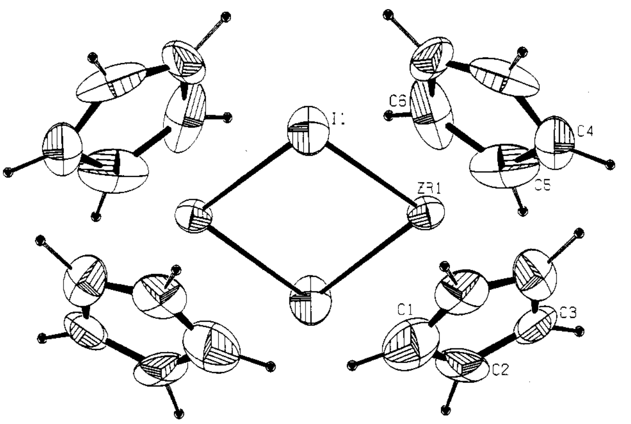

Figure 1. Molecular structure of $[Cp_2ZrI]_2$ showing thermal ellipsoids drawn at 50% level probability. Selected bond lengths (Å) and angles (deg) (estimated standard deviation in parentheses): Zr(1)–I(1) = 2.916 (1); I(1)–Zr(1)–I(1A) = 102.03 (3); Zr(1)–I(1)–Zr(1A) = 77.97 (3); Cp^1–Zr(1)–Cp^2 = 115.68 (3); Zr(1)···Zr(1A) = 3.669 (2).

experiments) as the only fulvalene-containing product. Considerable amounts of Cp'_2ZrCl_2 (35%, by NMR) remain unreacted, and new signals tentatively assigned to "Cp'_2Zr" have also been observed.[12]

This result clearly indicates that the fulvalene ligand originates only from the two cyclopentadienyl rings of the $Cp_2Zr(PMe_3)_2$ molecule. On the other hand, it is obvious that the bridging chlorine atoms of the complex **1** are provided by Cp'_2ZrCl_2. However, we were unable to understand why considerable amounts of unreacted Cp'_2ZrCl_2 invariably were present in the reaction mixtures, in spite of our effort to adjust the stoichiometry. In order to better clarify the role played by Cp'_2ZrCl_2 in this respect, we have carried out a comproportionation reaction between Cp_2ZrI_2 and $Cp_2Zr(PMe_3)_2$ in toluene. The reaction proceeds at room temperature, forming a deep purple solution. When the reaction progress is monitored by ^1H NMR, the disappearance of the starting materials is observed along with the formation of the fulvalene-bridged $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}I)]_2$[8a] and a growing narrow singlet at 4.97 ppm in the ^1H NMR spectrum [45% considering the singlet belonging to a bis(cyclopentadienyl) moiety]. The resulting solution was concentrated to a small volume, yielding black greenish[9] crystals (25%) upon cooling to −30 °C. The fulvalene-free compound showed the presence of a singlet at 4.97 ppm in the ^1H NMR spectrum (300 MHz) and a doublet at 102.04 ppm in the ^{13}C NMR spectrum (75 MHz). Analytical data were consistent with the formulation $[Cp_2ZrI]_2$ (**5**).

The structure of the molecule has been demonstrated by an X-ray diffraction analysis.[10] The unit-cell contains two discrete dimeric units, with the usually bent Cp_2Zr moieties linked by two bridging iodine atoms (Figure 1). The value of the intermetallic distance [3.669 (2) Å] is similar to those found in $[Cp_2Zr(\mu\text{-}PMe_2)]_2$[4] and $[Cp_2Zr(\mu\text{-}Cl)][Cp_2Zr(\mu\text{-}PMe_3)]$,[4] excluding once more the presence of a Zr–Zr bond. All the bond distances and angles are normal.

By analogy with $[ZrCl_3(PR_3)_2]_2$ complexes,[3a,d] $[Cp_2ZrI]_2$ is thermally unstable. It slowly disproportionates in solution at room temperature to Cp_2ZrI_2 and "Cp_2Zr".[12] Full decomposition can be achieved within few hours at 100 °C. This result tentatively suggests that the formation of Cp_2ZrCl_2 and "Cp_2Zr", observed in the comproportionation with Cp_2ZrCl_2, might be ascribed to the intermediate formation of the elusive $[Cp_2ZrCl]_2$. A higher thermal instability possibly might be responsible for the failure to characterize this species.[13] Further attempts to prepare $[Cp_2ZrCl]_2$ by the reaction between $[ZrCl_3(PR_3)_2]_2$ and CpNa in either ether or toluene at low temperature (−80/−30 °C) led only to mixtures of Cp_2ZrCl_2 and $Cp_2Zr(PR_3)_2$.

