Journal of Organometallic Chemistry 693 (2008) 2732–2738

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Disulfido iron–manganese carbonyl cluster complexes: Synthesis, structure, bonding and properties of the radical $CpFeMn_2(CO)_7(\mu_3\text{-}S_2)_2$

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ARTICLE INFO

Article history:
Received 15 May 2008
Accepted 16 May 2008
Available online 29 May 2008

Keywords:
Manganese
Iron
Disulfido
Radical
Molecular orbitals

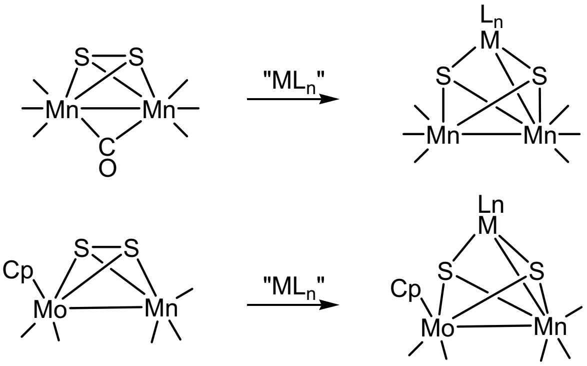
ABSTRACT

Two new compounds $CpFeMn_2(CO)_7(\mu_3\text{-}S_2)_2$ (**2**) and $Cp_3Fe_3Mn(CO)_4(\mu_3\text{-}S_2)_2(\mu_3\text{-}S)$ (**3**) were obtained by the treatment of $[CpFeMn(CO)_5(\mu_3\text{-}S_2)]_2$ (**1**) with CO at room temperature in the presence of room light. Compound **2** contains two triply bridging disulfido ligands on opposite sides of an open $FeMn_2$ triangular cluster. EPR and temperature-dependent magnetic susceptibility measurements show that it is paramagnetic with one unpaired electron per formula equivalent. The electronic structure of **2** was established by DFT and Fenske-Hall (FH) molecular orbital calculations which show that the unpaired electron occupies a low lying antibonding orbital that is located principally on the iron atom. The cyclic voltammogram of **2** exhibits one reversible one-electron oxidation wave at +0.34 V and one irreversible one-electron reduction wave at −0.66 V vs. Ag/AgCl. Compound **3** contains three iron atoms and one manganese atom with two triply bridging disulfido ligands and one triply bridging sulfido ligand and has no unpaired electrons. The molecular structures of compounds **2** and **3** were established by single crystal X-ray diffraction analyses.

1. Introduction

Transition metal complexes containing sulfido ligands present one of the most rich and varied fields of modern inorganic coordination chemistry [1]. Polynuclear metal–sulfur complexes exhibit a range of different structural types [2]. Mixed-metal sulfido cluster complexes have attracted attention because of possible synergistic effects [3] exhibited by certain types of heterogeneous metal sulfide catalysts [4].

Insertion of a metal group into the sulfur–sulfur bond of complexes containing the disulfido ligand is a convenient route for the synthesis of heteronuclear metal complexes with sulfido ligands [5]. Recently, we have reported the disulfido complexes $Mn_2(CO)_7(\mu\text{-}S_2)$ [6] and $CpMoMn(CO)_5(\mu\text{-}S_2)$ [7]. These complexes exhibit facile insertions of metal containing fragments into the S–S bond of the disulfido ligand to yield mixed metal cluster complexes containing two triply bridging sulfido ligands, Eqs. (1) and (2) [5a,5b,8].



(1)

Only a few mixed metal carbonyl complexes containing disulfido ligands have been reported [7]. We have now investigated the room temperature reaction of $[CpFeMn(CO)_5(\mu_3\text{-}S_2)]_2$ (**1**) with CO in the presence of light [9].

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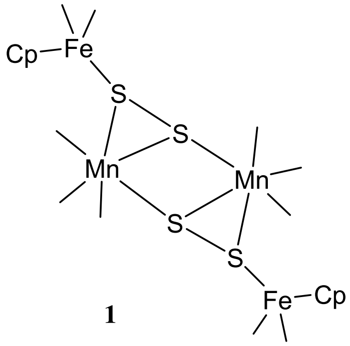
doi:10.1016/j.jorganchem.2008.05.029



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Two mixed metal complexes $CpFeMn_2(CO)_7(\mu_3\text{-}S_2)_2$ (**2**) and $Cp_3Fe_3Mn(CO)_4(\mu_3\text{-}S_2)_2(\mu_3\text{-}S)$ (**3**) were obtained. Both have been characterized crystallographically. The major product **2** is paramagnetic and has been studied by a combination of EPR, magnetic susceptibility, cyclic voltammetry and computational analyses. The results of these studies are reported herein.

