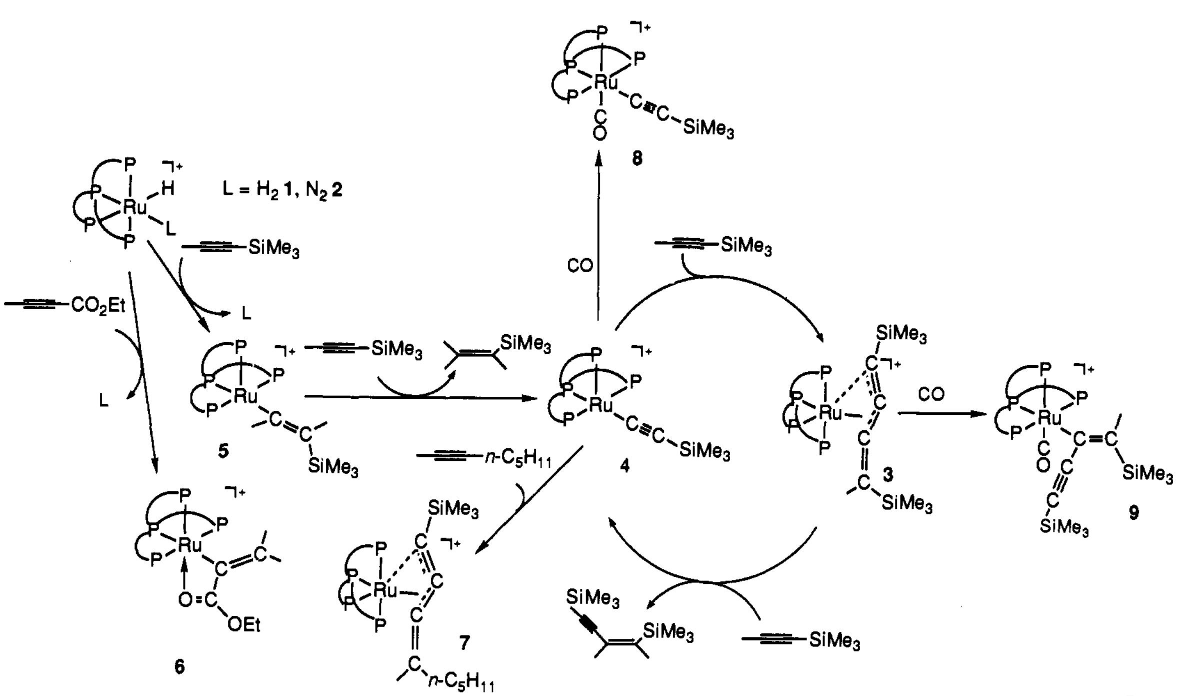
Scheme I



When **4** is reacted at 20 °C with an excess of $HC\equiv CSiMe_3$, we observe selective, catalytic production of (*Z*)-1,4-bis(trimethylsilyl)but-3-en-1-yne [substrate to catalyst ratio 100, 10 mL of THF, 6 h, 30% conversion, (*Z*)-$Me_3SiC\equiv CCH=CH(SiMe_3)$ 95%, (*E*)-$Me_3SiC\equiv CCH=CH(SiMe_3)$ 5%]. At reflux temperature the catalytic activity significantly increases (90% conversion, *Z* isomer 93%, *E* isomer 7%). The mixtures remain catalytically active. Similar conversion (90%) and selectivity (92% in the *Z* isomer) are found for the catalytic dimerization of $HC\equiv CPh$ to 1,4-diphenylbut-3-en-1-ynes by using **1** or **2** as catalyst precursors. For both 1-alkynes, the η^3-butenynyl complexes are the only species observable in the course of the catalysis ($^{31}P\{^1H\}$ NMR), suggesting that such complexes are reagents in the rate-determining step.

