

# A disulfide-bridged manganese carbonyl anion: synthesis, structure and reactivity of $[\text{Mn}_3(\text{CO})_{10}(\mu_3\text{-S}_2)_2]^-$

Richard D. Adams\*, Shaobin Miao

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208 USA

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## Abstract

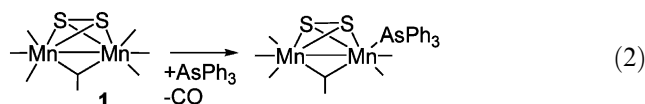
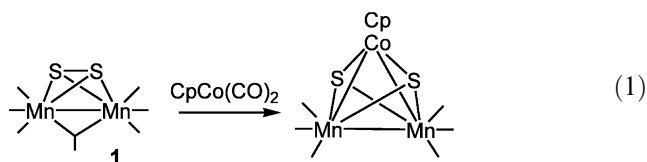
The reduction of  $\text{Mn}_2(\text{CO})_7(\mu\text{-S}_2)$ , (**1**) with sodium amalgam in THF provided the new monoanion  $[\text{Mn}_3(\text{CO})_{10}(\mu_3\text{-S}_2)_2]^-$ , (**3**) isolated in low yield as the  $[\text{Ph}_3\text{PMe}]$  salt. The reaction of  $\text{Mn}_4(\text{CO})_{15}(\mu_3\text{-S}_2)(\mu_4\text{-S}_2)$ , (**2**) with  $[\text{Ph}_3\text{PMe}]\text{I}$  provided the same salt  $[\text{Ph}_3\text{PMe}]$  [**3**] in a good yield, 68%. Anion **3** reacts  $[\text{CpFe}(\text{CO})_2(\text{acetone})]\text{BF}_4$  to yield the neutral mixed metal complex  $\text{CpFeMn}_3(\text{CO})_{12}(\mu_3\text{-S}_2)(\mu_4\text{-S}_2)$ , (**4**). The structures of [**3**] and **4** were determined by single crystal X-ray diffraction analyses. The core of the structure of **3** consists of two  $[\text{Mn}(\text{CO})_3]$  groups bridged by two disulfido ligands in a  $\mu_2\text{-}\eta^2$  fashion with an additional  $[\text{Mn}(\text{CO})_4]$  group that bridges the two disulfido ligands. The  $\text{CpFe}(\text{CO})_2$  group in **4** is bonded to a sulfur atom of one of the two disulfido ligands of the anionic grouping of **3**.

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**Keywords:** Manganese carbonyl; Cyclopentadienyliron; Sulfur; Disulfido ligand

## 1. Introduction

Chalcogen-containing transition metal carbonyl complexes have attracted much attention recently due to their versatile bonding modes and reactivities [1]. Compounds containing disulfido ligands are also of great interest [2]. Recently, we have been investigating the synthesis, structures and reactivities of manganese carbonyl compounds containing disulfido ligands including  $\text{Mn}_2(\text{CO})_7(\mu\text{-S}_2)$ , (**1**) [3] and  $\text{Mn}_4(\text{CO})_{15}(\mu_3\text{-S}_2)(\mu_4\text{-S}_2)$ , (**2**) [3,4]. Compound **1** exhibits a variety of interesting reactivities ranging from insertion of metal containing groups into the S–S bond of the disulfide

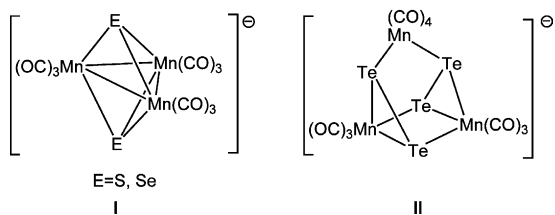


ligand eq. (1) [5] to ligand additions and substitutions at the manganese atoms, eq. (2) [6].

