



## Note

# Fe(CO)<sub>5</sub> promoted C–S bond activation and formation of an unusual C<sub>2</sub>S<sub>3</sub> ligand in [{Fe<sub>2</sub>(CO)<sub>6</sub>]<sub>2</sub>(μ-C<sub>2</sub>S<sub>3</sub>)}

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## ABSTRACT

Photolysis of a hexane solution containing Fe(CO)<sub>5</sub> and CS<sub>2</sub> leads to desulfurization and formation of a novel cluster [{Fe<sub>2</sub>(CO)<sub>6</sub>]<sub>2</sub>(μ-C<sub>2</sub>S<sub>3</sub>)} (**1**). Its molecular structure was determined by single crystal X-ray diffraction methods and shown to consist of two distinct Fe<sub>2</sub>(CO)<sub>6</sub> units linked by an unusual C<sub>2</sub>S<sub>3</sub> unit.

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## 1. Introduction

The activation and cleavage of selected bonds of small molecules by transition metal complexes is one of the challenging subjects of recent research. CS<sub>2</sub> has been shown to undergo a variety of reactions with transition metals, including insertion [1,2] and disproportionation [3–5], and there is a growing interest in the activation of CS<sub>2</sub> from catalytic and biological points of view. Cleavage of both C=S bonds of CS<sub>2</sub> is predicted to be exothermic process [6]. The cleavage of the C–S bonds is often observed in various transition metal complexes [7–12] in which chemistry has been explored for the hydrosulfurization of fossil products. In these complexes, the S<sup>2-</sup> ion derived from the C–S bond scission functions as a bridging ligand to link metal ions and metal cluster fragments and is generally of use in various cluster growth processes. An unusual CS<sub>2</sub> elimination and C–S bond cleavage has been observed in the reaction of [Zn(dmpzdtc)<sub>2</sub>] (dmpzdtc = 3,5-dimethylpyrazole-1-dithiocarboxylate) in MeCN and pyridine to form the cyclic octanuclear zinc sulfide complex[Zn<sub>4</sub>(μ-dmpz)<sub>5</sub>(μ-OH)(μ<sub>3</sub>-S)(py)<sub>2</sub>·py (dmpz = 3,5-dimethylpyrazole) [13]. In our previous studies, we have observed the insertion of CS<sub>2</sub> into Mo–acetylide bond to give complexes [(L)(Mo(CO)<sub>2</sub>(η<sup>2</sup>-S<sub>2</sub>CC≡CPh)] (L = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> and L = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) containing η<sup>2</sup>-S<sub>2</sub>C–C≡CPh and η<sup>3</sup>-S<sub>2</sub>C–C≡CPh ligands [1]. We have also observed the coupling of CS<sub>2</sub> with two ferrocene-

nylacetylene molecules leading to formation of 3,5-dithia-4-ethynylferrocenylcyclopentene ligand bonded with Fe<sub>2</sub>(CO)<sub>6</sub> moiety in a η<sup>1</sup>:η<sup>2</sup>:η<sup>1</sup>:η<sup>1</sup> fashion [2]. In this paper, we report the photochemical reaction of iron pentacarbonyl and CS<sub>2</sub> under inert atmosphere at 0 °C leading to the formation of a complex containing an unusual C<sub>2</sub>S<sub>3</sub> ligand.