2. Experimental

2.1. General data

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 Thermo-Nicolet Avatar 360 FTIR spectrophotometer. Electrospray mass spectrometric measurements were obtained on a MicroMass Q-Tof spectrometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ). $[CpFeMn(CO)_5(\mu_3\text{-}S_2)]_2$ was prepared by the published procedure [9]. Unless stated otherwise, all product isolations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

2.2. Reaction of $[CpFeMn(CO)_5(\mu_3\text{-}S_2)]_2$ (**1**) with CO

A solution of **1** (25 mg, 0.0329 mmol) in CH_2Cl_2 (10 mL) was stirred under CO atmosphere at room temperature in the presence of room light for 36 h. Note: No product was obtained when the reaction was performed in the dark. The solvent was then removed *in vacuo* and the residue was separated by TLC on silica gel using 1:1 hexane/CH_2Cl_2 solvent mixture to yield in order of elution 7.5 mg (41%) of brown–green $CpFeMn_2(CO)_7(\mu_3\text{-}S_2)_2$ (**2**) and 1.1 mg (5%) of $Cp_3Fe_3Mn(CO)_4(\mu_3\text{-}S_2)_2(\mu_3\text{-}S)$ (**3**). The known compound $[CpFe(CO)_2]_2$ can subsequently be eluted from the baseline in approx. 20% yield by using pure CH_2Cl_2 elution solvent [10,11]. Spectral data for **2**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2088(m), 2021(vs), 2010(s), 1972(m), 1951(m), 1932(m). Anal. Calc. for $C_{12}H_5FeMn_2O_7S_4$: C, 25.96; H, 0.91. Found: C, 25.62; H, 0.97%. Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2003(s), 1925(m), 1769(vw). ^1H NMR (in $CDCl_3$): $\delta = 4.94$ (s, 10H, Cp), 4.70 (s, 5H, Cp). MS (*e*/*z*): 691 (M+H).

2.3. Electrochemical measurements

Cyclic voltammetric experiments were conducted by using a CV-50W voltammetric analyzer purchased from Bioanalytical Systems, West Lafayette, IN. The experiments were done under a nitrogen atmosphere at room temperature in 10.0 mL of CH_3CN solution by using 1.0 mM solutions of compound **2** with 0.1 mol/L tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Cyclic voltammograms (CVs) were obtained by using a three-electrode system consisting of a platinum working electrode, a platinum counter and an Ag/AgCl reference electrode. Half-wave potentials ($E_{1/2}$) were calculated as the mean potential between the peak potential by use of the equation $E_{1/2} = (E_{pa} + E_{pc})/2$, where E_{pa} is the anodic peak potential and E_{pc} is the cathodic peak potential.

2.4. EPR measurements

Q-band (~34 GHz) EPR measurements were performed on samples dissolved in benzene on a Bruker E500 spectrometer. The magnetic field was calibrated with a built-in NMR teslameter and the frequency was recorded using a digital frequency counter. The temperature was varied between 300 and 4 K using a continuous flow liquid He cryostat. The measurements of $FeMn_2$ were made in benzene solutions, as a frozen glass, and also in a powder form.

2.5. Magnetic susceptibility measurements

Magnetic susceptibility experiments were carried out under a 100 Gauss magnetic field on powder samples of **2** using a Quantum Design MPMS XL SQUID Magnetometer. The temperature range was 1.8–200 K within an accuracy of 0.05 K.

2.6. Crystallographic analysis

Dark brown crystals of **2** suitable for diffraction analysis were obtained by slow evaporation of solvent from solutions in hexane/methylene chloride solvent mixtures at −20 °C. Brown crystals of **3** were grown from benzene/octane solvent mixture at 5 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). 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 [12]. Corrections for the Lorentz and polarization effects were also

Table 1
Crystallographic data for compounds **2** and **3**

Compound	**2**	**3**
Empirical formula	$C_{12}H_5FeMn_2O_7S_4$	$C_{19}H_{15}Fe_3MnO_4S_5$
Formula weight	555.13	690.10
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pnma*
a (Å)	11.6750(8)	9.6752(6)
b (Å)	10.3065(6)	13.2698(9)
c (Å)	30.3598(9)	17.8969(12)
$\alpha = \beta = \gamma$ (°)	90	90
V (Å^3)	3653.1(3)	2297.7(3)
Z	8	4
T (K)	296(2)	291(2)
ρ_{calc} (g/cm^3)	2.019	1.995
μ (Mo Kα) (mm^{-1})	2.634	2.874
Number of observations ($I > 2\sigma(I)$)	2717	1956
Number of parameters	230	150
Goodness-of-fit[a]	1.062	1.014
Maximum shift in final cycle	0.001	0.001
Residuals: R_1; wR_2[b]	0.0459; 0.0906	0.0451; 0.0997
Absorption Correction, maximum/minimum	1.000/0.877	1.000/0.866
Largest peak in difference map (e$^-$/Å^3)	0.735	0.630

[a] $GOF = [\Sigma_{hkl}(w(|F_{obs}^2| - |F_{calc}^2|))^2/(n_{data} - n_{vari})]^{1/2}$.

[b] $R_1 = \Sigma(\|F_{obs}| - |F_{calc}\|)/\Sigma|F_{obs}|$. $wR_2 = \{\Sigma[w(|F_{obs}^2 - F_{calc}^2|)^2/\Sigma[w(F_{obs}^2)^2]]\}^{1/2}$; $w = 1/\sigma^2(F_{obs}^2)$.