C–C Bond Formation between $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_6$ and CS_2 To Give the Triiron Complex $\{(\eta^5\text{-}C_5Me_4)CH_2CS_2\}Fe_3(CO)_8$

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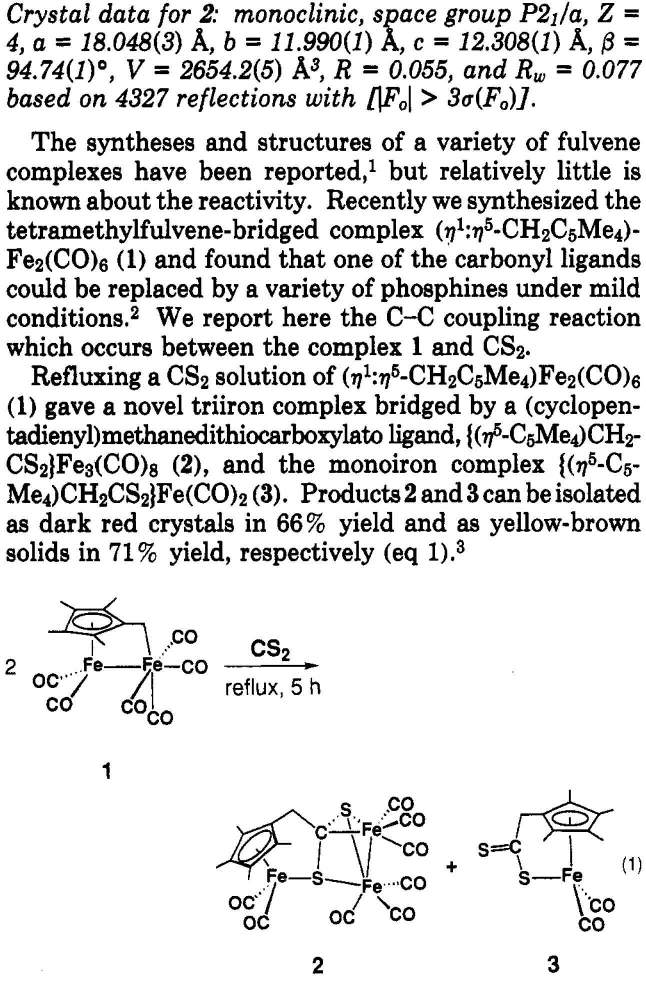
Summary: Reaction of the tetramethylfulvene-bridged complex $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_6$ (1) with CS_2 produces the triiron complex $\{(\eta^5\text{-}C_5Me_4)CH_2CS_2\}Fe_3(CO)_8$ (2) and the monoiron complex $\{(\eta^5\text{-}C_5Me_4)CH_2CS_2\}Fe(CO)_2$ (3) in high yields via C–C bond formation. X-ray crystallography of 2 shows that this complex contains a dithiocarboxylato ligand, $S_2CCH_2C_5Me_4$, which bridges three iron fragments in a novel coordination mode. Crystal data for 2: monoclinic, space group $P2_1/a$, $Z = 4$, $a = 18.048(3)$ Å, $b = 11.990(1)$ Å, $c = 12.308(1)$ Å, $\beta = 94.74(1)°$, $V = 2654.2(5)$ Å^3, $R = 0.055$, and $R_w = 0.077$ based on 4327 reflections with $[|F_o| > 3\sigma(F_o)]$.

The syntheses and structures of a variety of fulvene complexes have been reported,[1] but relatively little is known about the reactivity. Recently we synthesized the tetramethylfulvene-bridged complex $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_6$ (1) and found that one of the carbonyl ligands could be replaced by a variety of phosphines under mild conditions.[2] We report here the C–C coupling reaction which occurs between the complex 1 and CS_2.

Refluxing a CS_2 solution of $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_6$ (1) gave a novel triiron complex bridged by a (cyclopentadienyl)methanedithiocarboxylato ligand, $\{(\eta^5\text{-}C_5Me_4)CH_2CS_2\}Fe_3(CO)_8$ (2), and the monoiron complex $\{(\eta^5\text{-}C_5Me_4)CH_2CS_2\}Fe(CO)_2$ (3). Products 2 and 3 can be isolated as dark red crystals in 66% yield and as yellow-brown solids in 71% yield, respectively (eq 1).[3]



The structure of 2 was determined by the X-ray crystal structure analysis.[4] The ORTEP drawing of 2 shows that 2 contains the new highly bridging dithiocarboxylato ligand $S_2CCH_2C_5Me_4$, which is apparently formed by C–C bond formation between a carbon of CS_2 and an exo methylene carbon of 1, and this ligand connects three iron carbonyl fragments together (Figure 1).

