

## Methods to Functionalize Cluster Materials Based on Fullerenes and the Organometallic Cluster, $Cp_4Fe_4(CO)_4$

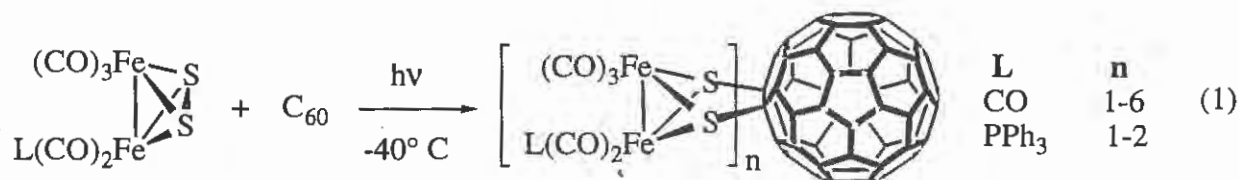
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Final Seminar

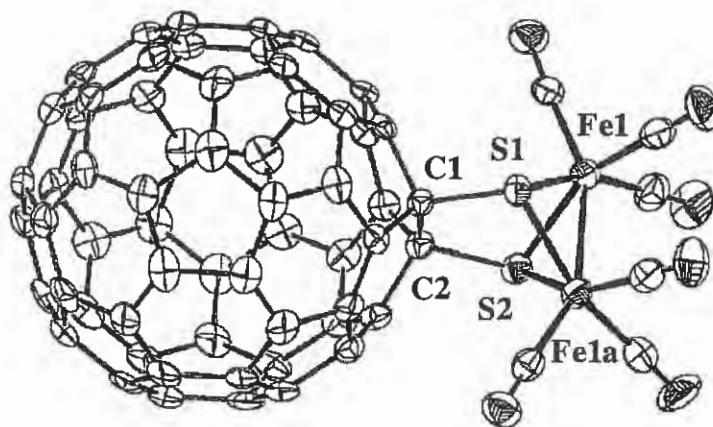
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**Iron Thiofullerene Derivatives of  $C_{60}$  and  $C_{70}$ .** Metal complexes figure prominently in the array of reagents that attack the carbon cages of  $C_{60}$ ,  $C_{70}$ , and  $C_{84}$ .<sup>1</sup> Fullerenes interact with metals most commonly via direct metal-cage bonding.<sup>2</sup> Cases where the fullerene binds to ligands are rare, although noteworthy examples are provided by Hawkins' pioneering studies on the osmylation of  $C_{60}$  and  $C_{70}$ .<sup>3</sup> The project focused on the development of sulfur modified derivatives or *thiofullerenes*, which would serve as thiolate ligands,  $C_{60}S_2^{2-}$ .

Our route utilized the reagent,  $Fe_2S_2(CO)_6$ , which adds to alkenes under photolytic conditions.<sup>4</sup> Toluene solutions of  $Fe_2S_2(CO)_6$  and  $C_{60}$  react under photolytic conditions to give the adducts  $C_{60}[S_2Fe_2(CO)_6]_n$ ,  $n = 1-6$  (eq 1).<sup>5</sup>



The adducts where  $n = 1-3$  have been isolated in compositional purity and characterized spectroscopically. Crystallographic studies of  $C_{60}S_2Fe_2(CO)_6$  show that the addition occurred at a 6,6 fusion and the S-S bond of the  $Fe_2$  reagent is cleaved to give a dithiolate with idealized  $C_{2v}$  symmetry (Figure 1).



