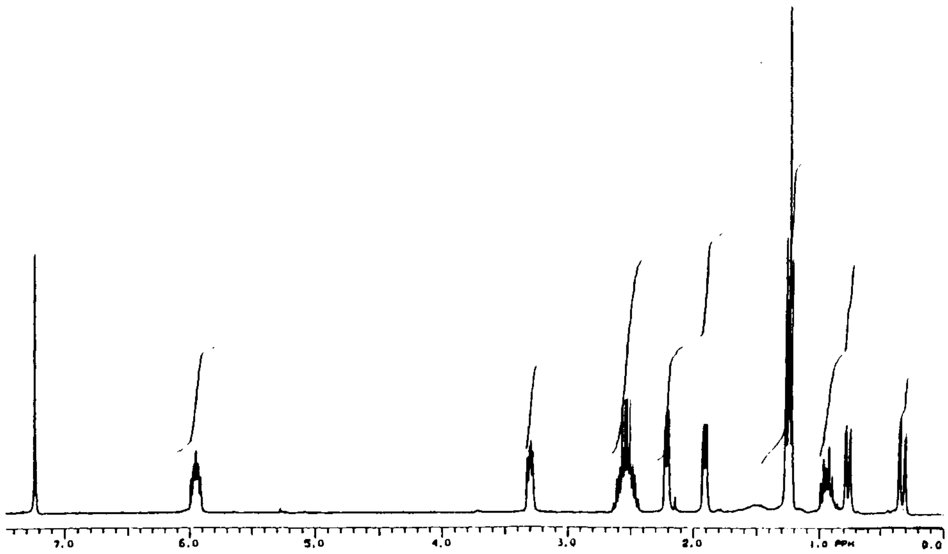


Figure 3. ^{1}H NMR spectrum for $(\mu-\eta^2,\eta^3-CH_2{=}CHCHCHCH_2)(\mu-EtS)Fe_2(CO)_5$, **20b**.

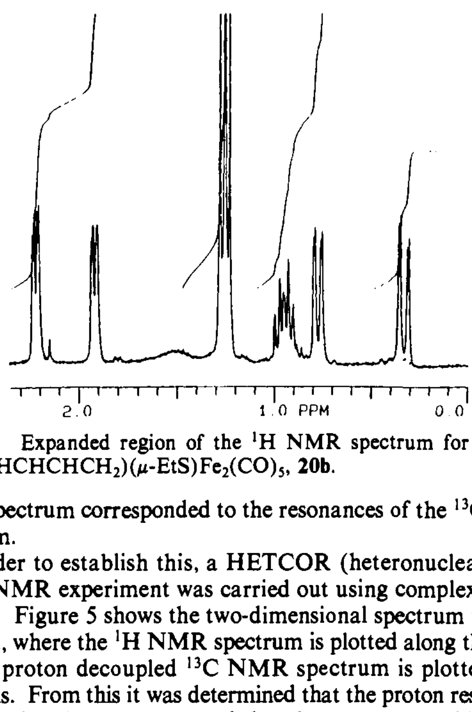


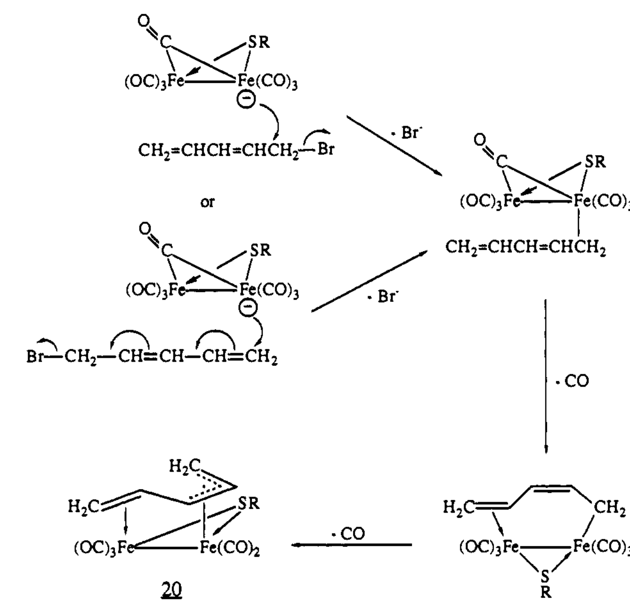
Figure 4. Expanded region of the ^{1}H NMR spectrum for $(\mu-\eta^2,\eta^3-CH_2{=}CHCHCHCH_2)(\mu-EtS)Fe_2(CO)_5$, **20b**.

NMR spectrum corresponded to the resonances of the ^{13}C NMR spectrum.

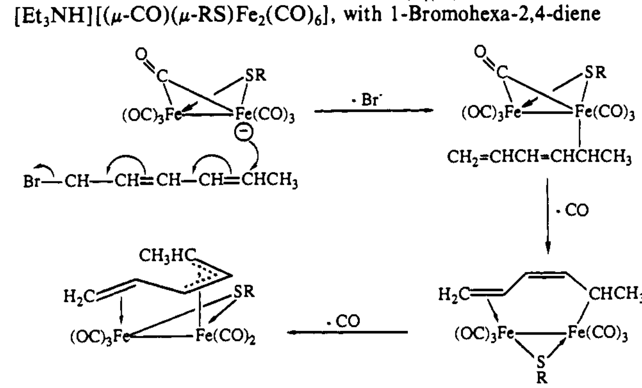
In order to establish this, a HETCOR (heteronuclear correlation) NMR experiment was carried out using complex **20a** (R = *t*-Bu). Figure 5 shows the two-dimensional spectrum that was obtained, where the ^{1}H NMR spectrum is plotted along the *y* axis and the proton decoupled ^{13}C NMR spectrum is plotted along the *x* axis. From this it was determined that the proton resonances at 0.36 and 2.29 ppm corresponded to the resonance at 29.28 ppm of the ^{13}C NMR spectrum. Thus, it was confirmed that one of these protons must have an anti orientation and the other must have a syn orientation to account for the large difference in chemical shift for the two protons. Likewise, the protons giving rise to resonances at 0.77 and 1.84 ppm were established to belong to the carbon atom giving rise to a signal at 36.70 ppm in the ^{13}C NMR spectrum. The remaining signals were assigned in a similar manner by matching a resonance on the 2-D map with the ^{1}H and ^{13}C NMR signals to which it corresponds. In the ^{13}C NMR spectrum the doublet at 89.63 was assigned as the central allylic carbon atom as the spectra for other η^3-allylic complexes of iron show a resonance in this region corresponding to this type of carbon atom.

