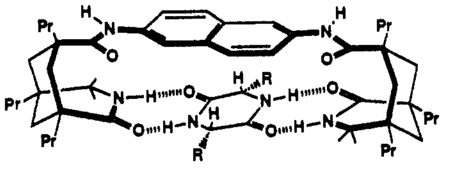
experimental[10] findings concerning the destabilizing effect of spectator atoms on nearby hydrogen-bonded arrays.



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Synthesis, Structure, and Electrochemical Properties of Mixed-Ligand Iron-Sulfur Cubane Clusters with Two Cp* and Two Dithiolene Ligands (Cp* = η-C_5H_5, η-C_5Me_5)

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Cubane clusters containing an M_4E_4 core (M = transition metal, E = chalcogen) are known to have different types of structures, especially with respect to the M-M bonding of the cubane core.[1] A large number of homo- and heterometallic clusters of this type have been synthesized, but mixed-ligand, homometallic cubane clusters are rare.[1,2] Since the nature of cubane clusters greatly depends on the ligand environment of each metal in the cluster,[3] it is significant to synthesize new mixed-ligand, homometallic metal-chalcogen cubane clusters and to investigate their structures and properties. We now report the first synthesis, structure, and electrochemical properties of iron-sulfur cubane clusters with two Cp* and two dithiolene ligands.

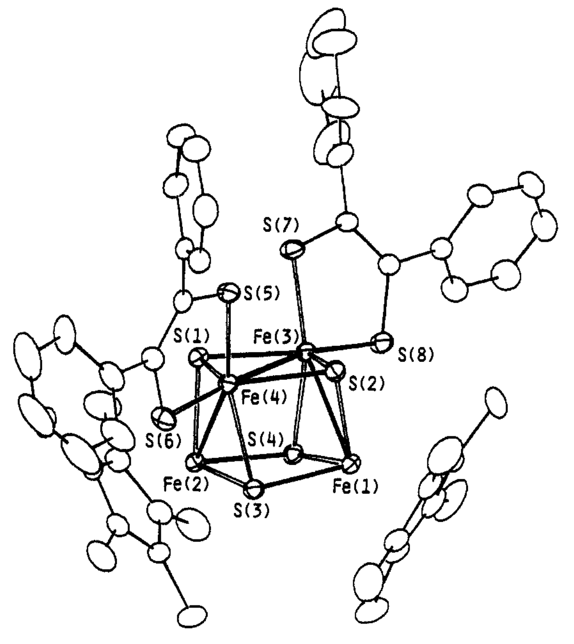
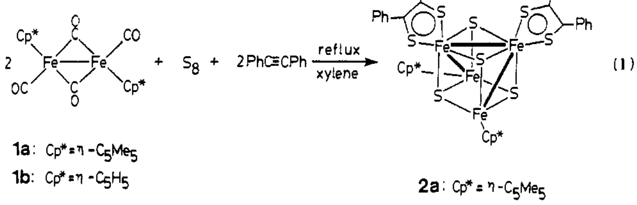


Figure 1. ORTEP diagram of $(\eta$-$C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4$ (**2a**) with thermal ellipsoids at the 30% probability level. Selected distances (Å): Fe(1)-Fe(3), 2.711 (1); Fe(2)-Fe(4), 2.717 (1); Fe(3)-Fe(4), 2.789 (1); Fe(1)···Fe(2), 3.400 (1); Fe(1)···Fe(4), 3.255 (1); Fe(2)···Fe(3), 3.270 (1) Å.

Reaction of a 1:0.5:2 molar ratio of $(\eta$-$C_5Me_5)_2Fe_2(CO)_4$ (**1a**), S_8, and PhC≡CPh in refluxing xylene for 120 h gave purple crystals of $(\eta$-$C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4$ (**2a**) as the major product in 51% yield. In a similar manner, the reaction of $(\eta$-$C_5H_5)_2Fe_2(CO)_4$ (**1b**) with S_8 and PhC≡CPh afforded $(\eta$-$C_5H_5)_2(Ph_2C_2S_2)_2Fe_4S_4$ (**2b**) in 32% yield (eq 1). In each case, a black powder, sparingly soluble in xylene, was also obtained as a byproduct, and in the latter case, the black powder was identified as the known cubane cluster $(\eta$-$C_5H_5)_4Fe_4S_4$ by mass and NMR spectroscopy.[4] This reaction is in sharp contrast to the reaction of $(\eta$-$C_5H_5)Co(CO)_2$ with S_8 and PhC≡CPh under similar conditions, which gives the mononuclear dithiolene complex $(\eta$-$C_5H_5)Co(S_2C_2Ph_2)$.[5]