It has been shown that the chalcogen elements and their oxides can be used as convenient sources for the preparation of mixed-metal clusters with transition metal anions under suitable conditions [7]. The chalcogen–manganese anions  $[\text{Mn}_3(\text{CO})_9(\mu_3\text{-S}_2)]^-$  and  $[\text{Mn}_3(\text{CO})_9(\mu_3\text{-Se}_2)]^-$  (**I**) [7h] were obtained from the reaction of elemental sulfur and selenium with  $\text{Mn}_2(\text{CO})_{10}\text{-KOH}$  in a molar ratio of 2:1, respectively. The sulfur–manganese anion  $[\text{Mn}_3(\text{CO})_9(\mu_3\text{-S}_2)]^-$  was also isolated from the reaction between  $[\text{Mn}(\text{CO})_5]^-$  and 5-substituted 1,3,4-oxathiazol-2-one [8]. Interestingly, the unusual tellurium–manganese anion  $[\text{Mn}_3(\text{CO})_{10}(\mu_3\text{-Te}_2)_2]^-$  (**II**), [7i] which could be a precursor to cubane clusters, was obtained from the reaction  $\text{K}_2\text{TeO}_3$  with  $\text{Mn}_2(\text{CO})_{10}$  in a molar ratio of 2:1 in MeOH.

\* Corresponding author. Tel.: +1-803-777-7187; fax: +1-803-777-6781

E-mail address: [adams@mail.chem.sc.edu](mailto:adams@mail.chem.sc.edu) (R.D. Adams).



Here we describe the synthesis and structure of the new anionic bis-disulfido cluster  $[\text{Mn}_3(\text{CO})_{10}(\mu_3\text{-S}_2)]^-$  (**3**) and the product obtained from its reaction with  $[\text{CpFe}(\text{CO})_2(\text{acetone})]\text{BF}_4$ .

## 2. Experimental

### 2.1. General

All reactions were performed under a nitrogen atmosphere using Schlenk techniques. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Nicolet 5DXBO FTIR spectrophotometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Compounds **1**, **2** [**3**] and  $[\text{CpFe}(\text{CO})_2(\text{acetone})]\text{BF}_4$  [**9**] were prepared according to the published procedures. Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å  $F_{254}$  glass plates.

### 2.2. Synthesis of $[\text{Ph}_3\text{PMe}][\text{Mn}_3(\text{CO})_{10}(\mu_3\text{-S}_2)_2]$

#### 2.2.1. Method 1

Compound **1** (40 mg, 0.11 mmol) was dissolved in THF in a 50 ml three-neck round-bottom flask containing sodium-amalgam. The mixture was stirred overnight at room temperature (r.t.). The solution was filtered and the solvent was removed in vacuo. The residue was dissolved in MeOH (10 ml) and a methanol solution (5 ml) containing 30 mg of  $[\text{Ph}_3\text{PMe}]\text{Br}$  was added. The mixture was stirred for another 30 min at r.t. and evaporated to dryness under vacuum. The red residue was then extracted into THF, and filtered to remove the excess  $[\text{Ph}_3\text{PMe}]^+$  and  $\text{Na}^+$  salts and then evaporated to dryness in vacuo. This residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and hexane was then added. On cooling to  $-20^\circ\text{C}$ , red crystals  $[\text{Ph}_3\text{PMe}][\text{Mn}_3(\text{CO})_{10}(\mu_3\text{-S}_2)_2]$  (10 mg, 11%) formed. Spectral data: IR  $\nu_{\text{CO}}$  ( $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ): 2083(w), 2011(s), 1991(s), 1954(w), 1911(m). Anal. Calc. for  $\text{C}_{29}\text{H}_{18}\text{Mn}_3\text{O}_{10}\text{PS}_4$ : C, 40.95; H, 2.13. Found: C, 41.23; H, 2.29%.

#### 2.2.2. Method 2

$[\text{Ph}_3\text{PMe}]\text{I}$  (50 mg) was added to a solution of **2** (40 mg, 0.052 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 ml). The mixture solution was stirred at r.t. for 24 h. The solvent was

then removed in vacuo and the residue was separated by TLC on silica gel using 1:1 hexane |  $\text{CH}_2\text{Cl}_2$  solvent mixture to yield 30 mg of  $[\text{Ph}_3\text{PMe}]$  [**3**], 68% yield.