The formation of the complexes **20** could have taken place either by an S_N2 or S_N2' mechanism, with the $[(\mu-CO)(\mu-RS)Fe_2(CO)_6]^-$ acting as an iron-centered nucleophile (its usual mode of reactivity[18]). As Scheme I shows, either mechanism would lead to the observed product. However, the use of a suitably substituted bromopentadiene in a reaction with $[(\mu-CO)(\mu-RS)Fe_2(CO)_6]^-$ should provide useful mechanistic information since the S_N2 and S_N2' mechanisms would lead to different products providing that the kinetic products are stable. Accordingly, we carried out the

Scheme I. Proposed Mechanism for the Formation of $(\mu-\eta^2,\eta^3-CH_2{=}CHCHCHCH_2)(\mu-RS)Fe_2(CO)_6$, **20**



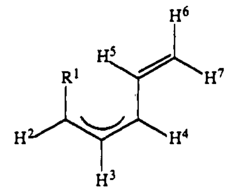
Scheme II. Possible Reaction Mechanism (S_N2') for the Reaction of $[Et_3NH][(\mu-CO)(\mu-RS)Fe_2(CO)_6]$, with 1-Bromohexa-2,4-diene



reactions of $[(\mu-CO)(\mu-t\text{-}BuS)Fe_2(CO)_6]^-$ and $[(\mu-CO)(\mu-PhS)Fe_2(CO)_6]^-$ with 1-bromohexa-2,4-diene, $CH_3CH{=}CHCH{=}CHCH_2Br$. The expected reaction course and product formed are shown in Schemes II and III.

The $(\mu-\eta^2,\eta^3$-hexadienyl$)(\mu-RS)Fe_2(CO)_5$ products (R = *t*-Bu, Ph, **24a** and **b**, respectively) of these reactions could be isolated by column chromatography (**24a**) or crystallization (**24b**).

Table III. ^{1}H NMR Data for the Organic Ligands in the Complexes **20** (R^1 = H) and **24** (R^1 = Me)[a]



	R^1	H^2	H^3	H_4	H_5	H_6	H^7
20a	0.77 dd (11.1, 2.3)	1.84 dd (5.6, 1.0)	5.91 m	3.26 m	0.99 m	0.36 dd (13.3, 1.9)	2.29 dd (6.4, 1.9)
24a		1.58 m	5.71 dd (9.7, 4.4)	3.14 dd (7.6, 5.5)	0.96 m	0.32 d (13.2)	2.25 d (7.2)
20c	1.00 dd (5.8, 1.5)	2.01 dd (2.4, 1.2)	6.07 m	3.57 dd (7.1, 5.0)	1.23 dt (13.5, 7.7)	0.68 dd (13.4, 2.1)	2.41 dd (7.2, 2.1)
24b[b]		1.72 m	5.82 dd (10.1, 5.1)	3.37 dd (8.0, 5.5)	1.12 dt (13.4, 7.8)	0.58 dd (13.2, 2.2)	2.30 dd (7.3, 2.1)

[a] All the spectra are recorded in $CDCl_3$ at room temperature. Coupling constants are given between brackets in Hz. [b] Major isomer.

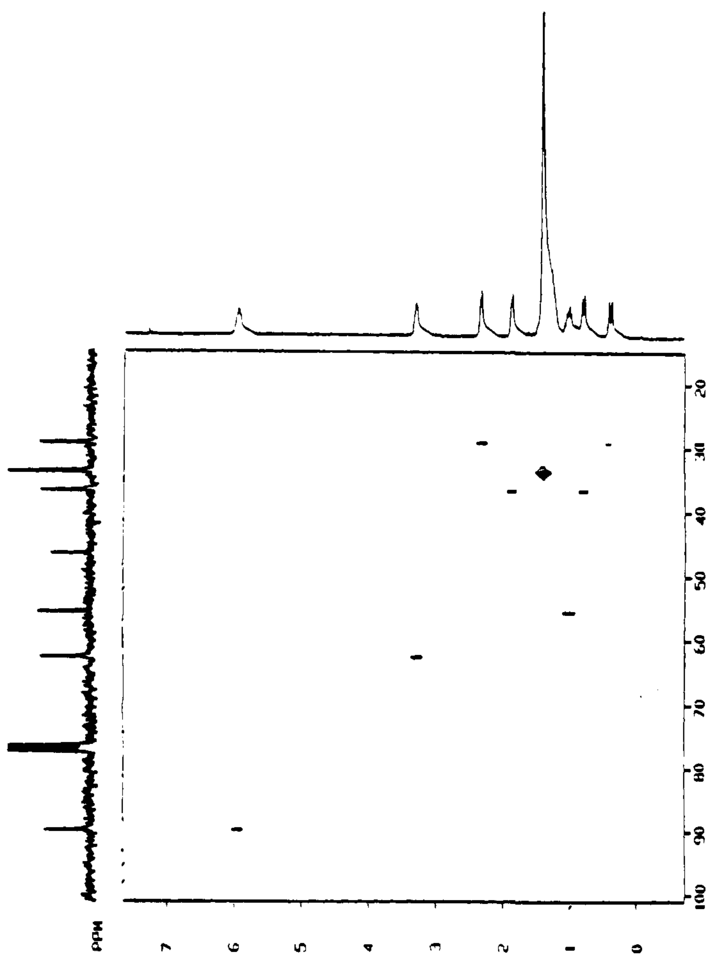


Figure 5. HETCOR NMR (^{1}H vs ^{13}C) spectrum for (μ-η^2,η^3-CH_2=CHCHCHCH$_2$)(μ-t-BuS)$Fe_2(CO)_5$, **20a**.