(1)

Compounds **2a** and **2b** were characterized by the usual spectroscopic methods.[6] The FAB mass spectra of **2a** and **2b** show molecular ion peaks centered at m/z = 1106 and 966, respectively. The ^1H NMR spectrum of **2a** (200 MHz) in $CDCl_3$ exhibits a methyl singlet (η-C_5Me_5) at 1.48 ppm and two Ph multiplets at 7.2-7.3 and 7.4-7.5 ppm. Similarly, the spectrum of **2b** shows

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(6) For **2a**: ^{13}C NMR ($CDCl_3$, 50 MHz) 10.6 (Me), 101.7 (η-C_5Me_5), 127.2, 127.8, 129.8, 141.7 (Ph), 174.1 (S=*C*Ph); MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe) m/z 1106 (M^+). Anal. Calcd for $C_{48}H_{50}Fe_4S_8 \cdot CH_2Cl_2$: C, 49.38; H, 4.40. Found: C, 49.30; H, 4.49. For **2b**: ^{13}C NMR ($CDCl_3$, 50 MHz) 89.3 (η-C_5H_5), 127.86, 127.92, 129.6, 141.6 (Ph), 179.0 (S=*C*Ph); MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe) m/z 966 (M^+). Anal. Calcd for $C_{38}H_{30}Fe_4S_8 \cdot CH_2Cl_2$: C, 44.55; H, 3.07. Found: C, 44.11; H, 3.36.

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a singlet assigned to cyclopentadienyl protons at 4.96 ppm in addition to Ph multiplets.

The X-ray diffraction study of a single crystal of **2a**·CH_2Cl_2[7] shows that a molecule of the cluster bears two η-C_5Me_5 and two diphenyldithiolene ligands on the four iron atoms, and its Fe_4S_4 core is highly distorted (Figure 1): Three Fe–Fe distances (Fe(1)–Fe(3), Fe(3)–Fe(4), and Fe(4)–Fe(2)) are much shorter (2.711 (1)–2.789 (1) Å) than the other three (3.255 (1)–3.400 (1) Å). The shorter Fe–Fe distances are somewhat longer than Fe–Fe single bond distances found in $[(\eta\text{-}C_5H_5)_4Fe_4S_4]$[4] and $[Fe_4(NO)_4S_4]$[8] (average 2.65 Å), but shorter than those with a bond order of $^3/_4$ in $[(\eta\text{-}C_5H_5)_4Fe_4S_4]^{2+}$ (2.83 Å).[9] The longer Fe–Fe distances correspond to the absence of interiron bonds. This localization of Fe–Fe bonds renders the top four-membered ring of Fe_2S_2 and the bottom one twisted with respect to each other by ca. 18°. Interestingly, the top and bottom four-membered rings of Fe_2S_2 are nearly planar[10] in contrast to those of other iron–chalcogen cubane clusters.[4,8,9,11-13]

The core structure of **2a** with three Fe–Fe single bonds is consistent with the metal fragment orbital model,[3,14] which predicts that the total bond order becomes 3 for this type of cubane cluster with 18 metal electrons: 12 electrons occupy the six metal–metal bonding orbitals, and the remaining six electrons occupy the low-lying metal–metal antibonding orbitals. There are two other iron–sulfur cubane clusters known to have 18 metal electrons and a total M–M bond order of 3, i.e., $[(\eta\text{-}C_5H_5)_4Fe_4S_4]^{2+}$[9] and $[Fe_4(S_2C_2(CF_3)_2)_4S_4]^{2-}$,[11] but, unlike **2a**, these clusters have four equivalent Fe–Fe bonds with a bond order of $^3/_4$ probably due to the higher symmetry of the cluster molecule.