Valuable mechanistic information on the catalytic cycle is provided by the isolation of (*E*)-$[(PP_3)Ru\{\eta^3\text{-}(SiMe_3)C_3CH(n\text{-}C_5H_{11})\}]BPh_4$ (**7**) by treatment of **4** with 1 equiv of $HC\equiv C\text{-}n\text{-}C_5H_{11}$. The geminal position of H and n-C_5H_{11} in the cross-coupling product **7** [$^3J(HH) = 6.3$ Hz] indicates that the alkyne has undergone a 1,2-hydrogen shift, which constitutes one of the known paths of the 1-alkyne to vinylidene tautomerization at metal centers.[7] Once the alkyne has rearranged to vinylidene, the butenynyl ligand may form via C–C bond formation between the α-carbons of cis vinylidene and alkynyl ligands.[4a] In accord with the proposed mechanism, when the metal coordination sphere of the σ-alkynyl **4** is saturated by CO, the six-coordinate complex $[(PP_3)Ru(CO)(C\equiv CSiMe_3)]BPh_4$ (**8**) forms and no further reactions with 1-alkynes occur.

The weak bonding interaction between ruthenium and the alkynyl moiety of the butenynyl ligand is present also in solution as shown by the reaction with CO in THF yielding the η^1-butenynyl (*E*)-$[(PP_3)Ru(CO)\{\eta^1\text{-}(SiMe_3)C_3CH(SiMe_3)\}]BPh_4$ (**9**). The facile unfastening of the alkynyl functionality in **3** is certainly an essential requisite for the occurrence of a catalytic cycle as it provides a free coordination site for the incoming 1-alkyne molecule (the replacement of **4** with **3** in the catlytic reactions at reflux temperature changes neither the conversion nor the selectivity).

Acknowledgment. C.B. thanks the EEC for Contract SC1.0027C.

Supplementary Material Available: Experimental details for the synthesis and characterization of all of the new complexes described in this paper and for the catalytic reactions and X-ray crystallographic data for **3** including experimental details, selected distances and angles, atomic coordinates, and thermal parameters (17 pages); listing of observed and calculated structure factors for **3** (59 pages). Ordering information is given on any current masthead page.

Thiolato- and Selenato-Bridged Dinuclear Iron Carbonyl Radicals

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Substantial advances have been made toward the understanding of reaction mechanisms of homogeneous catalysis through spectroscopic studies of photochemically generated, coordinatively unsaturated metal carbonyls and their reactions.[1] In particular, $Fe(CO)_5$ has an extensive odd-electron chemistry, which we are exploring by EPR spectroscopy. This report (a) exemplifies the variety of novel radical intermediates that can be obtained from organosulfur and -selenium compounds by photolysis of $Fe(CO)_5$ in the presence of H_2S and H_2Se and (b) draws attention to the

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† National Research Council of Canada.

‡ E. I. du Pont de Nemours and Company.

(1) For example: (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*: Academic Press: New York, 1979. (b) Poliakoff, M. *ACS Symp. Ser.* **1983**, *No. 211*, 35. (c) Weitz, E. *J. Phys. Chem.* **1987**, *91*, 3945.

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Table I. EPR Parameters for Thiolato- and Selenato-Bridged Iron Carbonyl Radicals at 173 K[a]

species	*g* factor	^1H	^{33}S	^{13}C	^{57}Fe	^{77}Se
1	2.0024	2.2 (1H)	2.9 (1S)	14.4 (2C) 3.7 (4C) 3.3 (2C)	3.9 (2Fe)	-
2	2.0076	32.4 (1H) 1.3 (2H)	3.7 (2S)	27.1 (2C) 5.2 (4C)	3.9 (2Fe)	-
2	2.0086	33.2 (1H) 1.3 (2H)	3.7 (2S)			
3	2.0446	26.1 (2H)	-	5.2 (6C?)[b]	-	-
3(Se)	2.0444	25.7 (2H)	-	5.1 (6C)	3.6 (2Fe)	4.5 (1Se)

[a] Units of the hyperfine interactions are gauss. [b] Not all lines of the septet were observed, but intensity ratios suggest six equivalent carbons.