### 2.3. Synthesis of $\text{CpFeMn}_3(\text{CO})_{12}(\mu_3\text{-S}_2)(\mu_4\text{-S}_2)$ (**4**)

To a solution of  $[\text{Ph}_3\text{PMe}]$  [**3**] (40 mg, 0.047 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 ml) was added  $[\text{CpFe}(\text{CO})_2(\text{acetone})]\text{BF}_4$  in  $\text{CH}_2\text{Cl}_2$  (10 ml). The solution was stirred at r.t. for 24 h. The solvent was then removed in vacuo and the residue was separated by TLC on silica gel by using 1:1 hexane |  $\text{CH}_2\text{Cl}_2$  solvent mixture to yield 10 mg of  $\text{CpFeMn}_3(\text{CO})_{12}(\mu_3\text{-S}_2)(\mu_4\text{-S}_2)$ , 28% yield. Spectral data: IR  $\nu_{\text{CO}}$  ( $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ): 2092(m), 2063(m), 2028(s), 2018(s), 2007(s), 1976(m), 1940(m), 1909(w). Anal. Calc. for  $\text{C}_{17}\text{H}_5\text{FeMn}_3\text{O}_{12}\text{S}_4$ : C, 27.22; H, 0.67. Found: C, 27.07; H, 0.93%.

### 2.4. Crystallographic analysis

The red crystals of  $[\text{Ph}_3\text{PMe}]$  [**3**] and **4** suitable for diffraction analysis were obtained by slow evaporation of solvent from solutions in hexane | methylene chloride solvent mixtures at  $-20^\circ\text{C}$ . The data crystals of  $[\text{Ph}_3\text{PMe}]$  [**3**] and **4** were mounted by gluing onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using  $\text{M-K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The unit cells were initially determined based on reflections selected from a set of three scans measured in orthogonal wedges of reciprocal space. The raw data frames were integrated with the SAINT+ program using a narrow-frame integration algorithm. Corrections for the Lorentz and polarization effects were also applied by using the program SAINT. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied for each analysis by using the program SADABS. Crystal data, data collection parameters, and results of the analyses for compounds  $[\text{Ph}_3\text{PMe}]$  [**3**] and **4** are listed in Table 1. Both structures were solved by a combination direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries and were refined by using the riding model. Refinements were carried out on  $F^2$  by the method of full-matrix least squares by using the SHELXTL program library with neutral atom scattering factors [10].

## 3. Results and discussion

The reduction of the well known iron compound  $\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)$  yields the dianion  $[\text{Fe}_2(\text{CO})_6(\mu\text{-S})_2]^{2-}$  [**11**] that has proved to be a valuable reagent over the

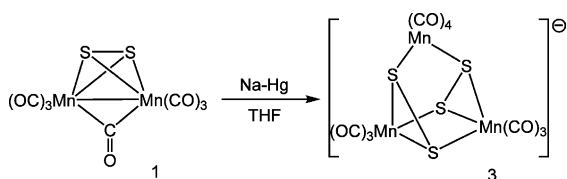
Table 1  
Crystallographic data for compounds [Ph<sub>3</sub>PMe] [3] and 4

Compound	[Ph <sub>3</sub> PMe] [3]	4
Empirical formula	C <sub>29</sub> H <sub>18</sub> Mn <sub>3</sub> O <sub>10</sub> PS <sub>4</sub>	C <sub>17</sub> H <sub>5</sub> Mn <sub>3</sub> FeO <sub>12</sub> S <sub>4</sub>
Formula weight	850.46	750.12
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.391(8)	9.3841(6)
<i>b</i> (Å)	11.969(9)	10.5030(7)
<i>c</i> (Å)	14.075(12)	13.7665(9)
$\alpha$ (°)	86.12(7)	85.0470(10)
$\beta$ (°)	72.56(8)	86.5530(10)
$\gamma$ (°)	88.10(7)	66.8480(10)
<i>V</i> (Å <sup>3</sup> )	1666(2)	1242.40(14)
<i>Z</i>	2	2
Temperature (K)	173(2)	296(2)
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.695	2.005
$\mu$ (Mo–K $\alpha$ ) (mm <sup>-1</sup> )	1.473	2.458
Number of observations ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	6955	5298
Number of parameters	425	334
Goodness of fit <sup>a</sup>	1.042	0.977
Maximum shift in final cycle	0.001	0.001
Residuals: <i>R</i> <sub>1</sub> ; <i>wR</i> <sub>2</sub> <sup>b</sup>	0.0335; 0.0803	0.0403; 0.1011
Absorption correction, max/min	SADABS, 1.000/ 0.898	SADABS, 1.000/ 0.828
Largest peak in difference map (e <sup>-</sup> /Å <sup>3</sup> )	0.623	0.576

<sup>a</sup>  $\text{GOF} = \left[ \sum |n_{\text{obs}} - n_{\text{calc}}|^2 / (n_{\text{data}} - n_{\text{vari}}) \right]^{1/2}$ .