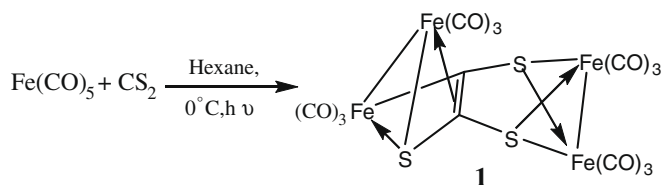
## 2. Results and discussion

When a solution of Fe(CO)<sub>5</sub> and CS<sub>2</sub> in hexane was photolyzed for 30 min at 0 °C, the novel cluster [{Fe<sub>2</sub>(CO)<sub>6</sub>]<sub>2</sub>(μ-C<sub>2</sub>S<sub>3</sub>)} (**1**) (10%) was isolated after chromatographic work-up (Scheme 1), along with known Fe<sub>3</sub>S<sub>2</sub>(CO)<sub>9</sub> (9%) and Fe<sub>2</sub>S<sub>2</sub>(CO)<sub>6</sub> (9%). The yield of **1** did not improve when CS<sub>2</sub> was used as the solvent in the photolysis reaction. In the thermolysis, compound **1** decomposes at 110 °C and did not form any Fe<sub>2</sub>S<sub>2</sub>(CO)<sub>6</sub>. Mass spectrum of **1** shows molecular ion peaks centered at *m/z* 679.6 and its infrared spectrum confirms the presence of terminally bonded carbonyls.

The molecular structure of **1** (Fig. 1) as established by single crystal X-ray diffraction methods, consists of two Fe<sub>2</sub>(CO)<sub>6</sub> units connected by a bridging C<sub>2</sub>S<sub>3</sub> unit such that the C<sub>2</sub>S<sub>2</sub> part of this ligand bonds to one Fe<sub>2</sub>(CO)<sub>6</sub> unit to complete the characteristic Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>(C=C) unit observed previously in complexes [Fe<sub>2</sub>(CO)<sub>6</sub>E<sub>2</sub>(HC=CPh)] (E = S, Se, Te) [14–20]. The third sulfur atom of the C<sub>2</sub>S<sub>3</sub> unit is unique in being the only sulfur atom to bond to the remaining two iron atoms of the cluster. A π-bond between the C=C double bond of the C<sub>2</sub>S<sub>3</sub> unit and the remaining iron atom completes the cluster framework. Consequently, an unusual ferrathiacyclobutene ring is formed, which is capped by a Fe(CO)<sub>3</sub>

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**Scheme 1.** Formation of  $[\{\text{Fe}_2(\text{CO})_6\}_2(\mu\text{-C}_2\text{S}_3)]$ .

group. Assuming that each S atom is a four-electron donor, then the 18-electron count around each iron atom is satisfied.