**Figure 1.** ORTEP drawing of  $C_{60}S_2Fe_2(CO)_6$  with thermal ellipsoids at 50%.

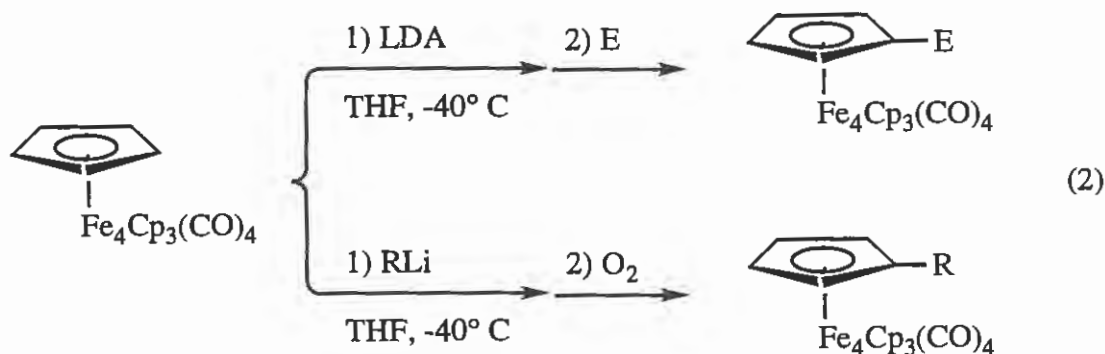
We were able to control the extent of functionalization by substituting one carbonyl ligand on  $Fe_2S_2(CO)_6$  with  $PPh_3$ . Thus photoaddition of  $Fe_2S_2(CO)_5(PPh_3)$  to  $C_{60}$  gave

$C_{60}[S_2Fe_2(CO)_5(PPh_3)]_n$ , where  $n = 1, 2$ .  $^{31}P\{^1H\}$  NMR spectroscopic studies show that the double adduct consists of multiple isomers. Photoaddition of  $Fe_2S_2(CO)_6$  to  $C_{70}$  gave a series of adducts  $C_{70}[S_2Fe_2(CO)_6]_n$  where  $n = 1-4$ . HPLC analysis shows one, four, and three isomers for the adducts, respectively.<sup>6</sup>

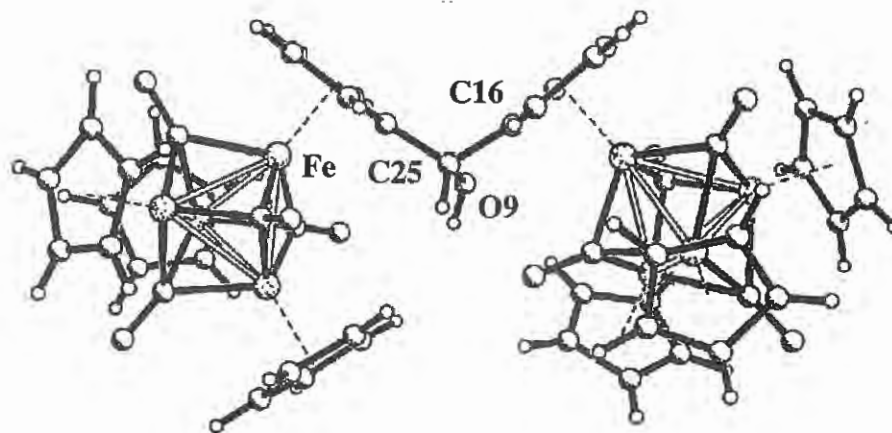
**Functionalization of  $Cp_4Fe_4(CO)_4$ : Comparisons and Contrasts to Ferrocene.** The functionalization of metal cyclopentadienyl compounds, while an old field, continues to be extremely fruitful. Ferrocenes continue to dominate the area,<sup>7</sup> but other cyclopentadienyl complexes, especially monometallic compounds, have been functionalized.<sup>8</sup> Advances in Cp functionalization has strongly contributed to the area of organometallic polymers, because polymerization processes are contingent on reactive functionalities.<sup>9,10</sup> Few clusters have been functionalized through cyclopentadienyl (Cp) ligands.<sup>11</sup> Cp functionalization is of interest based on considerations of scope and practicality: many Cp-containing clusters are known and the metal-Cp linkage is extremely robust.