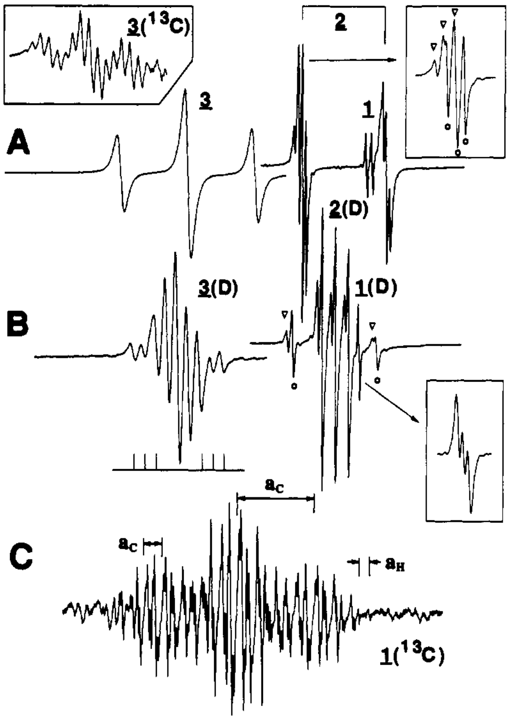
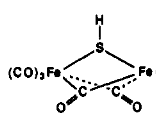
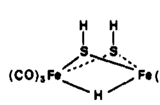


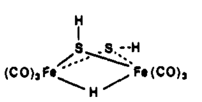
Figure 1. EPR spectra of (A) $Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}SH)$ (**1**), $Fe_2(CO)_6(\mu\text{-}SH)_2(\mu\text{-}H)$ (**2**) [inset (triangles, circles) shows two isomers of **2**], and $Fe_2(CO)_6(\mu\text{-}H)_2(\mu\text{-}SH)$ (**3**) [inset: $Fe(CO)_5$ enriched to 99% in ^{13}C]; (B) **1**, **2**, and **3** obtained by using 100% D_2S; and (C) **1** obtained by using $Fe(CO)_5$ enriched to 99% in ^{13}C.

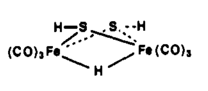
usefulness of extended Hückel molecular orbital (EHMO) calculations[2] in the interpretation of EPR results in organometallic chemistry.

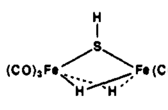
Low-temperature UV photolysis of $Fe(CO)_5$ in *n*-pentane in the presence of H_2S produces radicals **1**, **2**, and **3**. The spectrum

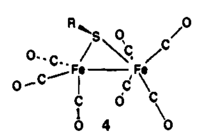

1


2a,a


2a,e


2e,e


3


4

of **1** consists of a doublet (1H = 2.2 G) with a *g* factor of 2.0024 (Figure 1A). Its identity is confirmed by using isotopically labeled precursors [D_2S, $H_2{}^{33}S$, $^{57}Fe(CO)_5$, $Fe(^{13}CO)_5$]. D_2S gives a 1:1:1 triplet (inset, Figure 1B). Labeling with ^{33}S and ^{57}Fe shows the presence of only one sulfur and two equivalent iron atoms. Enrichment in ^{13}C (Figure 1C) and analysis using computer simulation indicated 1H = 2.2 G, 2^{13}C = 14.4 G, 4^{13}C = 3.7 G, and 2^{13}C = 3.3 G. EHMO calculations suggest assignment of the large ^{13}C hyperfine splittings (hfs) to two bridging CO ligands (Figure 2).[3]

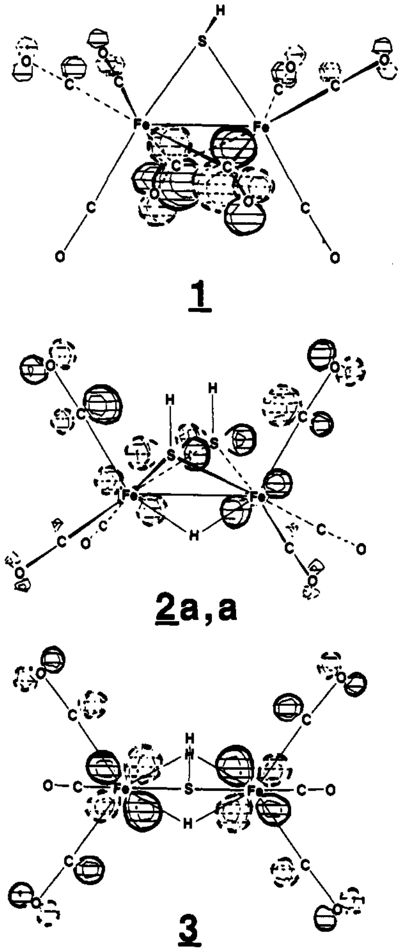


Figure 2. Contour plots of the SOMOs predicted by extended Hückel calculations for **1**, **2**(a,a), and **3**. The structures are based on that of $Fe_2(CO)_9$ with different bridging ligands.