Within the ferrathiacyclobutene ring of **1**, the C(13)–C(14) bond length of 1.333(7) Å is shorter than the respective C–C bond distances in the range of 1.40–1.46 Å in the complexes;  $[\text{Fe}_2(\text{CO})_{6-n}\{\text{P}(\text{OMe})\}_n\{\mu\text{-}(\text{CF}_3)_2\text{C}(\text{CF}_3)\text{S}\}]$  ( $n = 0, 1, 3$ ) [21],  $[\{\text{Fe}(\text{CO})_3\}_2\{\mu\text{-S}(\text{Me})\text{C}(\text{CF}_3)\text{C}(\text{CMeN}(\text{CH}_2)_2\text{NMe})\}]$ ,  $[\text{Fe}(\text{CO})_3\}_2\{\mu\text{-SMe}\}\text{C}(\text{CF}_3)\text{C}(\text{C}(\text{NMe})_2)\}]$  [22];  $[\text{Fe}_2(\text{CO})_5\text{PPh}_3(\text{CPh})\text{C}(\text{Ph})\text{S}]$  [23], *cis*- $[\text{Fe}_2(\text{CO})_4\{\mu\text{-SC}(\text{Ph})\text{CH}\}(\mu\text{-dppm})]$  [24],  $[\{\mu\text{-CF}_3\text{CC}(\text{CF}_3)\text{S}\}]\{\text{Fe}(\text{CO})_3\}_2]$  [25] and similar to that of 1.335 (7) and 1.37 (3) Å, respectively in the compounds  $[\{\text{Fe}(\text{CO})_3\}_2(\mu\text{-SC}(\text{NET})_2)]$  [26] and  $[\{\text{Fe}_2(\text{CO})_4\text{-}\{\text{P}(\text{OMe})_3\}_2\{\mu\text{-}(\text{CF}_3)\text{CC}(\text{CF}_3)\text{S}\}]\}]$  [21]. The bond length Fe(4)–S(3) = 2.2358(18) Å matches well with the Fe–S bond distances in related complexes;  $[\text{Fe}_2(\text{CO})_5\text{PPh}_3(\text{CPh})\text{C}(\text{Ph})\text{S}]$  [23], *cis*- $[\text{Fe}_2(\text{CO})_4\{\mu\text{-SC}(\text{Ph})\text{CH}\}(\mu\text{-dppm})]$  [24] and  $[\{\mu\text{-CF}_3\text{CC}(\text{CF}_3)\text{S}\}]\{\text{Fe}(\text{CO})_3\}_2]$  [25]. The bond angles S(3)–C(13)–C(14) = 105.4 (5)° and C(13)–C(14)–Fe(3) = 103.4 (4)° are similar to the corresponding angles in the complex  $[\{\text{Fe}(\text{CO})_3\}_2(\mu\text{-S})_2\{\text{C}(\text{NET})_2\}]$  [26]. The  $\text{Fe}_2\text{S}_2$  butterfly opens to a somewhat lesser degree (S(2)–C(13)–C(14) = 121.4 (5)° and S(1)–C(14)–C(13) = 112.6 (5)° in **1**, as compared to other related  $\text{Fe}_2\text{S}_2$  containing complexes:  $[\text{Fe}_2(\text{CO})_6\{\text{PrN}=\text{C}(\text{S})\text{-}(\text{S})\text{C}(\text{H})\text{N}(\text{H})\text{Pr}\}]$  and  $[\text{Fe}_2(\text{CO})_6(\text{Et})_2\text{NC}(\text{S})=\text{S}(\text{C})\text{N}(\text{Et})_2]$  in which the corresponding S–C–C angles average

116° [26]. The bond distances of C(13)–Fe(4) = 2.051 (6) and C(14)–Fe(4) = 2.129 (6) Å and the bond angles Fe(4)–C(13)–C(14) = 74.6 (4)° and Fe(4)–C(14)–C(13) = 68.3 (3)° indicate that the capping iron atom Fe(4) is slightly tilted towards the carbon atom C(13) which is bonded to the unique S atom.

Although the exact mechanism of formation of **1** is not known, investigation of reactions of  $\text{Ru}(\text{CO})_5$ ,  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  with  $\text{CS}_2$  under similar reaction conditions do not yield analogs of **1**. Formally, two molecules of  $\text{CS}_2$  must react, with one of them formally undergoing the loss of a sulfur atom. Formation of **1** can therefore be thought of being formed as a result of coupling of one  $\text{CS}_2$  with a CS on a  $\text{Fe}_4$  cluster support. The lost sulfur atom is consumed by iron carbonyl fragments as evidenced by the isolation of  $\text{Fe}_3\text{S}_2(\text{CO})_9$  and  $\text{Fe}_2\text{S}_2(\text{CO})_6$  from the reaction mixture.