Scheme III. Possible Reaction Mechanism (S_N2) for the Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$, with 1-Bromohexa-2,4-diene

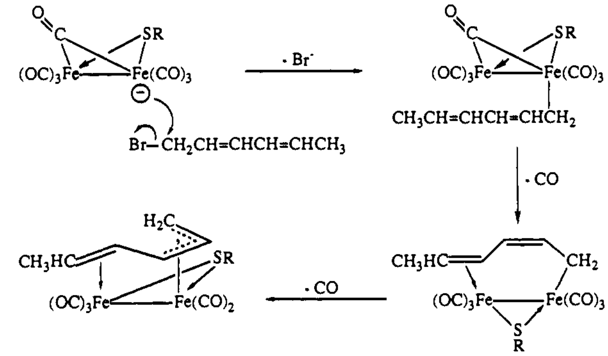


Table IV. Crystal Data for (η^2,η^3-CH_2=CHCHCHCH$_2$)(μ-PhS)$Fe_2(CO)_5$, **17c**

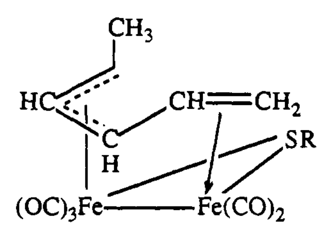
empirical formula	$C_{16}H_{12}Fe_2O_5S$
formula wt	428.04
crystal color, habit	red, prismatic
crystal dimension (mm)	0.150 × 0.120 × 0.120
crystal system	triclinic
no. reflcns used for unit cell determination (2θ range)	25 (25.2–30.1°)
ω scan peak width at half-height	0.34
lattice parameters	
a, Å	9.763 (6)
b, Å	11.132 (4)
c, Å	9.346 (4)
α, deg	111.71 (3)
β, deg	111.57 (4)
γ, deg	92.03 (5)
V, Å^3	860.2 (8)
space group	$P\bar{1}$ (no. 2)
Z value	2
D_{calc}	1.655 g/cm^3
F_{000}	428
μ(Mo Kα)	18.23 cm^{-1}

Complex **24b** was present as a 9:1 mixture of isomers, with that having the SPh equatorial most likely the major one. The position of the methyl group of the C_6H_9 ligand is easily deduced by comparing the ^{1}H NMR spectra of **24a** and **24b** and their pentadienyl analogues, **20a** and **20c** (Table III). The spectrum of **20a** shows two signals at δ 0.77 (dd, J = 11.1 and 2.3 Hz) and 1.84 (dd, J = 5.6 and 1.0 Hz), corresponding to H^1 and H^2. The ^{1}H NMR spectrum of the hexadienyl complex **24a** does not show these resonances but shows a multiplet at δ 1.58, which must be assigned to H^1.

The disposition of the methyl group as shown in **24a** was confirmed by the spin–spin coupling constants associated with the H^3 resonance which are indicative of neighboring trans (9.7 Hz) and cis (4.4 Hz) protons. For the rest of the hexadienyl ligand (H^4, H^5, H^6, H^7) the chemical shifts and spin–spin coupling constants are essentially the same as those for the analogous protons in the pentadienyl ligand in **20a**. The methyl proton signal appears as a doublet in the NMR spectrum of **24a**, partially hidden by the methyl proton signals of the *tert*-butyl group. In a ^{1}H NMR spectrum of **24a** taken in C_6D_6 the CH_3 resonance was clearly visible as a doublet (J = 5.4 Hz) at 1.07 ppm. A similar comparison may be made between the proton NMR spectra of **20c** and **24b** (major isomer) (Table III). The same hexadienyl ligand configuration is present in the minor isomer of **24b** as indicated by its ^{1}H chemical shifts and coupling constants (Experimental Section). These comparions of the proton NMR for

Table V. Final Positional Parameters for $(\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-}PhS)Fe_2(CO)_5$, **17c**