Fe(1) adopts the distorted-piano-stool geometry, while both Fe(2) and Fe(3) are distorted octahedral. There is a single bond between Fe(2) and Fe(3) (2.654(1) Å), but no bonding interaction between Fe(1) and Fe(2) (4.040(1) Å). Each of these pairs of iron atoms is bridged by the sulfur atoms of the dithiocarboxylato ligand. All of the carbonyl ligands are terminal. The distance between Fe(3) and C(19) in the S_2C portion is 2.004(5) Å, which clearly shows the existence of a single bond between them. Therefore, C(19) adopts a pseudotetrahedral geometry. Such a tetrahedral geometry at the carbon atom in an S_2C group is quite rare in dithiocarboxylato complexes. In many cases, the carbon atom in a dithiocarboxylato ligand does not interact with metals and stays planar. To our knowledge, there are only two examples of complexes

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(3) Synthesis and spectral data for 2 and 3: A solution of $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_6$ (1; 90 mg, 0.22 mmol) in CS_2 (10 mL, 0.17 mol) was refluxed for 5 h. After removal of the solvent, the residue was chromatographed on a silica gel flash column (i.d. 1.8 cm × 8 cm). Elution with hexane/benzene (1/1) and concentration of a dark red fraction gave $\{(\eta^5\text{-}C_5Me_4)CH_2CS_2\}Fe_3(CO)_8$ (2) as dark red crystals in 66% yield (43 mg, 0.071 mmol, the yield calculated on the assumption that two molecules of 1 produce one molecule each of 2 and 3). The eluent was then changed to benzene to collect a black band (10 mg, an unidentified product) and a yellow-brown band of $\{(\eta^5\text{-}C_5Me_4)CH_2CS_2\}Fe(CO)_2$ (3; 25 mg, 0.078 mmol; the yield based on the above assumption, 71%). Data for 2: ^{1}H NMR (200 MHz, C_6D_6) δ 0.83 (3H, s, Me), 1.00 (3H, s, Me), 1.23 (3H, s, Me), 1.41 (1H, d, $^2J_{HH} = 14.7$ Hz, CH_2), 1.84 (3H, s, Me), 2.27 (1H, d, $^2J_{HH} = 14.7$ Hz, CH_2); ^{13}C NMR (50 MHz, C_6D_6) δ 7.9 (Me), 8.6 (Me), 9.2 (Me), 9.8 (Me), 45.6 (CH_2), 88.0 (C_5Me_4), 95.3 (C_5Me_4), 98.4 (C_5Me_4), 99.5 (C_5Me_4), 103.5 (C_5Me_4), 129.7 ($-CS_2$), 211.2 (br, CO), 212.3 (CO), 212.5 (br, CO), 214.4 (CO); IR (KBr pellet) ν_{CO} 1950 (m), 1970 (s), 1980 (s), 2000 (s), 2020 (s), 2030 (s), 2075 (s), ν_{CS} 1278 (vw), 1030 (vw) cm^{-1}; mass (EI) m/z 602 (3, M$^+$), 574 (42, M$^+$ − CO), 546 (19, M$^+$ − 2CO), 518 (19, M$^+$ − 3CO), 490 (10, M$^+$ − 4CO), 462 (26, M$^+$ − 5CO), 434 (57, M$^+$ − 6CO), 406 (100, M$^+$ − 7CO), 378 (99, M$^+$ − 8CO). Anal. Calcd for $C_{19}H_{14}Fe_3S_2O_8$: C, 37.91; H, 2.34. Found: C, 37.96; H, 2.34. Data for 3: ^{1}H NMR (300 MHz, C_6D_6) δ 0.99 (6H, s, Me), 1.32 (6H, s, Me), 3.58 (2H, s, CH_2); ^{13}C NMR (75 MHz, C_6D_6) δ 8.6 (Me), 9.2 (Me), 50.3 (CH_2), 92.9 (C_5Me_4), 97.8 (C_5Me_4), 105.8 (C_5Me_4), 213.7 (CO), 259.6 (CS_2); IR (KBr pellet) ν_{CO} 2017 (vs), 1963 (vs), ν_{CS} 1093 (m), 1027 (vs); mass (EI) m/z 322 (28, M$^+$), 294 (33, M$^+$ − CO), 266 (30, M$^+$ − 2CO), 190 (100, M$^+$ − 2CO − CS_2); exact mass calcd for $C_{13}H_{14}FeO_2S_2$ 321.9785, found 321.9783. Anal. Calcd for $C_{13}H_{14}FeO_2S_2$: C, 48.46; H, 4.38. Found: C, 47.49; H, 4.15.

