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Synthesis and Reactivity of (η^6-C_6H_6)Mn$(CO)_2$SC(S)H and (η^6-$C_6(CH_3)_6$)Mn$(CO)_2$SC(S)H

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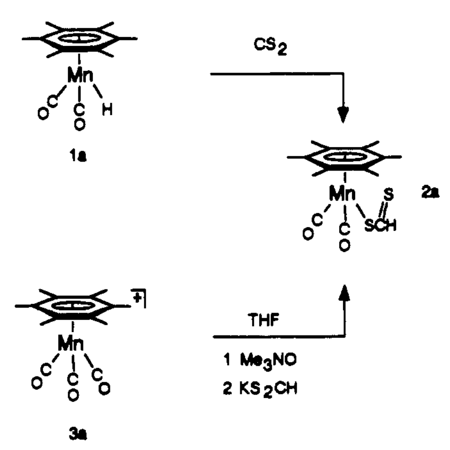
There are numerous examples in the literature that describe insertion of CS_2 into metal hydride bonds to produce metal-coordinated dithioformate ligands.[2-5] These metal hydride insertion reactions are believed to proceed by a mechanism that involves a four-centered intermediate that does not require an open coordination site for the reaction to occur, though this may not necessarily be true for all metal hydride compounds. Metal complexes that have an open coordination site or access to coordinative unsaturation by way of a rapid ligand dissociative process should be especially susceptible to nucleophilic attack by CS_2.[3] Kinetic studies of the reaction of CS_2 with the reactive metal hydride *trans*-$[PtH_2(P(C_6H_{11})_3)_2]$ suggest that the mechanism involves direct coordination of CS_2 to the metal prior to insertion into the Pt-H bond.[4] Early work in this field established, with careful spectroscopic and X-ray structural studies,[3,5] that sulfur was bound to the metal after insertion. It was also found that these ligands can be bound to the metal in either a mono- or bidentate fashion. The study of CS_2 insertion into metal hydride and metal-alkyl bonds is of interest as an extension of the analogous insertion reactions of CO_2[6] because CS_2 is much more reactive toward reduction or insertion than CO_2.

Scheme I



Scheme II

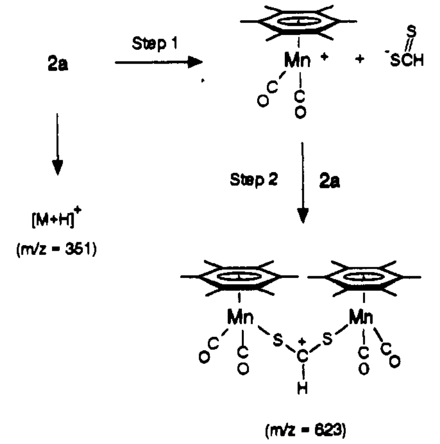


Table I. FAB MS Data[a] for (η^6-C_6Me_6)Mn$(CO)_2$SC(S)H and $[((\eta^6\text{-}C_6Me_6)Mn(CO)_2)_2S_2CH]PF_6$

		compd		
m/z	fragment[b]	**2a**[c] (initial)	**2a** + **5**[d] (60 min)	**5**-PF_6
623	$[Mn_2(HMB)_2(CO)_4S_2CH]$		29	72
567	$[Mn_2(HMB)_2(CO)_2S_2CH]$			2
511	$[Mn_2(HMB)_2S_2CH]$		14	32
405	$[Mn_2(HMB)(CO)_2S_2CH]$		7	16
351	$[Mn(HMB)(CO)_2S_2CH + H]$	14	17	14
349	$[Mn_2(HMB)S_2CH]$		32	73
322	$[(HMB)Mn(CO)S_2CH]$	2	2	7
294	$[(HMB)MnS_2CH]$	100	100	64
273	$[(HMB)Mn(CO)_2]$	6	16	41
245	$[(HMB)Mn(CO)]$	12	28	39
217	$[(HMB)Mn]$	34	75	74

[a] Numbers in table refer to relative abundances of the fragments. [b] HMB refers to hexamethylbenzene. [c] Initial spectrum of (η^6-C_6Me_6)Mn$(CO)_2$SC(S)H. [d] Spectrum of (η^6-C_6Me_6)Mn$(CO)_2$SC(S)H after 60 min under continuous FAB (fast atom bombardment) conditions.