atom	x	y	z	B(eq)
Fe(1)	0.1793 (1)	0.80922 (8)	0.2510 (1)	3.09 (3)
Fe(2)	0.3115 (1)	0.74669 (7)	0.0218 (1)	2.84 (3)
S(1)	0.4206 (2)	0.8633 (1)	0.3054 (2)	2.70 (4)
O(1)	0.5786 (6)	0.7841 (5)	−0.0399 (7)	6.5 (2)
O(2)	0.33458 (6)	0.4950 (4)	0.0479 (7)	6.7 (2)
O(3)	0.1133 (6)	0.6051 (6)	−0.3342 (6)	8.2 (2)
O(4)	0.1082 (6)	0.5384 (5)	0.2054 (7)	6.8 (2)
O(5)	0.2185 (7)	0.9111 (6)	0.5997 (6)	7.8 (3)
C(1)	0.5430 (6)	0.7738 (5)	0.4007 (6)	3.1 (2)
C(2)	0.5172 (7)	0.7232 (6)	0.5045 (7)	4.1 (2)
C(3)	0.6197 (8)	0.6596 (7)	0.5828 (8)	4.9 (3)
C(4)	0.747 (1)	0.6477 (7)	0.5561 (9)	5.7 (3)
C(5)	0.7774 (1)	0.6982 (7)	0.4538 (9)	5.3 (3)
C(6)	0.6756 (7)	0.7632 (6)	0.3804 (7)	4.3 (2)
C(7)	0.281 (1)	0.9290 (6)	0.0004 (8)	5.0 (3)
C(8)	0.1573 (8)	0.8960 (5)	0.0254 (7)	4.0 (2)
C(9)	0.1363 (7)	0.9651 (6)	0.1785 (7)	4.1 (2)
C(10)	0.0166 (8)	0.9180 (7)	0.2060 (9)	5.1 (3)
C(11)	−0.0559 (8)	0.7869 (8)	0.115 (1)	6.5 (3)
C(12)	0.4733 (7)	0.7675 (6)	−0.0157 (7)	4.0 (2)
C(13)	0.3279 (7)	0.5944 (6)	0.0426 (7)	4.0 (2)
C(14)	0.1892 (7)	0.6594 (6)	−0.1951 (8)	4.7 (2)
C(15)	0.1428 (7)	0.6424 (7)	0.2200 (8)	4.3 (2)
C(16)	0.2021 (8)	0.8725 (7)	0.4619 (9)	4.8 (3)
H(1)	0.4278	0.7318	0.5229	4.9
H(2)	0.6006	0.6246	0.6536	5.8
H(3)	0.8171	0.6038	0.6088	6.8
H(4)	0.8663	0.6883	0.4347	6.3
H(5)	0.6975	0.8017	0.3139	5.1
H(6)	0.3588	1.0012	0.0865	6.0
H(7)	0.2881	0.8798	−0.1032	6.0
H(8)	0.0810	0.8232	−0.0634	4.8
H(9)	0.2051	1.0443	0.2623	5.0
H(10)	−0.0142	0.9767	0.2869	6.1
H(11)	−0.1366	0.7555	0.1345	7.8
H(12)	−0.0251	0.7285	0.0348	7.8



24

Figure 6.

the respective pentadienyl and hexadienyl complexes lead us to the conclusion that the latter, **24a** and **24b**, have the structures shown in Figure 6. As in the case of the pentadienyl complexes, a HETCOR NMR experiment carried out with **24b** allowed assignments of all of the signals in its ^{13}C NMR spectrum.

The results obtained in the $CH_3CH{=}CHCH{=}CHCH_2Br$/ $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ reactions suggest that an S_N2' mechanism is operative (cf. Scheme II). A similar finding had been made in the case of the reaction of propargylic halides with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$.[18a] A second, in our opinion less likely, possibility is that these reactions proceed by a S_N2 process (Scheme III in the present case) and that rearrangment of the initially formed product leads to the finally observed product shown in Figure 6. We have no experimental evidence for or against this possibility and so favor the S_N2' mechanism.

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 and purged with nitrogen prior to use. Triethylamine was distilled under nitrogen from calcium hydride and purged with nitrogen prior to use. Ethyl, *tert*-butyl, and phenyl mercaptans were purged with nitrogen and used without further purification. Triiron dodecacarbonyl was prepared by a literature procedure.[20] Tribromophosphine, 1,4-pentadien-3-ol, and *trans,trans*-hexa-2,4-dien-1-ol were purchased from Aldrich, purged with nitrogen, and used without further purification. Literature procedures were followed for the preparation of 5-bromopenta-1,3-diene[21a] and 1-bromohexa-2,4-diene.[21b]

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 funnel was used. Further purification was achieved by column chromatography with a 450 × 25 mm medium pressure column using Sigma S-0507 230–400 mesh or Aldrich, 60 Å, 230–400 mesh silica gel. All chromatography was completed without exclusion of atmospheric moisture or oxygen. Solid products were recrystallized at −20 °C. All yields are based on Fe unless otherwise indicated.

Solution infrared spectra (NaCl windows) were obtained using a Perkin-Elmer 1600 Series FTIR instrument. Proton and carbon-13 NMR spectra were recorded on a Varian XL-300 spectrometer operating at 300 and 75.4 MHz, respectively. Electron impact mass spectra were obtained using a Finnigan-3200 mass spectrometer operating at 70 eV. Masses were correlated using the following isotopes: ^1H, ^{12}C, ^{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.

X-ray Crystallography. Structure of $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-}PhS)Fe_2(CO)_5$, 20c. A red, prismatic crystal of $(\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-}PhS)Fe_2(CO)_6$ (which had been grown in pentane/CH_2Cl_2 at −20 °C) having approximate dimensions of 0.150 × 0.120 × 0.120 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated Mo Kα radiation and a 12 KW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 25.20 < 2θ < 30.07° corresponded to a triclinic cell with dimensions given in Table IV. For $Z = 2$ and fw = 428.04, the calculated density is 1.655 g/cm³. On the basis of the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (no. 2).

The data were collected at a temperature of 23 ± 1 °C using the ω-2θ scan technique to a maximum 2θ value of 55.1 °C. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.34° with a take-off angle of 6.0°. Scans of (1.52 + 0.35 tan θ)° were made at speeds of 8.0°/min (in ω). The weak reflections ($I < 3.0\sigma(I)$) were rescanned (maximum of eight rescans), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal-to-detector distance was 310.0 mm.

Of the 4185 reflections which were collected, 3945 were unique (R_{int} = 0.040); equivalent reflections were merged. The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Mo Kα is 18.2 cm⁻¹. An empirical absorption correction[22] was applied which resulted in transmission factors ranging from 0.86 to 1.23. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[23] The non-hydrogen atoms were refined either anisotropically or isotropically. The final cycle of full-matrix least-squares refinement[24] was based on 1799 observed reflections ($I > 3.00\sigma(I)$) and 217 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and

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

(21) (a) Miginiac, P. *Ann. Chim.* **1962**, *7*, 445. (b) Jacobson, M. *J. Am. Chem. Soc.* **1955**, *77*, 2461.

(22) DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(23) (a) MITHRIL, an integrated direct methods computer program. *J. Appl. Cryst.* **1984**, *17*, 42–46. (b) Beurskens, P. T. DIRDIF: Direct Methods for Difference Structures. An automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, The Netherlands.