A full investigation on the reactivity of $[Cp_2ZrI]_2$ is in progress at the moment.

Supplementary Material Available: Tables of crystal data, anisotropic thermal parameters, atomic coordinates, bond lengths, bond angles, and torsion angles (8 pages); a listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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[9] Complex **5** is a deep red-purple solid. The emerald-green appearance of crystalline samples is a common feature for red Zr(III) derivatives.[3c,4]

[10] Crystal data: deep purple prism; crystal size (mm), 0.14 × 0.30 × 0.06; tetragonal; space group $P4_2nm$ (No. 102); a = 8.500 (3) Å, c = 13.774 (1) Å; Z = 2; V = 995.2 (5) $Å^3$; d(calcd) = 2.325 g cm^{-3}, μ(Mo) = 41.0 cm^{-1}; $F(000)$ = 652; scan mode = $\omega/2\theta$; scan width = 0.85 + 0.35 tan θ; T = 298 K; measured reflections 4178, range of hkl = h, $-10 \rightarrow 10$, k $0 \rightarrow 10$, l, $-16 \rightarrow 16$ ($2\theta_{max}$ = 52°); number of unique reflections, 561; number of reflections used in analysis, 522 [$I > 2.5\sigma(I)$]; structure solved by heavy-atom method; all the non-hydrogen atom positions were located and refined anisotropically; the carbon atoms of the cyclopentadienyl rings showed quite large thermal parameters probably due to libration motions as a common features for the complexes having this type of structure;[11] hydrogen atom positions were calculated and refined in the riding mode; number of variables 61; R = 0.026; R_w = 0.031, GOF = 1.806; $\omega = 1/[\sigma^2]$; largest remaining peak, −0.58, 0.80 e/$Å^3$; a final difference Fourier map did not show any significant residual feature; largest shift/esd, final cycle, 0.313.

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[12] Broad and undiagnostic signals have been reported for "Cp_2Zr".[8a] In our experiments "Cp_2Zr" showed a clean and well-solved NMR spectrum [^1H NMR (C_6D_6, δ (ppm)): "Cp_2Zr", 5.95 (s), 5.62 (s), 5.07 (pseudo-t), 4.33 (pseudo-t); "Cp'_2Zr", 5.67 (m), 1.91 (m)]. However, attempts to isolate this species were unsuccessful so far, and the structure remains not defined.

[13] Both green[13a] and red[13b–d] colors have been claimed for $[Cp_2ZrCl]_2$. (a) Fochi, G.; Guidi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1984**, 1253. (b) Cuenca, T.; Royo, P. *J. Organomet. Chem.* **1985**, *295*, 159. (c) Cuenca, T.; Royo, P. *J. Organomet. Chem.* **1985**, *293*, 61. (d) Samuel, E.; Guery, D.; Vedel, J.; Basile, F. *Organometallics* **1985**, *4*, 1073.

Isolation and X-ray Structure of an Intermediate in the Reaction of $(\mu\text{-}S)_2Fe_2(CO)_6$ with Thiolates: The $[(\mu\text{-}S)(\mu\text{-}S_2\text{-}t\text{-}Bu)Fe_2(CO)_6]^-$ Ion

Xintao Wu,[1] K. S. Bose, E. Sinn, and B. A. Averill*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

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Summary: Reaction of $(\mu\text{-}S_2)Fe_2(CO)_6$ (**1**) with 1 equiv of thiolate RS^- (R = Ph, $PhCH_2$, *i*-Pr) results in formation of the $[Fe_4S_4(CO)_{12}]^{2-}$ ion (**2**) containing two $[(\mu\text{-}S)_2Fe_2(CO)_6]^-$ units linked by a disulfide bond. Use of *t*-BuS^- results instead in a new green mixed disulfide, the $[(\mu\text{-}S)(\mu\text{-}S_2\text{-}t\text{-}Bu)Fe_2(CO)_6]^-$ ion (**3**), the structure of which has been determined as the Ph_4As^+ salt. These results suggest that similar mixed disulfides are intermediates in the reaction of thiolates with **1** to produce **2**.

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[1] Current address: Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, People's Republic of China.

