

Photoaddition of $\text{Fe}_2\text{S}_2(\text{CO})_6$ to C_{60}

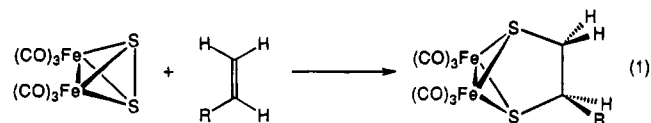
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There is intense interest in the functionalization of the fullerenes, especially as these molecular allotropes of carbon become increasingly available. Metal complexes figure prominently in the array of reagents that attack the C_{60} , C_{70} , and now C_{84} cages.¹ Fullerenes interact with metals most commonly via direct metal–cage bonding. Rarer are cases whereby the fullerene binds to ligands, the noteworthy examples are Hawkins' studies on the osmylation of C_{60} and C_{70} .² While not well developed, the ligand-based reactivity has the advantage of enhanced kinetic stability of the products and the potential for the decomplexation of modified fullerenes. The present work involves the reaction of C_{60} with sulfido ligands; as such, it represents a continuation of our interest in carbon sulfides.³ $c\text{-S}_8$ is known to cocrystallize with both C_{60} ⁴ and C_{70} ,⁵ but true thiofullerenes were unknown prior to this work.

Our approach is based on the findings by Seyferth, Lorenz, and co-workers that UV irradiation induces the addition of carbon–carbon multiple bonds across the S–S bond in the inorganic tetrahedrane $\text{Fe}_2\text{S}_2(\text{CO})_6$ (eq 1).^{6,7} A preliminary study



revealed that the photolysis of a solution of $\text{Fe}_2\text{S}_2(\text{CO})_6$ and C_{60} ⁸ affords soluble products whose fast atom bombardment (FAB) mass spectra revealed the presence of $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_n$ where $n = 1$ –6. Three considerations facilitated preparative-scale reactions of C_{60} and $\text{Fe}_2\text{S}_2(\text{CO})_6$. First, $\text{Fe}_2\text{S}_2(\text{CO})_6$, unlike C_{60} and most of its simple adducts,⁹ is very soluble in alkanes. Hence it is easy to remove excess $\text{Fe}_2\text{S}_2(\text{CO})_6$ from its reactions with fullerenes, whose solubility in alkanes is low. Second,

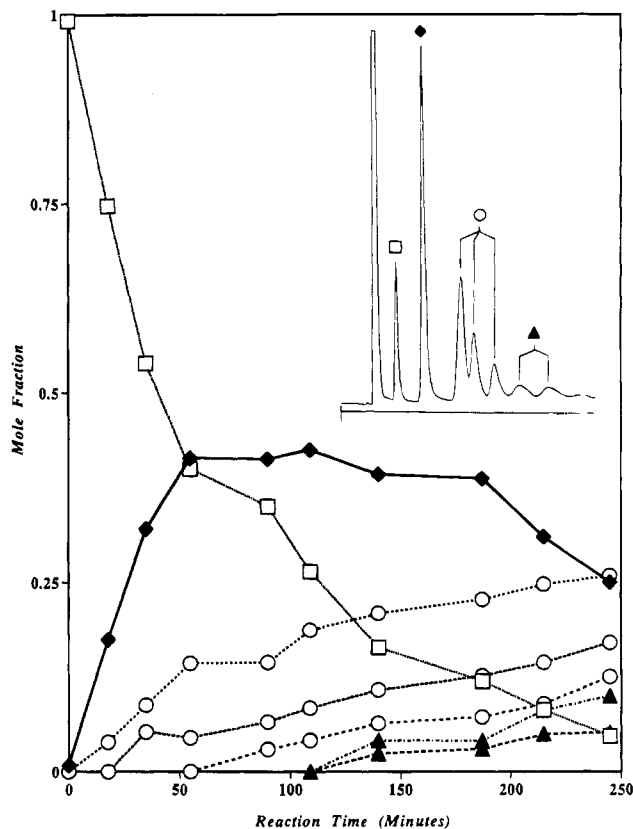


Figure 1. Time course for the reaction of $\text{Fe}_2\text{S}_2(\text{CO})_6$ and C_{60} (See footnote 13 for preparative details.) HPLC parameters: detection at 380 nm, flow rate = 1 mL/min, silica gel column, eluting with hexane. Inset: HPLC trace for the reaction mixture after 120 min. The peaks are assigned as follows: unreacted C_{60} (open square), $\text{C}_{60}\text{S}_2\text{Fe}_2(\text{CO})_6$ (filled diamond), isomers of $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_2$ (open circle), and isomers of $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_3$ (filled triangle). The same labels apply to the graph.