Radical **2** shows the large hfs of a bridging proton (ca. 32.5 G), and a *g* factor of ca. 2.0080. Of the three possible isomers **2**(a,e), **2**(e,e), and **2**(a,a), only two are discernible in Figure 1A (inset: triangles, circles) as the superposition of two 1:2:1 triplets in a ca. 1:3 intensity ratio. We are unable to assign these spectra to specific isomers. The presence of the two isomers is more obvious from the experiment with D_2S (Figure 1B). The spectrum of perdeuterio **2** consists of two sets of 1:1:1 triplets of slightly different *g* factors and deuterium hfs, again in an approximate

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[2] MO calculations were performed by using the Du Pont implementation of the extended Hückel method. (a) Pensak, D. A.; McKinney, R. J. *Inorg. Chem.* **1979**, *18*, 3407. (b) Pensak, D. A.; McKinney, R. J. *Inorg. Chem.* **1979**, *18*, 3413.

[3] The Cartesian coordinates used for **1** were those of $Fe_2(CO)_6(\mu\text{-}CO)_3$ (Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* **1974**, 800) in which one bridging CO was replaced by an SH group having *d*(FeS) = 2.1 Å and *d*(SH) = 1.1 Å. The SH bond lies in the molecular plane of symmetry forming an angle of 120° with the FeSFe plane.

1:3 ratio. In the wings of the spectrum, lines can be seen due to $Fe_2(CO)_6(\mu\text{-}SD)_2(\mu\text{-}H)$ (triangles, circles). The unexpected presence of this hydrogen-containing isotopomer could be due to a large kinetic isotope effect. Isotopic labeling (Table I) shows the presence of two strongly interacting ^{13}C nuclei. EHMO calculations lead us to assign these interactions to two terminal CO ligands trans to the bridging hydrogen (Figure 2).[4]

Radical **3** has two bridging hydrogens (2H = 26.1 G) and a large positive *g* shift (Figure 1A). With D_2S a 4.1-G quintet was obtained, together with additional lines in the wings belonging to $Fe_2(CO)_6(\mu\text{-}SD)(\mu\text{-}H)(\mu\text{-}D)$ (Figure 1B). With $Fe(^{13}CO)_5$, each line of the triplet becomes a binomial septet due to the six terminal carbonyls. With H_2Se, a radical analogous to **3** was obtained containing two equivalent iron atoms and a single selenium atom as established by isotopic enrichment (Table I).

This work is currently being extended to include the photolysis of mercaptans and disulfides with $Fe(CO)_5$. Preliminary results have shown that radicals analogous to **1**, **2**, and **3** containing bridging SR groups are formed, as well as an asymmetric species, **4**.

Acknowledgment. We are indebted to R. Dutrisac (NRCC) and S. A. Hill (Du Pont) for technical assistance.

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(4) EHMO calculations were performed on **2a**, using the atomic coordinates of $Fe_2(CO)_6(\mu\text{-}CO)_3$ with two SH groups and a hydrogen [d(FeH) = 1.5 Å] replacing the bridging CO's.

Electrochemical Reduction and Oxidation of C_{60} Films

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We describe the first electrochemical study of films of C_{60} on platinum electrodes. The cyclic voltammetry (CV) of such films in tetra-*n*-butylammonium [$(TBA)AsF_6$]/MeCN, showing an unusual hysteresis, differs from the CV of dissolved C_{60} and suggests that large structural or resistive changes occur on reduction. The structure of C_{60} has been investigated by a number of techniques.[1-5] The CV of C_{60} dissolved in solvents such as CH_2Cl_2 and THF shows that C_{60} is reduced easily with three reversible CV reductions at −1.07, −1.43, and −1.92 V vs Fc/Fc$^+$ (where Fc is ferrocene).[4-6] No oxidation waves were seen.