Results and Discussion

While exploring the reactivity of (η^6-C_6Me_6)Mn$(CO)_2$H (**1a**),[7] it was observed that CS_2 will react with this metal hydride at room temperature to produce the red complex (η^6-C_6Me_6)Mn$(CO)_2$SC(S)H (**2a**) as the major product (Scheme I). This reaction proceeds either in CS_2 or in other aprotic solvents such as THF or CH_2Cl_2 with CS_2 added in stoichiometric amounts. Under carbon monoxide pressure, the reaction does not display any rate retardation, suggesting that insertion proceeds by a concerted mechanism rather than a carbonyl dissociative process. An alternate synthesis of **2a** has been achieved by using the reaction of Me_3NO with $[(\eta^6\text{-}C_6Me_6)Mn(CO)_3]PF_6$ (**3a**) in THF to produce (η^6-C_6Me_6)Mn$(CO)_2(THF)^+$ (**4a**),[7c,8] followed by addition of KSC(S)H. The ^1H NMR and IR spectral data for **2a** can be used as the basis for a postulated structure. The ^1H NMR spectrum reveals a singlet peak for the six equivalent methyl groups on the arene ring, suggesting the presence of η^6-$C_6(CH_3)_6$, and a single proton peak at δ 11.44, a characteristic shift for dithioformate protons.[1,9] The infrared spectrum of **2a**, in the carbonyl stretching region, is consistent with two carbonyls bound to the metal, implying that the dithioformate ligand must be

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(9) Monodentate versus bidentate coordination of dithioformate ligands cannot be differentiated by ^1H NMR spectroscopy. For a typical range of dithioformate ^1H NMR values, see ref 1.

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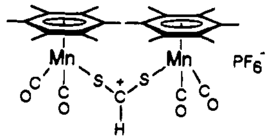
monodentate if an 18-electron count on manganese is to be satisfied. In addition, the peaks in the IR (KBr) spectrum at 1245, 1011, and 647 cm^{-1} are consistent with reported assignments for bending and stretching modes of monodentate dithioformate ligands in other transition-metal complexes.[2]

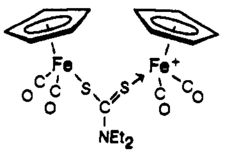
During characterization and reactivity studies, **2a** was observed to display a unique mode of decomposition. Although moderately stable in THF solution, over a period of days at room temperature or a period of hours at elevated temperature (40-50 °C), decomposition of **2a** was observed to give other carbonyl-containing products as monitored by IR spectroscopy. This decomposition was also observed with solid samples stored for several weeks under nitrogen in sample vials at −20 °C. A GC mass spectrum of the gas above **2a** in the sample vials revealed the presence of CS_2. The FAB MS of **2a** provided evidence for the identity of the decomposition product.

The FAB mass spectrum of **2a**, with 3-nitrobenzyl alcohol as the matrix solvent, displayed an ion corresponding to the protonated molecular ion at *m/z* 351. Several other significant fragment ions observed in the spectrum (Table I) correspond to fragmentation of the parent molecule. In addition to the expected fragmentation peaks arising from **2a**, a small peak was observed at *m/z* 623. Aged samples were found to contain this peak, with increased relative intensity dependent on the sample age and temperature of storage. Repurification of **2a**, followed immediately by FAB MS analysis, resulted in a marked decrease in the intensity of the ion at *m/z* 623. As indicated in Table I, its abundance increased again over time especially if the sample was allowed to remain in the instrument continuously subjected to FAB conditions. Scheme II presents a proposed mechanism for the formation of **5**. This process probably involves dissociation of the dithioformate ligand from manganese followed by attack of the uncoordinated sulfur from a second molecule of **2a**. These steps afford the proposed complex $[((\eta^6\text{-}C_6Me_6)Mn(CO)_2)_2(\mu\text{-}S_2CH)]^+$ (**5**, *m/z* 623), which would be positively charged and detectable by the mass spectrometer. It is noteworthy to add that the FAB MS of the dithioformate complex, deuterated on the dithioformate ligand, produced ions corresponding to *m/z* 352 and 624, which is consistent with the deuterated species **2a**-d_1 and **5**-d_1, respectfully. This indicates that the ion corresponding to the decomposition product **5** could not have arisen from the formation of a CS_2-bridged species, with the chemical formula $((\eta^6\text{-}C_6Me_6)Mn(CO)_2)_2(\mu\text{-}CS_2)$, followed by protonation of the molecule by the matrix solvent under FAB conditions.

A reaction similar to step 2 in Scheme II was reported by Astruc,[10] in which an iron dithiocarbamate complex, $CpFe(CO)_2SC(S)N(Et_2)$, was observed to react with $CpFe(CO)_2(THF)^+$ or $Cp^*Fe(CO)_2(THF)^+$ to form an isolable cationic dithiocarbamate-bridged bimetallic species **6**. In addition, Lotz[11] recently reported the formation of the thiophenoxy-bridged bimetallic species, $[((\eta^6\text{-}C_6R_6)Mn(CO)_2)_2SPh]PF_6$ (**7**), by the reaction of $[(\eta^6\text{-}C_6R_6)Mn(CO)_2(THF)]PF_6$ with $(\eta^6\text{-}C_6R_6)Mn(CO)_2SPh$. The reaction sequence of Scheme II would require sufficient lability of the dithioformate ligand on **2a** to permit substitution by the uncoordinated sulfur atom of the dithioformate ligand of a second molecule of **2a** to produce **5**.