although $\text{Fe}_2\text{S}_2(\text{CO})_6$ undergoes competing photodimerization,¹⁰ the product $\text{Fe}_4\text{S}_4(\text{CO})_{12}$ is insoluble in all solvents.¹¹ Third, the synthesis of $\text{Fe}_2\text{S}_2(\text{CO})_6$ was recently optimized.¹²

Our studies have focused on the reaction of toluene solutions of C_{60} with a 10-fold excess $\text{Fe}_2\text{S}_2(\text{CO})_6$ at -20°C .¹³ The product distribution vs time is presented in Figure 1. The data indicate that under these conditions the optimized yield of $\text{C}_{60}\text{S}_2\text{Fe}_2(\text{CO})_6$ is $\sim 70\%$. It is also evident that $\text{C}_{60}\text{S}_2\text{Fe}_2(\text{CO})_6$ is

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- (13) Typical conditions (see Figure 1): A stirred solution of 0.105 g of C_{60} (0.145 mol) and 0.495 g of $\text{Fe}_2\text{S}_2(\text{CO})_6$ (1.44 mol) in 80 mL of toluene (Pyrex flask) was irradiated (Spectronic Blacklamp, $\lambda_{\text{max}} = 365\text{ nm}$) at -20°C for 1.25 h. An analytical sample was prepared by cooling a warm toluene solution. Anal. Calcd for $\text{C}_{66}\text{Fe}_2\text{O}_6\text{S}_2$: C, 74.47; Fe, 10.49; S, 6.02. Found: C, 73.97; H, 0.94; N, 0.93; Fe, 10.37; S, 5.89.

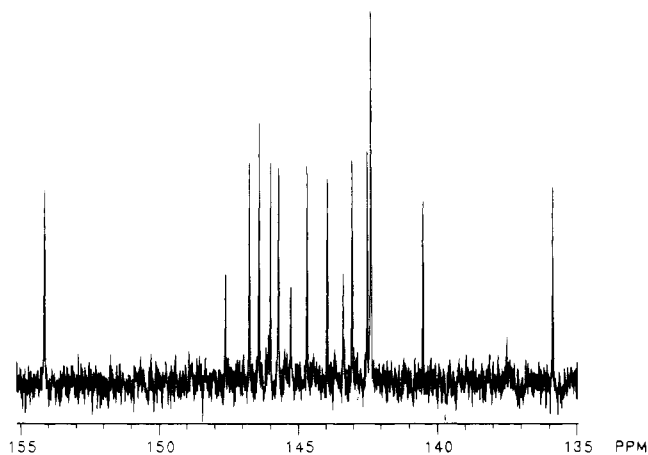
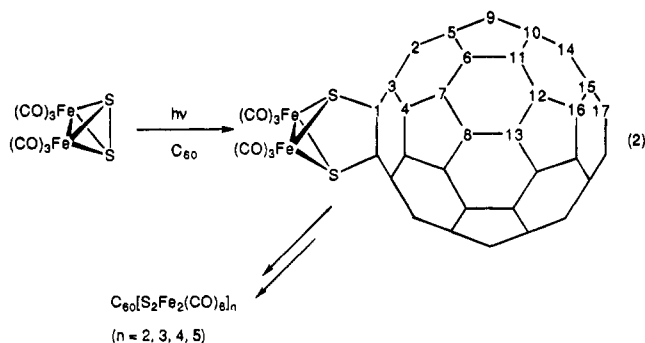


Figure 2. 125 MHz ^{13}C NMR spectrum of $\text{C}_{60}\text{S}_2\text{Fe}_2(\text{CO})_6$ in CS_2 solution (24 mg sample in 0.7 mL; 716 pulses, 8 s delay time).

reactive toward further equivalents of $\text{Fe}_2\text{S}_2(\text{CO})_6$. Workup entailed simply filtration of the reaction mixture, evaporation, and washing of the residue with hexane. Preparative-scale separations of $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_n$ were accomplished by gel filtration on Bio-Beads SX-3, eluting with toluene. The purity and identity of the fractions were verified by HPLC and mass spectrometric analyses. As expected, the elution proceeded in the order of molecular size, the initial fraction consisting of small amounts of $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_3$. After this band, we collected yellow brown fractions of $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_2$ and $\text{C}_{60}\text{S}_2\text{Fe}_2(\text{CO})_6$, in that order. The slowly eluting violet C_{60} was easily separated from the functionalized fullerenes (eq 2).