(24) Least-Squares: Function minimized, $\sum w(|F_o| - |F_c|)^2$; where $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz–polarization factor, and p = p-factor.

weighted agreement factors of $R = 0.035$ and $R_w = 0.040$. Goodness of fit indicator = 1.22.

The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.35 and −0.28 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[25] Anomalous dispersion effects were included in F_{calc};[26] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[27] All calculations were performed using the TEXSAN[28] crystallographic software package of Molecular Structure Corporation.

Standard in situ Preparation of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$. A 100-mL Schlenk flask equipped with a rubber septum and a stir-bar was charged with 1.50 g (2.98 mmol) of $Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged successively with 30 mL of THF, 3.00 mmol of the appropriate thiol, and 0.42 mL (0.30 g, 3.00 mmol) of triethylamine. The mixture was stirred for 15 min at room temperature during which time slow gas evolution and a gradual color change from dark green to brown-red were observed. The resulting $[Et_3NH][(\mu\text{-}CO)\text{-}(\mu\text{-}RS)Fe_2(CO)_6]$ reagent solution then was used in situ without further purification.

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ with 5-Bromopenta-1,3-diene. To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ reagent solution (2.98 mmol) was added 0.33 mL (3.00 mmol) of 5-bromopenta-1,3-diene by syringe. The mixture was stirred at room temperature for 1 h, during which time a color change to bright red and the formation of a white precipitate were observed. The solvent was removed in vacuo to leave a red oil which was dissolved in pentane and filtered through a thin pad of silicic acid to remove decomposition materials. Pentane eluted an orange band which was followed closely by a bright red band. Because the bands could not be separated in this manner, they were collected together and separated using medium pressure column chromatography. Pentane eluted an orange band which gave 0.29 g (0.64 mmol, 43% based on S, a/e:e/e = 1.5) of $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[29] Continued elution with pentane removed a deep red band which yielded 0.65 g (1.59 mmol, 53%) of $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_5$, **20a**, as an air-stable, deep red, crystalline solid after recrystallization from pentane, mp 90.0–92.0 °C: IR (CCl_4, cm^{-1}) 2976 (w), 2940 (w), 2898 (w), 2863 (w), 1720 (w), 1691 (m), 1641 (m), 1494 (m), 1472 (m), 1458 (m), 1392 (s), 1232 (m), 1156 (s), 1039 (w), 990 (w), 904 (w); terminal carbonyl region (CCl_4, cm^{-1}) 2046 (vs), 1994 (vs), 1980 (vs), 1969 (vs), 1937 (s). ^1H NMR ($CDCl_3$, 300 MHz) δ 0.36 (dd, ^1J = 13.34 Hz, ^2J = 1.87 Hz, 1 H, $CH_2CHCHCH{=}CH_2$ syn), 0.77 (dd, ^1J = 11.14 Hz, ^2J = 2.31 Hz, 1 H, $CH_2CHCHCH{=}CH_2$ syn), 0.99 (m, 1 H, $CH_2CHCHCH{=}CH_2$), 1.37 (s, 9 H, $SC(CH_3)_3$), 1.84 (dd, ^1J = 5.60 Hz, ^2J = 1.04 Hz, 1 H, $CH_2CHCHCH{=}CH_2$ anti), 2.29 (dd, ^1J = 6.42 Hz, ^2J = 1.89 Hz, 1 H, $CH_2CHCHCH{=}CH_2$ anti), 3.26 (m, 1 H, $CH_2CHCHCH{=}CH_2$), 5.91 (m, 1 H, $CH_2CHCHCH{=}CH_2$); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 29.28 (t, J = 159.2 Hz, $CH_2CHCHCH{=}CH_2$), 33.75 (q, J = 127.4 Hz, $SC(CH_3)_3$), 36.70 (t, J = 160.2 Hz, $CH_2CHCHCH{=}CH_2$), 46.55 (s, $SC(CH_3)_3$), 55.68 (d, J = 162.1 Hz, $CH_2CHCHCH{=}CH_2$), 62.70 (d, J = 170.3 Hz, $CH_2CHCHCH{=}CH_2$), 89.63 (d, J = 167.8 Hz, $CH_2CHCHCH{=}CH_2$), 210.94 (broad s, terminal COs), 217.23, 219.02 (both s, terminal COs); mass spectrum (EI) m/z (rel intensity) 408 (M^+, 0.6), 380 ($M^+ - CO$, 1), 352 ($M^+ - 2CO$, 2), 324 ($M^+ - 3CO$, 10), 296 ($M^+ - 4CO$, 6), 268 ($M^+ - 5CO$, 13), 212 $(Fe_2SH(CH_2{=}CHCHCHCH_2)^+$, 41), 184 $(Fe_2S(CH_2{=}CHCH)^+$, 12), 169 $(Fe_2S(CH{=}C)^+$, 8), 144 (Fe_2S^+, 63), 142 $(FeSH(CH_2{=}CHCHCH)^+$, 10), 121 ($FeCH_2{=}CHCHCHC^+$, 8), 67 ($CH_2{=}CHCHCHCH_2^+$, 31), 56 (Fe^+, 19), 41 ($CH_2{=}CHCH^+$ + 1H, 100). Anal. Calcd for $C_{14}H_{16}Fe_2O_5S$: C, 41.20; H, 3.96. Found: C, 41.36; H, 4.04. (The mass spectra of all other complexes prepared were characterized, as was that of **20a**, by the presence of M^+ and $[M^+ - nCO]$ fragment ions (n = 1–5), and the mass spectral data for the other complexes are provided in the supplementary material.)