C_{60} is insoluble in MeCN so that films cast on electrode surfaces [Pt, Au, or glassy carbon (GC)] can be studied in this medium. The films were prepared by evaporation on the electrode surface of a few microliters of a solution of C_{60} in CH_2Cl_2 or benzene. Typical voltammograms[7] for the reduction of C_{60} films (Figures 1 and 2) show four reduction peaks with cathodic peak potentials (E_{pc}) at −1.17, −1.39, −1.88, and −2.24 V vs Fc/Fc$^+$. The first three peak potentials are close to those reported for dissolved C_{60}[4,6] and probably represent successive one-electron-transfer reactions. However, the behavior on scan reversal is different than that of dissolved C_{60}. The anodic peaks are displaced to potentials far positive of the cathodic peaks (ca. 0.5 V for the first wave and ca. 0.2 V for the second).

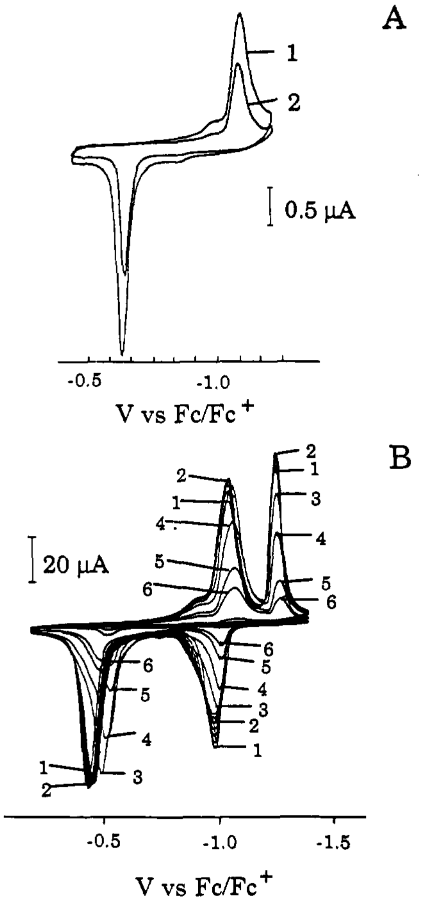

Figure 1. Cyclic voltammograms of a film of C_{60} on a platinum electrode in a solution of MeCN; supporting electrolyte: 0.1 M $(TBA)AsF_6$. Reversible reduction processes: (A) First reduction. (1) v = 200 mV/s; (2) v = 100 mV/s. (Electrode diameter: 250 μm). (B) Second reduction and effect of continuous scanning at 200 mV/s. (1) First cycle; (2) 10th cycle; (3) after 5 min; (4) after 10 min; (5) after 20 min; (6) after 25 min. (Electrode diameter: 1 mm.)

The film was stable in the presence of TBA$^+$ on Pt, Au, or GC electrodes. Continuous scanning over the first pair of waves, or over both the first and second pairs, showed small changes in peak potentials and a slow and continuous decrease in peak currents, with the waves almost gone after 2 h of scanning at 200 mV/s (Figure 1B). The film was less stable for scans beyond the third or fourth reduction waves. The peak widths at half-height, $\Delta E_{p,1/2}$ (55–70 mV for the first cathodic wave and 30–55 mV for the first anodic wave), were significantly less than those expected for a surface-confined species (91 mV)[8] at scan rates (v) below 200 mV/s. In this region of v a plot of the peak current, i_p, against v was linear and intersected the origin, as expected for a surface-confined species. To obtain a more quantitative estimate of the state of reduction of the film, a known amount of C_{60} (2 μL of 1 mM C_{60} in benzene) was dropped on a 3-mm-diameter GC

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(5) Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 8983.

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(7) Electrochemical experiments were conducted in a glovebox under a He atmosphere. The counter electrode was a Pt foil; a Ag wire was used as a quasi-reference electrode. All potentials are referenced to the Fc/Fc$^+$ couple, which was used as an internal standard. Electrochemical experiments and working electrode fabrication followed the procedures described in the following: Garcia, E.; Kwak, J.; Bard, A. J. *Inorg. Chem.* **1988**, *27*, 4377.

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