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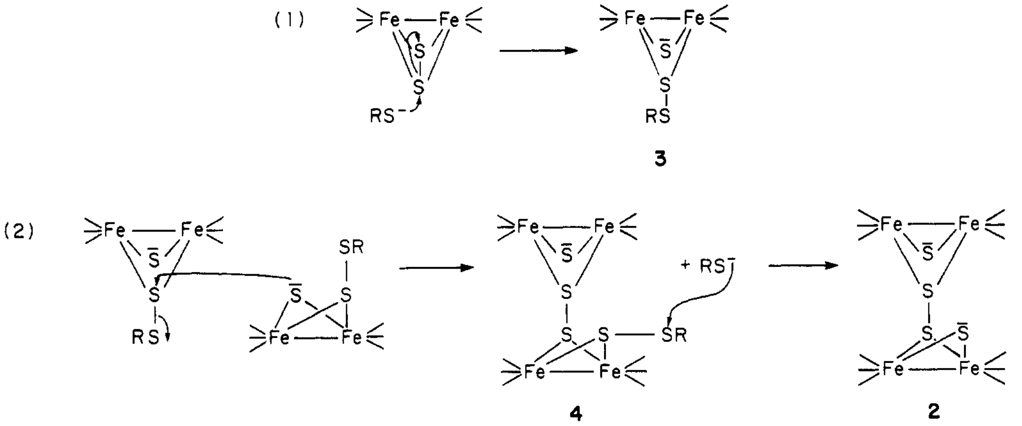
Scheme I



The chemistry of (μ-dithio)bis(tricarbonyl)iron ((μ-S_2)-$Fe_2(CO)_6$, 1)[2,3] has been of substantial recent interest. Seyferth et al.[4] have demonstrated that the S_2^{2-} unit of 1 exhibits reactivity comparable to an organic disulfide, in that reduction produces a dianion that behaves as a typical dithiolate, undergoing alkylation,[4-6] protonation,[6,7] metalation,[4,6-9] and olefin addition[10] reactions. In addition, 1 reacts with transition metals in low oxidation states via an oxidative addition reaction,[11-14] producing a variety of novel heterometallic sulfide-bridged clusters. We have shown[15] that a presumed intermediate in the formation of the $[(\mu\text{-}S)_2Fe_2(CO)_6]^{2-}$ ion, namely, $[(\mu\text{-}S)(\mu\text{-}SH)Fe_2(CO)_6]^-$, spontaneously dimerizes to form the $[Fe_4S_4(CO)_{12}]^{2-}$ ion (2), containing an *interdimer* disulfide bond similar to that in the $(PhS)Fe_2(CO)_6S_2Fe_2(CO)_6(SPh)$ molecule recently reported by Seyferth et al.[16] We report herein that 2 is also formed readily by reaction of 1 with stoichiometric amounts of thiolate and that the sterically hindered thiolate *t*-BuS⁻ permits the isolation and structure determination of a mixed disulfide intermediate, the $[(\mu\text{-}S)(\mu\text{-}S_2\text{-}t\text{-}Bu)Fe_2(CO)_6]^-$ ion (3).

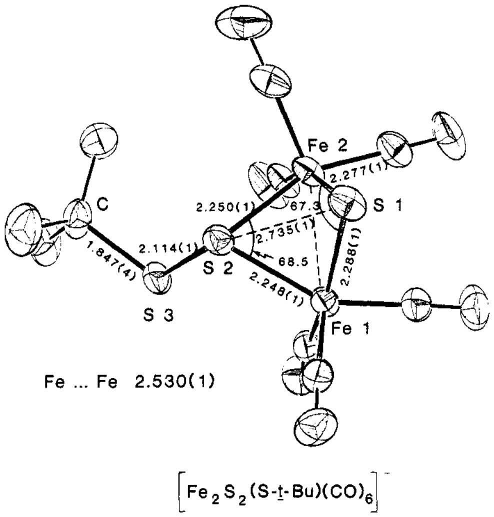


Figure 1. Structure of the $[Fe_2S(S_2\text{-}t\text{-}Bu)(CO)_6]^-$ ion, showing the atomic labeling scheme and selected distances and angles.

Addition of 1 equiv of LiSR (R = Ph, $PhCH_2$, or *i*-Pr; prepared from RSH plus 1 equiv of *n*-BuLi in THF) to $(\mu\text{-}S)_2Fe_2(CO)_6$ in THF or *i*-PrOH at room temperature with stirring followed after 1 h by addition of 1.3 equiv of $Ph_4As^+Cl^-$ in *i*-PrOH and cooling to −20 °C overnight produces deep green needle-shaped crystals of $(Ph_4As)_2[Fe_4S_4(CO)_{12}]$, identified by its crystal morphology and optical and IR spectra, in 40–60% yield. The Et_4N^+ salt was also isolated in pure form[17] in 40% yield by addition of $Et_4N^+Br^-$ (3 equiv) to the $Fe_2S_2(CO)_6$/LiSPh reaction mixture and cooling to −20 °C. Use of LiS-*t*-Bu in an analogous procedure results in dark green crystals of a new compound,[18] identified by elemental analysis,[17] ^{1}H NMR spectrum,[18] and X-ray structure determination[19] as the