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ with 5-Bromopenta-1,3-diene. A similar procedure was used in the reaction of 2.98 mmol of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ with 3.0 mmol of 5-bromopenta-1,3-diene. In the initial filtration chromatography, pentane eluted an orange band which was followed closely be a deep red band. Because the bands could not be separated in this manner, they were collected together and separated using medium pressure column chromatography. Pentane eluted an orange band which gave 0.31 g (0.76 mmol, 51% based on S, a/e:e/e = 1.9) of $(\mu\text{-}EtS)_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[30] Continued elution with pentane removed a deep red band which yielded 0.55 g (1.45 mmol, 48%) of $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-}EtS)Fe_2(CO)_5$, **20b**, as an air-stable, deep red, crystalline solid after recrystallization from pentane, mp 48.0–49.0 °C: ^1H NMR ($CDCl_3$, 300 MHz) δ 0.34 (dd, ^1J = 13.04 Hz, ^2J = 2.78 Hz, 1 H, $CH_2CHCHCH{=}CH_2$ syn), 0.78 (dd, ^1J = 10.54 Hz, ^2J = 2.09 Hz, 1 H, $CH_2CHCHCH{=}CH_2$ syn), 0.95 (dt, ^1J = 13.01, ^2J = 7.60 Hz, 1 H, $CH_2CHCHCH{=}CH_2$), 1.26 (t, J = 7.23 Hz, 3 H, SCH_2CH_3), 1.92 (d, J = 6.95 Hz, 1 H, $CH_2CHCHCH{=}CH_2$ anti), 2.22 (dd, ^1J = 7.34 Hz, ^2J = 2.40 Hz, 1 H, $CH_2CHCHCH{=}CH_2$ anti), 2.54 (m, 2 H, SCH_2CH_3), 3.30 (dd, ^1J = 7.68 Hz, ^2J = 5.02 Hz, 1 H, $CH_2CHCHCH{=}CH_2$), 5.96 (m, 1 H, $CH_2CHCHCH{=}CH_2$); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 18.03 (q, J = 127.6 Hz, SCH_2CH_3), 27.45 (t, J = 156.6 Hz, $CH_2CHCHCH{=}CH_2$), 35.14 (t, J = 141.2 Hz, SCH_2CH_3), 37.25 (t, J = 160.4 Hz, $CH_2CHCHCH{=}CH_2$), 54.33 (d, J = 159.1 Hz, $CH_2CHCHCH{=}CH_2$), 63.84 (d, J = 168.6 Hz, $CH_2CHCHCH{=}CH_2$), 89.27 (d, J = 166.8 Hz, $CH_2CHCHCH{=}CH_2$), 210.50, 216.58, 218.36 (all s, terminal COs). Anal. Calcd for $C_{12}H_{12}Fe_2O_5S$: C, 37.92; H, 3.19. Found: C, 38.00; H, 3.22.

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}PhS)Fe_2(CO)_6]$ with 5-Bromopenta-1,3-diene. A similar reaction was carried out using 2.98 mmol of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}PhS)Fe_2(CO)_6]$ and 3.0 mmol of 5-bromopenta-1,3-diene. In the initial filtration chromatography, pentane eluted an orange band which was followed closely by a deep red band. Because the bands could not be separated in this manner, they were collected together and separated using medium pressure column chromatography. Pentane eluted an orange band which gave 0.45 g (0.90 mmol, 60% based on S) of $(\mu\text{-}PhS)_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[31] Continued elution with pentane removed a deep red band which yielded 0.40 g (0.93 mmol, 31%) of $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCH_2)(\mu\text{-}PhS)Fe_2(CO)_5$, **20c**, as an air-stable, deep red, crystalline solid after recrystallization from pentane/CH_2Cl_2 (2:1 v/v), mp 138.0–139.0 °C. ^1H NMR (CD_2Cl_2, 300 MHz) δ 0.68 (dd, ^1J = 13.38 Hz, ^2J = 2.13 Hz, 1 H, $CH_2CHCHCH{=}CH_2$ syn), 1.00 (dd, ^1J = 5.84 Hz, ^2J = 1.49 Hz, 1 H, $CH_2CHCHCH{=}CH_2$ syn), 1.23 (dt, ^1J = 13.51 Hz, ^2J = 7.66 Hz, 1 H, $CH_2CHCHCH{=}CH_2$), 2.01 (dd, ^1J = 2.40 Hz, ^2J = 1.21 Hz, 1 H, $CH_2CHCHCH{=}CH_2$ anti), 2.41 (dd, ^1J = 7.24 Hz, ^2J = 2.13 Hz, 1 H, $CH_2CHCHCH{=}CH_2$ anti), 3.57 (dd, ^1J = 7.08 Hz, ^2J = 4.98 Hz, 1 H, $CH_2CHCHCH{=}CH_2$), 6.07 (m, 1 H, $CH_2CHCHCH{=}CH_2$), 7.28 (m, 3 H, Ph), 7.54 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 28.91 (t, J = 158.5 Hz, $CH_2CHCHCH{=}CH_2$), 36.63 (t, J = 160.0 Hz, $CH_2CHCHCH{=}CH_2$), 55.07 (d, J = 159.4 Hz, $CH_2CHCHCH{=}CH_2$), 63.64 (d, J = 168.5 Hz, $CH_2CHCHCH{=}CH_2$), 89.61 (d, J = 166.8 Hz, $CH_2CHCHCH{=}CH_2$), 127.61 (d, J = 161.1 Hz, Ph), 128.69 (d, J = 161.4 Hz, Ph), 131.62 (d, J = 163.2 Hz, Ph), 137.92 (s, ipso Ph), 210.07 (broad s, terminal COs), 216.19, 218.62 (both s, terminal COs). Anal. Calcd for $C_{16}H_{12}Fe_2O_5S$: C, 44.89; H, 2.83. Found: C, 45.00; H, 2.94.