<sup>b</sup>  $R_1 = \sum (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum |F_{\text{obs}}|$ ,  $wR_2 = \left\{ \sum [w(|F_{\text{obs}} - F_{\text{calc}}|)^2] \right\}^{1/2}$ ,  $w = 1/\sigma^2(F_{\text{obs}})$ .

years [2a]. Accordingly, we investigated the reduction of **1**. The reduction of **1** with sodium amalgam in THF provided the new cluster anion **3** isolated in low yield as the [Ph<sub>3</sub>PMe] salt, Scheme 1. This salt was characterized by IR spectroscopy and single crystal X-ray diffraction analysis. The infrared spectrum of [Ph<sub>3</sub>PMe] [3] shows five absorptions consistent with terminal carbonyl ligands only. The structure of the anion **3** is shown in Fig. 1. Selected bond distances and angles are listed in Table 2. The structure can be viewed as consisting of two [Mn(CO)<sub>3</sub>] groups bridged by two S<sub>2</sub> fragments in a  $\mu_2$ - $\eta^2$  fashion. Finally, the two disulfido ligands are bridged by a Mn(CO)<sub>4</sub> group. The anion **3** is structurally similar to that of [Mn<sub>3</sub>(CO)<sub>10</sub>( $\mu_3$ -Te<sub>2</sub>)<sub>2</sub>]<sup>-</sup> [7i] and CrFe<sub>2</sub>(CO)<sub>10</sub>( $\mu_3$ -Se<sub>2</sub>)<sub>2</sub> [12] and can be regarded as an inorganic analogue of the organic quadricyclane. The two S–S bonding distances (2.0745(17) and 2.080(2) Å) are similar to those found in **2**, S–S = 2.0771(13) and



Scheme 1.

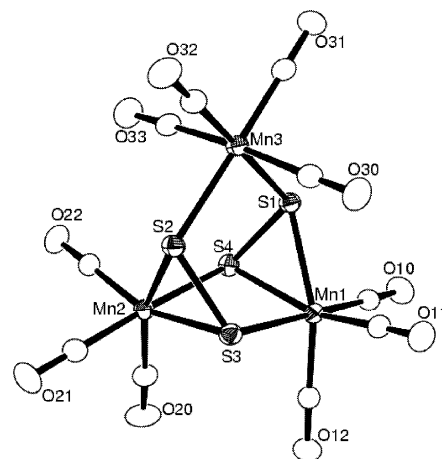


Fig. 1. An ORTEP diagram of the molecular structure of anion **3** showing 40% thermal ellipsoid probabilities.

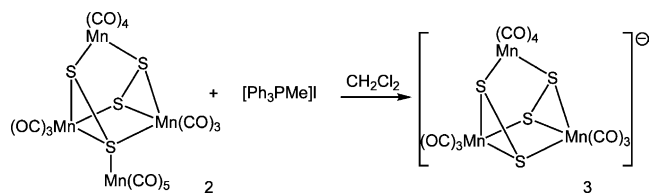
Table 2  
Selected intramolecular bond distances (Å) and angles (°) for [Ph<sub>3</sub>PMe][Mn<sub>3</sub>(CO)<sub>10</sub>( $\mu_3$ -S<sub>2</sub>)<sub>2</sub>]<sup>-</sup><sup>a</sup>