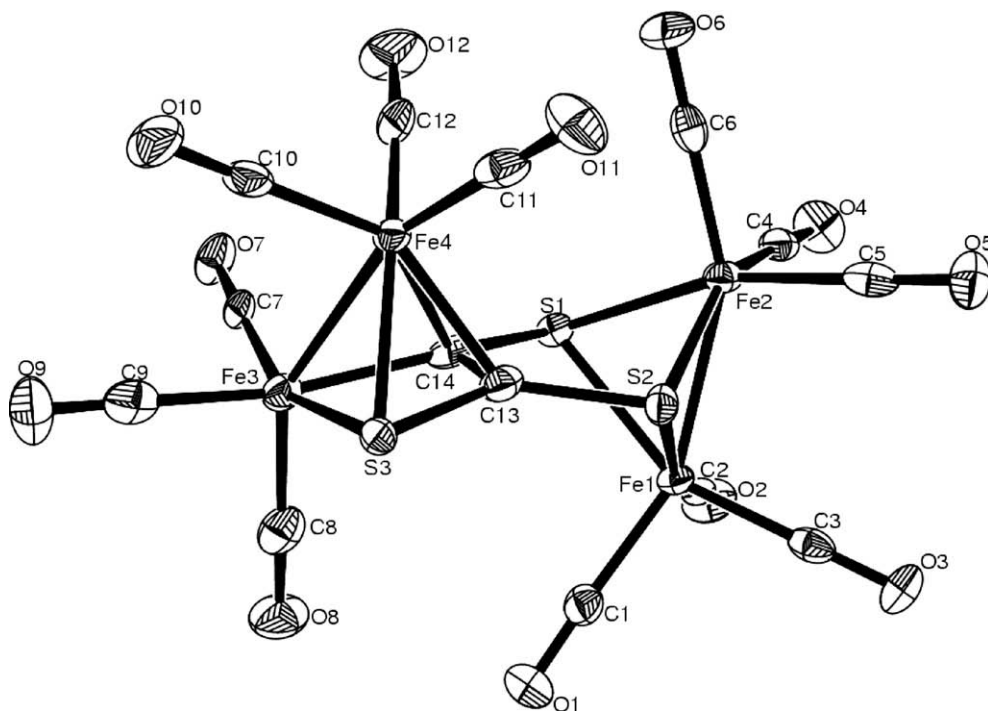
### 3. Conclusion

The low temperature photochemical reaction of  $\text{Fe}(\text{CO})_5$  and  $\text{CS}_2$  leads to desulfurization and formation of an unusual  $\text{C}_2\text{S}_3$  ligand containing a C=C double bond in the complex  $[\{\text{Fe}_2(\text{CO})_6\}_2(\mu\text{-C}_2\text{S}_3)]$ . Activation of C=S bond is selective for the reaction with  $\text{Fe}(\text{CO})_5$ . The unique  $\text{C}_2\text{S}_3$  ligand acts as a bridge between two  $\text{Fe}_2(\text{CO})_6$  units and forms an unusual ferrathiacyclobutene ring.

### 4. Experimental

#### 4.1. General procedure

All reactions and manipulations were performed using standard Schlenk line techniques under an inert atmosphere of pre-purified argon. Solvents were purified, dried, and distilled under an argon atmosphere prior to use. Infrared spectra were recorded on a Nicolet 380 FT-IR spectrometer as hexane solutions in 0.1 mm path



**Fig. 1.** ORTEP diagram of  $[\{\text{Fe}_2(\text{CO})_6\}_2(\mu\text{-C}_2\text{S}_3)]$  (**1**) with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): C(13)–C(14) = 1.333(7), S(3)–C(13) = 1.754(6), C(14)–Fe(3) = 1.978(6), Fe(3)–S(3) = 2.2699(17), Fe(4)–S(3) = 2.2358(18), Fe(4)–C(13) = 2.2051(6), Fe(4)–C(14) = 2.129(6), Fe(4)–C(13) = 2.051(6), Fe(4)–C(14) = 2.129(6); Fe(3)–S(3)–C(13) = 80.4 (2), C(13)–C(14)–Fe(3) = 103.4 (4), C(14)–Fe(3)–S(3) = 70.68 (7), Fe(4)–S(3)–C(13) = 60.4 (2), Fe(4)–S(3)–Fe(3) = 68.07 (5), Fe(4)–Fe(3)–C(14) = 54.81 (16), S(2)–C(13)–C(14) = 121.4 (5), C(13)–C(14)–S(1) = 112.6 (5), Fe(2)–S(1)–Fe(1) = 65.15 (5), Fe(2)–S(2)–Fe(1) = 65.83 (5), Fe(4)–C(13)–C(14) = 47.6(4) and Fe(4)–C(14)–C(13) = 68.3(3).