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(17) Anal. Calcd for $(Et_4N)_2Fe_4S_4(CO)_{12}$ ($C_{28}H_{40}Fe_4N_2O_{12}S_4$): C, 35.47; H, 4.25; N, 2.95. Found: C, 35.72; H, 4.17; N, 2.99. Calcd for $(Ph_4As)_2[Fe_2S(S_2\text{-}t\text{-}Bu)(CO)_6]$ ($C_{34}H_{30}AsFe_2O_6S_3$): C, 50.00; H, 3.58; As, 9.18; Fe, 13.68; S, 11.78. Found: C, 50.85; H, 4.01, As, 9.93; Fe, 13.47; S, 17.22.

(18) Preparation of (Ph_4As)**3**: A 1.0 M solution of LiS-*t*-Bu (0.58 mL) in THF was added slowly under N_2 to 200 mg of $Fe_2S_2(CO)_6$ (0.58 mmol) in 15 mL of *i*-PrOH, producing a dark green solution. Addition of $Ph_4As^+Cl^-$ (300 mg) in 7 mL of *i*-PrOH, followed by cooling to −20 °C overnight, gave dark green crystals of analytically pure[17] (Ph_4As)**3** in 86% yield. IR spectrum (MeCN): ν_{CO} 2041 (m), 1999 (vs), 1959 (s), 1950 (s) cm^{-1}. Electronic spectrum (DMF): λ (ϵ) 572 nm (3370 M^{-1} cm^{-1}), 410 (sh), 328 (13 250). ^{1}H NMR spectrum (CD_3CN): δ 7.68 (m, 20, *Ph*$_4$As$^+$), 1.37 (s, 9, *t-Bu*) versus TMS.

(19) Measurements were performed on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The θ–2θ scan technique was used as previously described[20a] to record intensities for all nonequivalent reflections with $10 < 2\theta < 50°$. Intensities were corrected for Lorentz polarization effects and for absorption. A total of 3807 reflections with $F_o^2 > 3\sigma(F_o^2)$[20b] were used in the refinement. The crystal used was an irregular slab with dimensions 0.325 mm × 0.49 mm × 0.10 mm. (Ph_4As)**3** crystallizes in space group $P1$ with $a = 11.398$ (5) Å, $b = 13.109$ (6) Å, $c = 14.316$ (6) Å, $\alpha = 102.14°$, $\beta = 109.11°$, $\gamma = 106.03°$, and $Z = 2$. Heavy atoms were located by a three-dimensional Patterson synthesis, while remaining non-hydrogen atoms were located by Fourier syntheses. Full-matrix least-squares refinement[20a] was carried out with anisotropic temperature factors for non-hydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinement for three cycles and then held fixed. Final refinement converged at $R = 5.1\%$ and $R_w = 6.0\%$.

Ph$_4$As$^+$ salt of the $[(\mu\text{-S})(\mu\text{-S}_2\text{-}t\text{-Bu})\text{Fe}_2(\text{CO})_6]^-$ ion (**3**). The compound is air-stable for brief periods in the solid state and is stable in solution in aprotic solvents room temperature for prolonged periods in the absence of oxygen.

The crystal structure of the Ph$_4$As$^+$ salt of **3** shows that the anion contains a $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6$ unit linked via a disulfide bond to a *t*-BuS unit in a pseudoequatorial fashion[21] (e-linked[9]). Selected distances and angles are given in Figure 1. The $(\mu\text{-S})_2\text{Fe}(\text{CO})_6$ unit has a conformation similar to that in $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$,[22] $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$,[23] $(\mu\text{-RS})(\mu\text{-RHgS})\text{Fe}_2(\text{CO})_6$,[9] $[\text{Fe}_4\text{S}_4(\text{CO})_{12}]^{2-}$,[15] and $(\mu\text{-PhS})\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6(\mu\text{-SPh})$,[16] with a dihedral angle of 88.91° between the FeS$_2$ planes. Although a number of examples of both η^1-[24] and η^2-coordinated[25] persulfide units are now known, there appear to be only two crystallographically characterized examples of bridging persulfides analogous to that in **3**, namely, $\{[(\text{C}_5\text{H}_5)\text{Cr}(\text{NO})]_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-S}_2\text{-}t\text{-Bu})\}$[26] (**4**) and $[\text{Mo}_2(\text{NTol})_2(\text{S}_2\text{P}(\text{OEt})_2)_2\text{S}(\text{O}_2\text{CMe})(\text{SSEt})]$[27] (**5**). The S–S bonds in **4** and **5**, at 2.076 (4) and 2.068 (2) Å, respectively, are only marginally shorter than that in **3**, and the M–S–M angles at the bridging persulfide are ca. 10° (**4**) and 2° (**5**) larger than that in **3**. As found for **2**, the iron bonds to the disulfide sulfur (S2) in **3** are actually 0.03–0.04 Å shorter than those to the bridging sulfide (S1). The disulfide bond (S2-S3) in **3** is ca. 0.05 Å shorter than in **2**, approaching a normal S–S single bond value[27] (as seen in **4**[26]). This is not, however, accompanied by a compensating increase in the "nonbonded" S1···S2 distance, which is actually 0.04 Å less in **3** than in **2** and is thus well within the range reported for S···S bonding interactions.[28] The long S2–S3 and short S1···S2 distances in **3** are consistent with a delocalized bonding description involving all three sulfur atoms, as originally suggested for **2**[15] and supported by recent theoretical calculations.[29]