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ with 1-Bromohexa-2,4-diene. The same procedure was used in the reaction of 2.98 mmol of $[EtNH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ with 0.36 mL (3.08 mmol) of $CH_3CH{=}CHCH{=}CHCH_2Br$ in THF. The crude product, a red oil, was dissolved in pentane and filtered through a thin pad of silica gel. Purification of the products was achieved by medium pressure column chromatography. Pentane eluted an orange band which gave 0.09 g (0.18 mmol, 12% based on S, a/e:e/e = 3.6) of $[(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6]$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[30] Continued elution with pentane removed a deep red band which yielded 0.28 (22%) of $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCHCH_3)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_5$, **24a**, as an air stable, deep red, crystalline solid after recrystallization from pentane, mp 85–88 °C. IR (Nujol cm^{-1}) 2045 vs, 1991 vs, 1966 vs, 1934 s, 1908 m, 1364 w, 1154 w, 1032 vw, 905 vw, 848 vw, 682 vw, 617 vw, 591 w; terminal carbonyl region (pentane, cm^{-1}) 2047 s, 1993 vs, 1980 s, 1969 m, 1936 m; ^1H NMR (C_6D_6, 300 MHz) δ 0.10 (dd, J = 13.4 and 2.1 Hz, 1 H, $CH_3CHCHCHCH{=}CH_2$, syn), 0.57 (dt, J = 13.4 and 7.8 Hz, 1 H, $CH_3CHCHCHCH{=}CH_2$), 1.07 (d, J = 5.4 Hz, 3 H, $CH_3CHCHCHCH{=}CH_2$), 1.20 (m, 1 H, $CH_3CHCHCHCH{=}CH_2$), 1.32 (s, 9 H, $SC(CH_3)_3$), 1.86 (dd, J = 7.3 and 2.1 Hz, 1 H, $CH_3CHCHCHCH{=}CH_2$, anti), 2.70 (dd, J = 8.3 and 5.6 Hz, 1 H, $CH_3CHCHCHCH{=}CH_2$), 5.14 (dd, J = 9.6 and 5.0 Hz,

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1 H, $CH_3CHCHCHCH{=}CH_2$); ^1H NMR spectrum in $CDCl_3$ Table I; ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 18.44 (q, J = 123.6 Hz, $CH_3CHCHCHCH{=}CH_2$), 28.55 (t, J = 164.6 Hz, $CH_3CHCHCHCH{=}CH_2$), 33.77 (q, J = 128.8 Hz, $C(CH_3)_3$), 46.29 (s, $C(CH_3)_3$), 53.07 (d, J = 163.6 Hz, $CH_3CHCHCHCH{=}CH_2$), 55.23 (d, J = 160.2 Hz, $CH_3CHCHCHCH{=}CH_2$), 58.75 (d, J = 169.0 Hz, $CH_3CHCHCHCH{=}CH_2$), 92.52 (d, J = 16.7 Hz, $CH_3CHCHCHCH{=}CH_2$), 211.39 (br, terminal COs), 217.64 and 219.64 (s, terminal COs); mass spectrum (EI) m/z (rel density) 422 (M^+, 5), 394 ($M^+ - CO$, 7), 366 ($M^+ - 2CO$, 19), 388 ($M^+ - 3CO$, 18), 310 ($M^+ - 4CO$, 22), 282 ($M^+ - 5CO$, 51), 226 ($(Fe_2SH(CH_3CHCHCHCH{=}CH_2)^+$, 100), 224 ($Fe_2SH(CH_3CHCHCHCH{=}CH_2)^+$ −2 H, 55), 222 ($Fe_2SH(CH_3CHCHCHCH{=}CH_2)^+$ −4 H, 14), 171 ($Fe_2S(CH{=}CH_2)^+$, 11), 145 (Fe_2SH^+, 35), 144 (Fe_2S^+, 57), 81 ($CH_3CHCHCHCH{=}CH_2^+$, 22), 79 ($CH_3CHCHCHCH{=}CH_2^+$ −2 H, 24), 77 ($CH_3CHCHCHCH{=}CH_2^+$ −4 H, 8), 66 ($CHCHCHCH{=}CH_2^+$, 12), 57 (Fe^+, 28), 52 ($CHCHCHCH^+$, 16). Anal. Calcd for $C_{15}H_{18}Fe_2O_5S$: C, 42.69; H, 4.30. Found: C, 42.75; H, 4.35.