(a) Bond distances			
Mn(1)–S(1)	2.3316(19)		
Mn(1)–S(4)	2.355(3)		
Mn(1)–S(3)	2.382(2)		
Mn(2)–S(2)	2.339(2)		
Mn(2)–S(3)	2.364(3)		
Mn(2)–S(4)	2.3785(19)		
Mn(3)–S(1)	2.3520(19)		
Mn(3)–S(2)	2.3533(19)		
S(1)–S(4)	2.080(2)		
S(2)–S(3)	2.0752(17)		
C–O	1.144(3)(av)		
(b) Bond angles			
S(1)–Mn(1)–S(4)	52.68(7)	S(3)–S(2)–Mn(2)	64.44(7)
S(1)–Mn(1)–S(3)	93.48(6)	S(3)–S(2)–Mn(3)	112.88(6)
S(4)–Mn(1)–S(3)	84.36(7)	Mn(2)–S(2)–Mn(3)	118.80(7)
S(2)–Mn(2)–S(3)	52.36(6)	S(1)–S(4)–Mn(1)	63.09(7)
S(2)–Mn(2)–S(4)	92.47(7)	S(1)–S(4)–Mn(2)	112.48(7)
S(1)–Mn(3)–S(2)	89.21(7)	Mn(1)–S(4)–Mn(2)	94.01(7)
S(4)–S(1)–Mn(1)	64.23(7)	S(2)–S(3)–Mn(1)	63.20(7)
S(4)–S(1)–Mn(3)	112.67(7)	S(2)–S(3)–Mn(1)	111.31(6)
Mn(1)–S(1)–Mn(3)	117.80(6)	Mn(2)–S(3)–Mn(1)	93.69(7)
S(3)–Mn(2)–S(4)	84.23(7)		

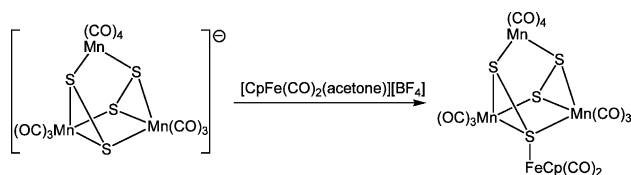
<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

2.0924(12) Å [4,5a], and the structurally related compound [(C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Ru<sub>2</sub>Rh(NCMe)( $\mu$ -S<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> (2.082(3) and 2.099(3) Å) [13]. The Mn–S bond distances (2.331(2)–2.382(2) Å) are similar to those in **2** (2.3098(10)–2.3817(9) Å). If each disulfido ligand is viewed as a six-electron donor in anion **3**, then each of the manganese atoms achieves an 18-electron configuration.

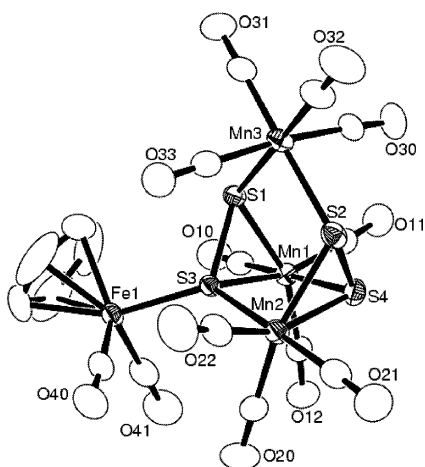
Upon seeing the close similarity of the structure of the anion **3** to that of the cluster of compound **2**, it was decided to attempt to obtain **3** from **2**, by cleaving the



Scheme 2.



Scheme 3.

Fig. 2. An ORTEP diagram of the molecular structure of **4** showing 40% thermal ellipsoid probabilities.

appended  $\text{Mn}(\text{CO})_5$  group with  $\text{I}^-$ . Indeed, the reaction of **2** with  $[\text{Ph}_3\text{PMe}]\text{I}$  in  $\text{CH}_2\text{Cl}_2$  provided the  $[\text{Ph}_3\text{PMe}]$  salt of the monoanion **3** in a much better yield 68%, Scheme 2.

$[\text{Ph}_3\text{PMe}]$  [**3**] is very stable and is unreactive toward reagents such as  $\text{MeI}$  and  $[\text{Mn}(\text{CO})_5(\text{CH}_3\text{CN})]\text{PF}_6$ ,  $[\text{Cu}(\text{NCMe})_4]\text{BF}_4$ ,  $[\text{Ph}_3\text{PAu}]\text{Cl}$  or even the activated species  $[\text{Ph}_3\text{PAu}]\text{BF}_4$  at room temperature. However, this cluster does react with the more reactive iron compound  $[\text{CpFe}(\text{CO})_2(\text{acetone})]\text{BF}_4$ .