Compound **3** must arise by nucleophilic attack of RS$^-$ on the bridging S$_2^{2-}$ unit of **1** (Scheme I, reaction 1), in a reaction analogous to that proposed[4] for the reaction of hydride and alkyllithium reagents with **1** to produce $[(\mu\text{-S})(\mu\text{-SH})\text{Fe}_2(\text{CO})_6]^-$ and $[(\mu\text{-S})(\mu\text{-SR})\text{Fe}_2(\text{CO})_6]^-$, respectively. We postulate that **3** is not stable for most thiolates and spontaneously dimerizes to form **2**, presumably via intermediate **4**, with elimination of RSSR as shown in Scheme I, reaction 2. The fact that the reaction stops at **3** for R = *t*-Bu must be due to steric hindrance of nucleophilic attack by a second molecule of **3**; electronic factors should most favor formation of **2** with *t*-BuS$^-$, since it is the strongest reductant of the thiolates examined. Compound **3** is stable both in solution as well as in the solid state, differing from **2** in the former respect; thus it may prove to be an even more convenient precursor to the $[(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6]^{2-}$ dianion than **2** and a useful reagent for cluster syntheses.

Acknowledgment. This research was supported by grants from the U.S. Department of Agriculture Competitive Research Grants Office (82-CRCR-1-1123 and 86-CRCR-1-2033).

Supplementary Material Available: Tables of atomic coordinates, interatomic distances and angles, and thermal parameters (5 pages); a listing of calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

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A Double Intramolecular Ring Metalation: Formation, Spectroscopic Characterization, and Molecular Structure of $(\text{C}_5\text{Me}_3(\text{CH}_2)_2)\text{Ta}(\text{H})_2(\text{PMe}_3)_2$

Steven T. Carter,[1a] William Clegg,[1b]
Vernon C. Gibson,*,[1c] Terence P. Kee,[1c] and
Robert D. Sanner[1a,d]

Department of Chemistry
George M. Bateman Physical Sciences Centre
Arizona State University, Tempe, Arizona 85287
Department of Chemistry
University Science Laboratories, South Road
Durham DH1 3LE, U.K., and
Department of Inorganic Chemistry, The University
Newcastle upon Tyne NE1 7RU, U.K.

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Summary: Treatment of (C$_5$Me$_5$)TaCl$_4$ with sodium amalgam in THF solution containing PMe$_3$ gives rise to the compound $(\text{C}_5\text{Me}_3(\text{CH}_2)_2)\text{Ta}(\text{H})_2(\text{PMe}_3)_2$ (**1**), in which two ring methyl C–H bonds have been cleaved. NMR and X-ray crystallographic studies show that the abstracted hydrogens remain bound to the metal and the resulting ring methylene groups are located on adjacent ring-carbon atoms, being best described as sp^2, olefin-type CH$_2$ groups. Migration of the metal-bound hydrogens back to the C$_5$Me$_3$(CH$_2$)$_2$ ligand is shown by the reaction of **1** with CO affording (C$_5$Me$_5$)Ta(CO)$_2$(PMe$_3$)$_2$.

The importance of the pentamethylcyclopentadienyl ligand (η^5-C$_5$Me$_5$ or Cp*) in contemporary organometallic chemistry coupled with recent interest in C–H activation[2] and the reactivity of metal–hydrocarbyl fragments[3] has led

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(1) (a) Arizona State University. (b) University of Newcastle upon Tyne, U.K. (c) University of Durham, U.K. (d) Present address: Lawrence Livermore National Laboratory, Livermore, CA 94550.

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