To examine the functionalization of a metal cluster, we selected  $Cp_4Fe_4(CO)_4$  because it has been well studied<sup>12</sup> and is easily prepared by the thermal decomposition of  $[CpFe(CO)_2]_2$ .<sup>13</sup> Additional advantages for this cluster are that it is electroactive, reversibly undergoing both reduction and oxidation, and it absorbs strongly at  $\sim 400$  nm which facilitates spectroscopic and chromatographic analysis.<sup>14</sup>

Cluster 1 can be alkylated and arylated using organolithium reagents to give the derivatives  $(C_5H_4R)Cp_3Fe_4(CO)_4$ . This reaction is competitive with reduction of  $Cp_4Fe_4(CO)_4$  by the organolithium reagent. A more versatile method for functionalizing  $Cp_4Fe_4(CO)_4$  involves its deprotonation using lithium diisopropyl amide (LDA) followed by treatment with electrophiles to give  $(C_5H_4X)_nCp_{n-x}Fe_4(CO)_4$  ( $X = C(OH)HCH_3, CO_2H, CHO, SPh, PPh_2$ ) (eq 2).<sup>15</sup>

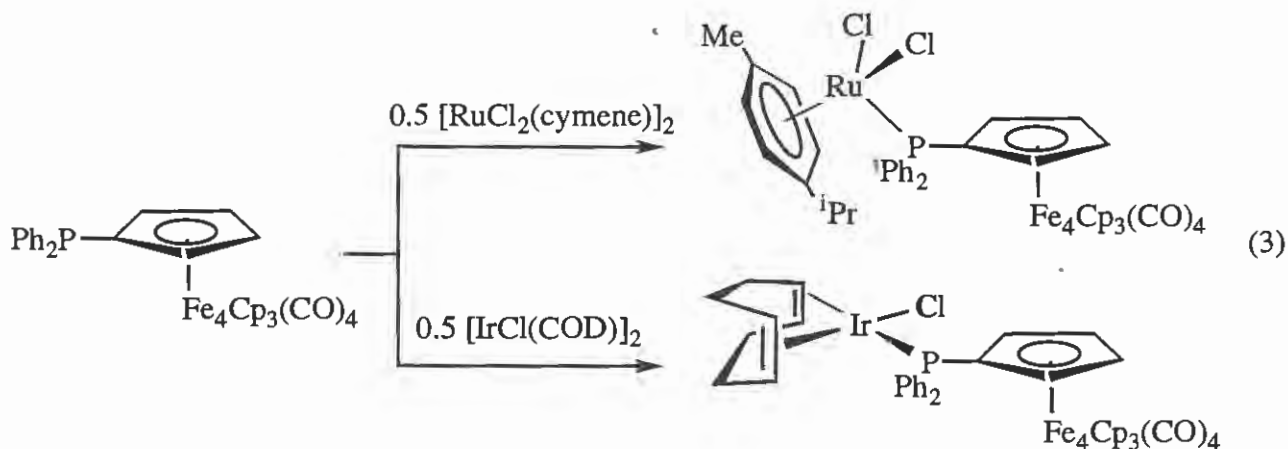


The reactivity of the lithiated clusters towards organic electrophiles led us to investigate routes to diclusters. Treatment of  $(C_5H_4CHO)Cp_3Fe_4(CO)_4$  with the lithiated cluster gave the double cluster,  $[(C_5H_4)Cp_3Fe_4(CO)_4]_2CHOH$ . Single crystal X-ray diffraction was employed to characterize  $[(C_5H_4)Cp_3Fe_4(CO)_4]_2CHOH$  (Figure 2).



**Figure 2.** ORTEP drawing of  $[(C_5H_4)Cp_3Fe_4(CO)_4]_2CHOH$  with thermal ellipsoids at 50%.

The use of the cluster as a ligand was demonstrated by the synthesis of the adducts  $(C_5H_4PPh_2ML_n)Cp_3Fe_4(CO)_4$ , where  $ML_n = RuCl_2(cymene)$ ,  $IrCl(COD)$  (eq 3).



Single crystal X-ray diffraction was employed to characterize  $(C_5H_4PPh_2RuCl_2(cymene))Cp_3Fe_4(CO)_4$ .

In closing, it is useful to compare the chemical properties of  $Cp_4Fe_4(CO)_4$  and ferrocene, both of which are thermally robust CpFe compounds that, to some extent, can be viewed as sandwich compounds. Overall, the reactivity of  $Cp_4Fe_4(CO)_4$  indicated that it is more electron-deficient than ferrocene, hence it is deprotonated by milder base, e.g., LDA, and it is susceptible to reduction by RLi. Because of its relatively greater acidity as well as the presence of multiple reactivity sites, there is every prospect to expect a rich chemistry to evolve for  $Cp_4Fe_4(CO)_4$ .

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