The reaction of  $[\text{Ph}_3\text{PMe}]$  [**3**] with  $[\text{CpFe}(\text{CO})_2(\text{acetone})]\text{BF}_4$  in  $\text{CH}_2\text{Cl}_2$  yielded the cluster  $\text{CpFeMn}_3(\text{CO})_{12}(\mu_3\text{-S}_2)(\mu_4\text{-S}_2)$ , (**4**) in 28% yield, Scheme 3. Compound **4** was characterized by IR spectroscopy and single crystal X-ray diffraction analysis. The infrared spectrum of **4** shows several absorptions consistent with terminal carbonyl ligands only. A diagram of the molecular structure of **4** is shown in Fig. 2. Selected bond distances and angles are listed in Table 3. The structure of the  $\text{Mn}_3(\text{CO})_{10}(\mu_3\text{-S}_2)(\mu_4\text{-S}_2)$  portion of **4** is similar to that found in **2** and **3**. The  $\text{CpFe}(\text{CO})_2$  group

Table 3  
Selected intramolecular bond distances and angles for **4**<sup>a</sup>

(a) Bond distances			
Mn(1)–S(1)	2.3138(8)		
Mn(1)–S(3)	2.3236(8)		
Mn(1)–S(4)	2.3658(8)		
Mn(2)–S(2)	2.2972(9)		
Mn(2)–S(4)	2.3414(8)		
Mn(2)–S(3)	2.3891(8)		
Mn(3)–S(1)	2.3229(8)		
Mn(3)–S(2)	2.3415(9)		
Fe(1)–S(3)	2.2773(7)		
S(1)–S(3)	2.0843(9)		
S(2)–S(4)	2.0747(11)		
C–O	1.129(4)(av)		
(b) Bond angles			
S(1)–Mn(1)–S(3)	53.42(2)	S(4)–S(2)–Mn(2)	64.53(3)
S(1)–Mn(1)–S(4)	92.86(3)	S(4)–S(2)–Mn(3)	112.98(4)
S(3)–Mn(1)–S(4)	82.43(3)	Mn(2)–S(2)–Mn(3)	118.24(3)
S(2)–Mn(2)–S(4)	53.13(3)	S(1)–S(3)–Fe(1)	116.10(4)
S(2)–Mn(2)–S(3)	91.25(3)	S(1)–S(3)–Mn(1)	63.05(3)
S(4)–Mn(2)–S(3)	81.56(3)	Fe(1)–S(3)–Mn(1)	123.81(3)
S(1)–Mn(3)–S(2)	90.02(3)	S(1)–S(3)–Mn(2)	113.60(3)
S(3)–S(1)–Mn(1)	63.53(3)	Mn(1)–S(3)–Mn(2)	96.16(3)
S(3)–S(1)–Mn(3)	109.62(3)	S(2)–S(4)–Mn(1)	112.39(4)
Mn(1)–S(1)–Mn(3)	119.88(3)	S(2)–S(4)–Mn(2)	62.34(3)
Fe(1)–S(3)–Mn(2)	126.21(3)	Mn(2)–S(4)–Mn(1)	96.32(3)

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

is bonded to one of sulfur atoms of one of the bridging disulfido ligands. The Fe–S distance at 2.2773(7) Å is unexceptional. The two S–S bond distances (2.0749(11) and 2.0842(9) Å) are also very similar to those observed in  $[\text{Ph}_3\text{PMe}]$  [**3**].

One of the most interesting features of this research is the absence of evidence for the reduced dimanganese species  $[\text{Mn}_2(\text{CO})_7(\mu\text{-S})]^{2-}$ . Instead, the bis(disulfido)trimanganese anion **3** which may be derived from some tetramanganese precursor similar to **2** was formed, and indeed **2** is a much better precursor to anion **3** than **1**. Anion **3** is not a strong nucleophile, but is capable of adding a  $\text{CpFe}(\text{CO})_2$  grouping at one of the sulfur atoms to yield the a new mixed metal complex **4**.

#### 4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC 194950 and 194951 for compounds  $[\text{Ph}_3\text{PMe}]$  [**3**] and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>].

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