(4) Crystal data for 2: $C_{19}H_{14}Fe_3S_2O_8 \cdot {}^1/_2C_6H_5CH_3$, $M_n = 638.06$, monoclinic, space group $P2_1/a$ (variant of No. 14); $a = 18.048(3)$ Å, $b = 11.990(1)$ Å, $c = 12.308(1)$ Å, $\beta = 94.74(1)°$, $V = 2654.2(5)$ Å^3, $Z = 4$, $D_c = 1.62$ g cm^{-3}, $F(000) = 1848$, μ (Mo Kα) = 6.22 cm^{-1}. Diffraction data were collected in the ω–2θ scan mode ($3° < 2\theta < 60°$). Final $R = 0.055$ ($R_w = 0.077$) for 4327 unique reflections (with $|F_o| > 3\sigma(F_o)$). The structure was solved by the heavy-atom method and was refined by use of block-diagonal least-squares procedures. All non-hydrogen atoms were located and refined anisotropically. The hydrogen atoms bonded to a methylene atom were located from the difference maps and isotropic thermal parameters. The positions of hydrogen atoms on the aromatic ring of solvent toluene were calculated and fixed. The solvent toluene was disordered between two orientations related by the inversion at the center of the six-membered ring. Therefore, a 50% occupancy factor was adopted for the methyl carbon atom and the atom was located.

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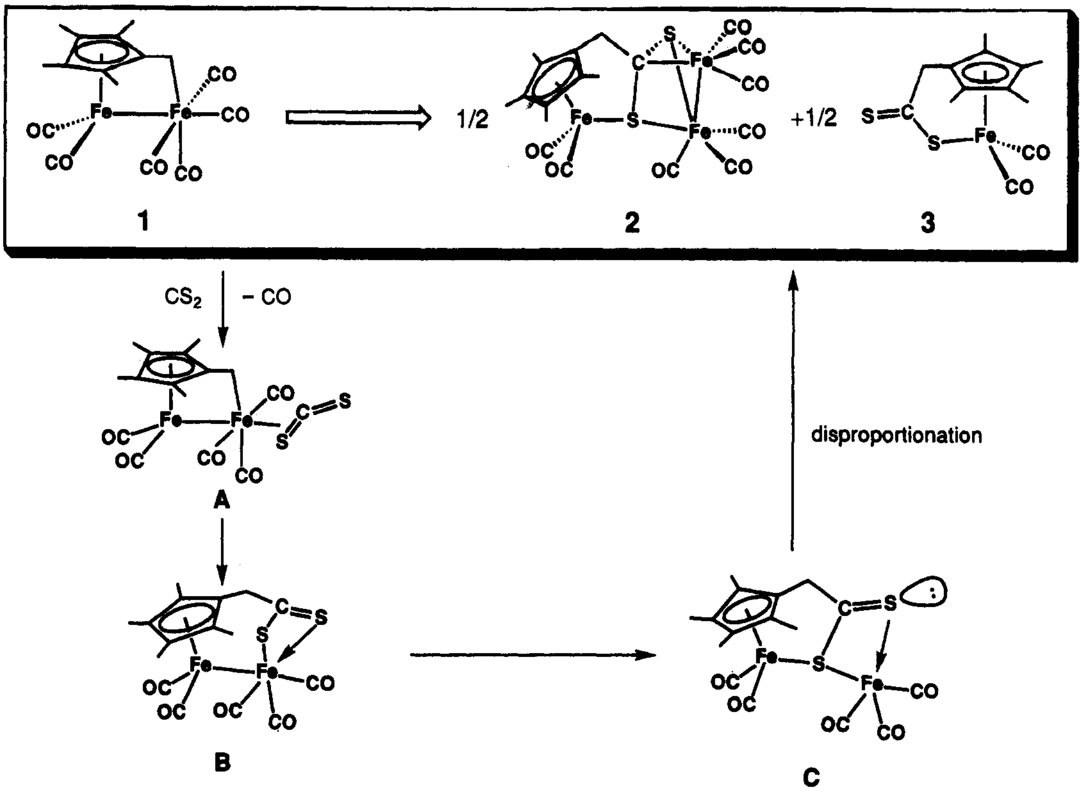
Scheme 1