length NaCl cells. Iron pentacarbonyl and CS<sub>2</sub> were purchased from Fluka and SD Fine-Chem, respectively, and these were used without further purification. TLC plates were purchased from Merck (20 × 20 cm silica gel 60 F<sub>254</sub>). Photochemical reactions were carried out using double-walled quartz vessels and a 125 W immersion type mercury lamp operating at 366 nm, manufactured by Applied Photophysics Ltd. X-ray crystallographic data was collected from single-crystal (0.21 × 0.17 × 0.14 mm<sup>3</sup>) mounted on a Oxford Diffraction XCALIBUR-S CCD system equipped with graphite-monochromated Mo K $\alpha$  radiation (0.71070 Å). The data were collected by the  $\omega$ -2 $\theta$  scan mode, and absorption correction was applied by using Multi-Scan. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least squares against  $F^2$  using SHELXL-97 software [27]. *Crystal Data of 1*: C<sub>14</sub>Fe<sub>4</sub>S<sub>3</sub>O<sub>12</sub>;  $M = 679.72$ ; triclinic, space group  $P\bar{1}$ ;  $a = 6.5744(19)$  Å,  $b = 11.075(3)$  Å,  $c = 15.194(4)$  Å;  $\alpha = 102.54(2)^\circ$ ,  $\beta = 96.89(2)^\circ$ ,  $\gamma = 103.52(2)^\circ$ ;  $V = 1032.9(5)$  Å<sup>3</sup>;  $Z = 2$ ;  $D_c = 2.186$  Mg m<sup>-3</sup>; absorption coefficient 3.119 mm<sup>-1</sup>  $F(0\ 0\ 0) = 664$ ; Crystal size = 0.21 × 0.17 × 0.14 mm<sup>3</sup>; data collection 2.97° <  $\theta$  < 25.00°,  $-7 \leq h \leq 7$ ,  $-12 \leq k \leq 13$ ,  $-18 \leq l \leq 17$ ; reflections collected/unique 10116/3617; goodness-of-fit on  $F^2 = 1.025$ ; final  $R$  indices  $R_1 = 0.0517$  and  $wR_2 = 0.0758$  [ $I = 2\sigma(I)$ ], and  $R_1 = 0.0888$  and  $wR_2 = 0.0839$ ; maximum and minimum residual electron densities = 0.617 and  $-0.531$  e Å<sup>-3</sup>, respectively.

#### 4.2. Synthesis of $[\{\text{Fe}_2(\text{CO})_6\}_2(\mu\text{-C}_2\text{S}_3)]$ (**1**)

A hexane solution (60 mL) containing carbon disulfide (0.12 mL, 2 mmol) and iron pentacarbonyl (0.27 mL, 2 mmol) was photolyzed for 30 min at 0 °C. The solvent was removed in vacuo, the residue was dissolved in dichloromethane and subjected to chromatographic work-up using high performance silica gel TLC plates. Elution with hexane yielded the yellow compound  $[\text{Fe}_2(\text{CO})_6(\mu\text{-S})_2]$  (7 mg, 9%), maroon compound  $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})_2]$  (10 mg, 9%) and yellow compound (**1**)  $[\{\text{Fe}_2(\text{CO})_6\}_2(\mu\text{-C}_2\text{S}_3)]$  (15 mg, 10%). IR Data  $\nu$  (CO) cm<sup>-1</sup>: 2074 (s), 2054 (vs), 2047 (s), 2012 (vs) and 1959 (w); mass ( $m/z$ ): 679.6 [M], 651.5 [M-CO], 623.6 [M-2CO], 595.6 [M-3CO], 539.6 [M-5CO], M.P. 184–188 °C (decomposed).

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#### Appendix A. Supplementary material

CCDC 724619 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.05.023](https://doi.org/10.1016/j.jorganchem.2009.05.023).

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