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SPh)Fe_2(CO)_6]$ with 1-Bromohexa-2,4-diene. A reaction of 2.98 mmol of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}PhS)Fe_2(CO)_6]$ with 3.08 mmol of 1-bromohexa-2,4-diene was carried out as described above. The solvent was removed in vacuo to leave a red oily solid which was dissolved in pentane/CH_2Cl_2 (3:1, v/v) and filtered through a thin pad of silica gel, eluting with the same mixture. Concentration of the solution in vacuo and cooling overnight to −20 °C led to 0.45 g (1.02 mmol, 34%) of $(\mu\text{-}\eta^2,\eta^3\text{-}CH_2{=}CHCHCHCHCH_3)(\mu\text{-}PhS)Fe_2(CO)_5$, **24b**, as an air stable, deep red, crystalline solid, mp 145–148 °C: ^1H NMR ($CDCl_3$, 300 MHz) δ −0.10 (dd, J = 13 and 2 Hz, $CH_3CHCHCHCH{=}CH_2$, syn, minor isomer), 0.58 (dd, J = 13.3 and 2.2 Hz, $CH_3CHCHCHCH{=}CH_2$, syn, major isomer), 0.85 (m, $CH_3CHCHCHCH{=}CH_2$, minor isomer), 1.12 (dt, J = 13.4 and 7.8 Hz, $CH_3CHCHCHCH{=}CH_2$, major isomer), 1.44 (d, J = 5.2 Hz, $CH_3CHCHCHCH{=}CH_2$, minor isomer), 1.49 (d, J = 5.9 Hz, $CH_3CHCHCHCH{=}CH_2$, major isomer), 1.72 (m, $CH_3CHCHCHCH{=}CH_2$, both isomers), 2.18 (dd, J = 7 and 2 Hz, $CH_3CHCHCHCH{=}CH_2$, anti, minor isomer), 2.30 (dd, J = 7.3 and 2.1 Hz, $CH_3CHCHCHCH{=}CH_2$, anti, major isomer), 3.37 (dd, J = 8.0 and 5.5 Hz, $CH_3CHCHCHCH{=}CH_2$, major isomer), 3.42 (dd, J = 8 and 5 Hz, $CH_3CHCHCHCH{=}CH_2$, minor isomer), 5.82 (dd, J = 10.1 and 5.1 Hz, $CH_3CHCHCHCH{=}CH_2$, major isomer), 6.11 (dd, J = 9 and 4.5 Hz, $CH_3CHCHCHCH{=}CH_2$, minor isomer), 6.95 (m, 2 H Ph, minor isomer), 7.05 (m, 3 H Ph, minor isomer), 7.28 (m, 3 Ph, major isomer), 7.53 (m, 2 H Ph, major isomer); ratio major/minor isomer 9/1. ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 18.60 (q, J = 126.7 Hz, $CH_3CHCHCHCH{=}CH_2$), 28.14 (t, J = 157.8 Hz, $CH_3CHCHCHCH{=}CH_2$), 53.37 (d, J = 160.6 Hz, $CH_3CHCHCHCH{=}CH_2$), 54.57 (d, J = 160.4 Hz, $CH_3CHCHCHCH{=}CH_2$), 59.82 (d, J = 169.4 Hz, $CH_3CHCHCHCH{=}CH_2$), 92.47 (d, 164.8 Hz, $CH_3CHCHCHCH{=}CH_2$), 127.53 (d, J = 162.1 Hz, C-4 Ph), 128.62 (d, J = 158.4 Hz, Ph), 131.74 (d, J = 163.6 Hz, Ph), 137.98 (s, ipso Ph), 210.12 (br, terminal COs), 216.65 and 219.34 (s, terminal COs); major isomer. Anal. Calcd for $C_{17}H_{14}Fe_2O_5S$: C, 46.19; H, 3.19. Found: C, 45.97; H, 3.23.

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Supplementary Material Available: IR and mass spectral data, X-ray structure report, tables of positional parameters, bond distances and angles, and torsion or conformation angles (23 pages); table of calculated and observed structure factors (27 pages). Ordering information is given on any current masthead page.

Isotopic Labeling Investigation of the Oxygenation of Nickel-Bound Thiolates by Molecular Oxygen

Patrick J. Farmer, Touradj Solouki, Daniel K. Mills, Takako Soma, David H. Russell, Joseph H. Reibenspies, and Marcetta Y. Darensbourg*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received September 19, 1991*

Abstract: Discrete compounds resulting from the oxidation and oxygenation of nickel thiolate complexes have been isolated, separated, and characterized. Molecular oxygen or hydrogen peroxide reacted with [N,N'-bis(mercaptoethyl)-1,5-diazacyclooctane]nickel(II), (BME-DACO)Ni^{II} (**1**), to produce two oxygenates, [(mercaptoethyl)(sulfinatoethyl)diazacyclooctane]nickel(II), (MESE-DACO)Ni^{II} (**2**), and [bis(sulfinatoethyl)diazacyclooctane]nickel(II), (BSE-DACO)Ni^{II} (**3**), as well as a trimetallic, $[(BME\text{-}DACO)Ni]_2Ni^{2+}$ (**4**). Matrix-assisted laser desorption (MALD) ionization was used to obtain Fourier transform ion cyclotron resonance (FT-ICR) mass spectra on isotopomers of **2** and **3**. Isotopic labeling experiments ($^{18}O_2/^{16}O_2$ mixtures) demonstrated that both oxygens in the sulfinate ligand of **1** were derived *from the same* dioxygen molecule. The molecular structures of **2** and **4** were determined by X-ray crystallography. Crystallographic data are given as a, b, c; β; space group, Z, 2θ range, unique observed reflections, $R(R_w)$ (%). (MESE-DACON)Ni^{II}: 8.306 (3), 12.258 (3), 12.773 (4) Å; 101.36 (3)°, $P2_1/n$, 4, 4.0°/50.0°, 2047 ($I > 2.0\sigma(I)$), 2.85 (3.61). $\{[(BME\text{-}DACO)Ni]_2Ni\}Br_2$: 7.144 (2), 10.931 (2), 17.296 (3) Å; 91.72 (2)°, $P2_1/c$, 4, 4.0°/50.0°, 2053 ($I > 2.0\sigma(I)$), 4.46 (4.84). The pseudo-square-planar NiN_2S_2 complex **2** has cis sulfur donor atoms and a tetrahedral twist of 18.4°. The $Ni\text{-}S_{sulfinato}$ distance of 2.140 (1) Å is significantly shorter than the $Ni\text{-}S_{thiolate}$ distance, 2.163 (1) Å. The trimetallic **4** contains a staircaselike structure where two molecules of **1** serve as metallothiolate ligands to the central Ni^{2+} creating an NiS_4 square plane (dihedral angle between best square planes = 103.4°).

Introduction

The synthetically vexing air sensitivity of anionic transition-metal thiolate complexes generally reflects ill-understood chemical reactions which, if controlled, might prove useful in the preparation of organic disulfides, sulfoxides, and sulfinic acids. In addition, such reactions are of import to loss of activity of both industrial and enzymatic catalysts which contain sulfided metal centers. The slow reaction of solutions of the complex [N,N'-bis(mercaptoethyl)-1,5-diazacyclooctane]nickel(II), (BME-DACO)Ni^{II} (**1**),[1] with O_2 provided opportunity to isolate and characterize products that result from both electron transfer and oxygenation at sulfur, eq 1. This paper reports those results as well as an isotopic labeling

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