Each of the cyclic voltammograms of **2a** and **2b** in a 0.1 M $(n\text{-}Bu)_4NBF_4/CH_2Cl_2$ solution exhibits four reversible redox waves, indicating the existence of five discrete species $[Cp^*{}_2(Ph_2C_2S_2)_2Fe_4S_4]^n$ for which $n = -2, -1, 0, +1$, and $+2$. The formal potentials for the redox waves of $Cp^*{}_2(Ph_2C_2S_2)_2Fe_4S_4$ ($E_{1/2}$) are −1.13, −0.55, +0.20, and +0.64 ($Cp^* = \eta\text{-}C_5Me_5$) and −0.92, −0.40, +0.41, and +0.84 ($Cp^* = \eta\text{-}C_5H_5$) V vs SCE, respectively. The $E_{1/2}$'s of **2a** are about 200 mV more negative than those of **2b** and are probably due to the electron-donating effect of 10 methyl groups on the Cp rings of **2a**.

Bulk electrolysis of **2a** was performed at +0.20 V vs SCE on a platinum working electrode in a 1:1 mixture of CH_2Cl_2 and CH_3CN in the presence of 0.1 M NH_4PF_6 as supporting electrolyte. Nearly 1 equiv of charge required for the one-electron oxidation of **2a** was passed, and the salt of the monocationic cluster $[(\eta\text{-}C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4](PF_6)$ (**3**)[15] was obtained as dark purple crystals in 92% yield. The same product was obtained in high yield by the oxidation with ferricinium hexafluorophosphate. The ^{1}H NMR spectrum of **3** exhibits typical paramagnetic shifts and line broadening.

We have little information so far on the mechanism for the formation of **2**. However, in the early stage of the reaction of **1a**, S_8, and PhC≡CPh, TLC analysis showed a strong spot of $[(\eta\text{-}C_5Me_5)_2Fe_2S_4]$ (**4**), which is known to be formed in high yield by the reaction of **1a** and S_8 under milder conditions (toluene reflux).[16] Furthermore, we observed that the reaction of **4** with PhC≡CPh in a refluxing xylene solution provided **2a**. These results are consistent with a mechanism involving **4** as one of the intermediates.

Supplementary Material Available: Tables of atomic positional and thermal parameters and bond distances and angles for **2a** (17 pages); listing of observed and calculated structure factors for **2a** (43 pages). Odering information is given on any current masthead page.

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(7) Single crystals of **2a**·CH_2Cl_2 were grown by layering ether on the CH_2Cl_2 solution of **2a** at room temperature: space group $P2_1/a$, $a = 20.679$ (3) Å, $b = 20.130$ (3) Å, $c = 12.742$ (2) Å, $\beta = 104.97$ (2)°, $V = 5124$ (1) Å^3, $Z = 4$, $d_{measd} = 1.54$ g cm^{-3}. Diffraction data were collected at 21 °C by the ω–2θ scan technique (3° < 2θ < 60°) using a Rigaku AFC-6A diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (MULTAN) and refined via block-diagonal least-squares methods using anisotropic thermal parameters for non-hydrogen atoms of the cluster molecule and isotropic thermal parameters for hydrogen atoms and for atoms of CH_2Cl_2. Molecules of CH_2Cl_2 were disordered. For 9193 unique reflections with $|F_o| > 3\sigma(F_o)$, final $R = 0.069$ ($R_w = 0.102$).

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Direct Conversion of Vinylic Organocopper Compounds to Allylic Zinc and Copper Organometallics

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Nucleophilic allylic organometallics have proven to be very efficient reagents for the formation of new carbon–carbon bonds with a variety of organic electrophiles.[1] Unfortunately, the most reactive allylic reagents (metal = Li, K, Mg, Zn) are often difficult to prepare due to their high reactivity and to side reactions during their preparation such as Wurtz coupling. Alternative syntheses such as oxidative additions or metalations of allylic halides using activated metals,[2] transmetalations,[3] homologation of vinyl organometallics,[4] and hydrometalation of dienes[5] have been successfully developed.

We report herein a new method allowing a very efficient direct conversion of alkenylcopper[6] compounds **1** to allylic zinc and copper reagents **2** mediated by (iodomethyl)zinc iodide[7] (**3**) (Scheme I). Thus the addition of ICH_2ZnI (**3**) (1.7 equiv) to an alkenylcopper **1** in THF at −30 °C leads to a fast methylene homologation reaction.[8] The resulting highly reactive allylic

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