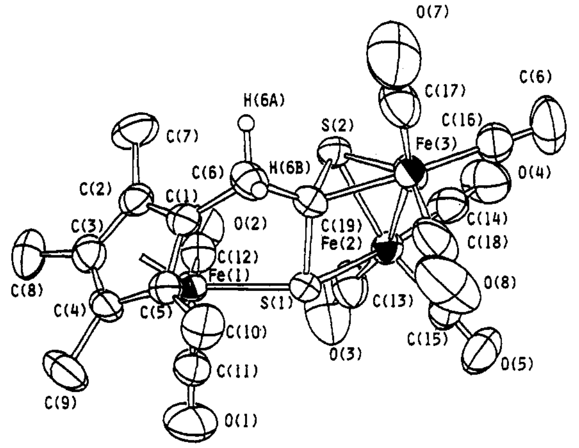


Figure 1. ORTEP diagram and numbering scheme of **2** with thermal ellipsoids drawn at the 30% level. Selected distances (Å): Fe(2)–Fe(3), 2.654(1); Fe(1)–S(1), 2.277(1); Fe(2)–S(1), 2.318(2); Fe(2)–S(2), 2.261(1); Fe(3)–S(2), 2.195(2); Fe(3)–C(19), 2.004(5); S(1)–C(19), 1.793(5); S(2)–C(19), 1.786(7); C(6)–C(19), 1.512(9).

containing a dithiocarboxylato ligand similar to **2**, the iron complex (η^5-C_5H_5)Fe(η^3-S_2CMe-*S,C,S'*)(dppm) (**4**)[5a] and the ruthenium complex (η^5-C_5H_5)Ru[1-Ph_2P-2-{S_2CCH(Me)C_6H_4}] (**5**).[5b] In these complexes, two sulfur atoms and a carbon atom of the dithiocarboxylato group are all coordinated to a central metal.

The C–S bonds (1.793(5), 1.786(7) Å) in **2** are the longest observed in dithiocarboxylato complexes.[5–7] This can be attributed to a reduced π-bonding interaction in these bonds caused by adopting the above-mentioned unique coordination mode. The Fe–S bond lengths are in the normal range for those of iron dithiocarboxylato complexes.

The ^{1}H NMR spectrum of **2** shows four nonequivalent methyl signals and the AB pattern signal of one methylene group. The ^{13}C NMR spectrum of **2** (in C_6D_6) also shows four methyl signals and five ring carbon signals. The methylene signal is observed at 45.6 ppm. The signal at 129.7 ppm can be assigned to the carbon of the S_2C portion. This signal appears at much higher field than the corresponding signals of other complexes containing a dithiocarboxylato ligand such as (C_5H_5)(Ph_3P)Ru(η^2-S_2CC_2Ph) (211.9 ppm ($CDCl_3$)).[6] The high-field shift of the S_2C signal of **2** can be reasonably explained by the enhanced sp^3 character of the carbon as well as the electronic effect of the metal directly bound to it. In fact, complex **5**, having a coordination mode of the S_2C portion similar to that for **2**, shows a signal for the S_2C portion at a similar high field (150.6 ppm ($CDCl_3$)).[5]

Complex **2** shows four ^{13}C signals in the carbonyl region, i.e. two sharp signals at 212.4 and 214.4 ppm and two broad signals at 211.2 and 212.5 ppm. The sharp signals are assigned to the two carbonyls attached to Fe(1), while the broad signals can be assigned to the two sets of three carbonyls bound to Fe(2) and Fe(3). The broadness of the latter signals indicates that three carbonyls on each metal are exchanging on the NMR time scale.

The ^{1}H NMR spectrum of compound **3** shows two methyl signals and one methylene signal at 0.99, 1.32, and 3.58 ppm, respectively. In the ^{13}C NMR spectrum of **3**, besides the signals for the C_5Me_4 portion, the signals for the exo methylene, carbonyl ligands, and the S_2C group appear at 50.3, 213.7, and 259.6 ppm, respectively. The mass spectrum of **3** clearly shows the parent peak at *m/z* 322 and the fragment peaks for successive loss of two carbonyls.

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These data are consistent with the proposed structure of **3**.

A plausible mechanism for the formation of **2** is illustrated in Scheme 1. In the previous paper, we reported that one of the CO groups of the $Fe(CO)_4$ part of **1** is readily replaced by a phosphine under mild conditions.[2] Therefore, in the present reaction, the first step can be also the replacement of the CO by a donor ligand, i.e. the solvent CS_2. Subsequent migration of the methylene carbon from the metal center onto the carbon of CS_2 gives the intermediate B. A similar migration of an organic group is known for a few ruthenium complexes.[5b,6] The species B then rearranges to C, probably to reduce strain in the molecule. Finally, the disproportionation of C, including the transfer of a $Fe(CO)_3$ unit, results in the formation of **2** and **3**.

Supplementary Material Available: Listings of crystal data, atomic coordinates, thermal parameters, interatomic distances, and bond angles for **2** and a figure giving the ^1H NMR spectrum for **3** (10 pages). Ordering information is given on any current masthead page.

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