Relying on gel filtration, we could obtain >50 mg samples of $\text{C}_{60}\text{S}_2\text{Fe}_2(\text{CO})_6$ which are >95% purity, on the basis of HPLC analysis. The ^{13}C NMR spectrum of $\text{C}_{60}\text{S}_2\text{Fe}_2(\text{CO})_6$ features 15 lines for the cage, where 17 are expected (Figure 2).¹⁴ Assuming comparable relaxation times for all carbon centers, four of the expected 17 resonances should have 0.5 relative intensity, as these signals arise from pairs of equivalent carbon atoms that lie on the two mirror planes (C1, C8, C13, and C17

(14) ^{13}C NMR (CS_2 solution, C_6D_6 lock): 154.1, 147.6, 146.7, 146.4, 146.0, 145.7, 145.2, 144.7, 143.9, 143.3, 143.0, 142.5, 142.3, 140.5, 135.8 ppm. The peak at 142.3 ppm is of double intensity. This ^{13}C NMR spectrum shows a broad signal at 208 ppm which may be assigned to slowly exchanging (turnstile mechanism) Fe-CO.

in eq 2). On the basis of the intensities in the spectrum, at least two resonances are coincident; hence we can account for 16 of 17 possible signals. The chemical shifts (135.8–154.1 ppm) are comparable to the nonfunctionalized carbon centers in $\text{C}_{60}\text{O}_2\text{OsO}_2(t\text{-Bupy})_2$ (137–153 ppm).^{2,15} The IR spectrum of $\text{C}_{60}\text{S}_2\text{Fe}_2(\text{CO})_6$ shows four ν_{CO} bands, also as predicted for a molecule of C_{2v} symmetry.¹⁶ The redox properties of the modified fullerenes were evaluated by cyclic voltammetry on 1,2-dichlorobenzene solutions.¹⁷ We observed three reduction steps for $\text{C}_{60}\text{S}_2\text{Fe}_2(\text{CO})_6$, at -460, -840, and -1288 mV (vs Ag/AgCl). These waves correspond to quasireversible processes on the basis of the relative anodic and cathodic currents.

Gel chromatography afforded pure fractions corresponding to the double- and triple-addition compounds $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_n$ ($n = 2, 3$). Under typical conditions, the combined yield of these species was ~20%. The HPLC trace for the double-addition product consisted of three peaks, indicating the presence of at least three isomers. Eight isomers of $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_2$ are possible.¹⁸ Samples of $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_3$ were identified by FABMS which showed the absence of single- and double-addition compounds. The triple-addition compound represents one of the highest nuclearity (108 atoms) molecular inorganic compounds known. The IR spectra of $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_n$ are almost identical for $n = 1-3$, indicating that there is little electronic coupling between the two $\text{Fe}_2\text{S}_2(\text{CO})_6$ sites. The fullerene cage is sensitive to the degree of addition as shown by the electronic spectra. UV maxima for the series $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_n$ shift to higher energies with increasing n , i.e. 336 ($n = 0$), 332 ($n = 1$), 320 ($n = 2$), and 318 nm ($n = 3$).

In summary, our studies have uncovered the first sulfido derivatives of C_{60} . The approach is probably more general since many metal sulfides add unsaturated organic compounds.¹⁹ Metal sulfide/fullerene hybrids are of potentially broader interest in view of the novel electronic materials derived from metal dithiolato complexes.²⁰

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Supplementary Material Available: Text giving preparative details and figures showing IR, NMR, and mass spectra (14 pages). Ordering information is given on any current masthead page.

- (15) For C_{60}O , the shifts for the unfunctionalized carbon atoms are 140–146 ppm (Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P.; Jones, D. R.; Gallager, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103). We do not observe a resonance that can be unambiguously assigned to the S-functionalized carbon.
- (16) IR data (CS_2 solutions): for $\text{C}_{60}\text{S}_2\text{Fe}_2(\text{CO})_6$, 2076, 2040, 2011, 2001 cm^{-1} ; for $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_2$, 2076, 2041, 2011, 2003 cm^{-1} ; for $\text{C}_{60}[\text{S}_2\text{Fe}_2(\text{CO})_6]_3$, 2076, 2041, 2012, 2002 cm^{-1} ; for $\text{Fe}_2\text{S}_2(\text{CO})_6$, 2080, 2040, 2001 cm^{-1} .
- (17) Conditions: scan rate 200 mV/s, supporting electrolyte NBu_4PF_6 , IR compensation, Pt working electrode, BAS-100 instrument. For background literature on the redox properties of fullerenes, see: Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W. *J. Am. Chem. Soc.* **1994**, *116*, 1359.
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