5-PF$_6$



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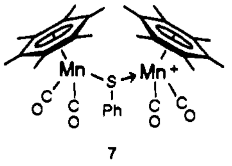

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In an attempt to synthesize **5** by an independent route, **4a** was reacted with **2a**, producing $[((\eta^6\text{-}C_6Me_6)Mn(CO)_2)_2(\mu\text{-}S_2CH)]PF_6$ (**5**-PF_6). This compound is assigned the same structure as **5**, but with PF_6^- as the counterion. Unlike compounds **6** and **7**, **5**-PF_6 displays only two infrared CO stretching bands. In addition, the ^1H NMR spectrum has equivalent proton resonances for the two methylated arene rings, indicating that the arenes are hexahapto and equivalent. These observations suggest that the positive charge is equally distributed between the two manganese atoms rather than localized on one. In addition, the CO stretching frequencies of **5**-PF_6 are approximately 6 wavenumbers higher than those in **2a**, indicating that the electron-donating ability of the sulfur atoms is not greatly altered by the presence of the positive charge. The chemical shift of the bridging dithioformate proton (δ 10.75) is consistent with that of a compound reported by Hawthorne,[12] which contains a cationic dithioformate bridge between boron atoms of two dicarbollide ligands in a cobalt complex. As anticipated, the FAB MS of **5**-PF_6 (Table I) gives rise to fragments that are identical with those produced by **5**.

The bridging S_2CH fragment of **5**-PF_6 can be displaced from one of the $(\eta^6\text{-}C_6Me_6)Mn(CO)_2$ fragments by the addition of 1 equiv of KS_2CH to a CH_2Cl_2 solution of **5**-PF_6, producing 2 equiv of **2a** after 6 h, as shown in eq 1. Likewise, **2a** can be displaced

$$\mathbf{5}\text{-}PF_6 + KS_2CH \rightarrow 2(\mathbf{2a}) \quad (1)$$

$$\mathbf{5}\text{-}PF_6 + CH_3Li \rightarrow \mathbf{2a} + \underset{\mathbf{8}}{(\eta^6\text{-}C_6Me_6)Mn(CO)_2CH_3} \quad (2)$$

from **5**-PF_6 by the addition of CH_3Li (eq 2), producing the methyl derivative $(\eta^6\text{-}C_6Me_6)Mn(CO)_2CH_3$[7b,13] (**8**) and a small amount of $((\eta^6\text{-}C_6Me_6)Mn(CO)_2)_2$[14] (**9**). The formation of **9** in the reaction probably arises from a reaction between a liberated molecule of **2a** with CH_3Li, since it has been observed that **2a** will react with CH_3Li in THF to produce **8** and **9**. This is similar to the reaction of $(\eta^6\text{-}C_6Me_6)Mn(CO)_2I$ with CH_3Li, which also produces **8** and **9**.[14] These results suggest that the carbon of the bridging S_2CH, although positively charged, is not very accessible for nucleophilic addition, and that the preferred mode of attack involves displacement of one end of the bridging S_2CH unit from a $(\eta^6\text{-}C_6Me_6)Mn(CO)_2$ fragment, producing **2a** and $(\eta^6\text{-}C_6Me_6)Mn(CO)_2L$ (L = CH_3 or SC(S)H).

Unlike **1a**, $(\eta^6\text{-}C_6H_6)Mn(CO)_2H$ (**1b**) did not react with CS_2 to form the dithioformate insertion product **2b**, analogous to **2a**. There is apparently a sufficient reduction of hydridic character in **1b** relative to **1a** to prevent insertion of CS_2. This decrease in electron density is confirmed by a 30 wavenumber increase in the infrared CO stretching frequencies of **1b** relative to **1a**.[15] In an attempt to synthesize **2b** by another route, $[(\eta^6\text{-}C_6H_6)Mn(CO)_3]PF_6$ (**3b**) was treated with Me_3NO in THF for 30 min at 0 °C, followed by the addition of KSC(S)H. **2b** prepared in this way displayed much lower stability than that of the permethylated derivative **2a**. It did not display the mode of decomposition leading to a dithioformate-bridged dimanganese species. In solution at room temperature, **2b** shows evidence of decomposition over a period of hours and is stable in the solid state for only a few days at −20 °C. The mass spectrum of **2b** displays only the expected fragmentation pattern, and there is no evidence for the formation of a bimetallic species.

Experimental Section

General Procedures. All reactions and manipulations were performed under nitrogen or argon by using Schlenk or glovebox techniques. All solvents were dried and deoxygenated prior to use. Microanalyses were

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performed by Desert Analytics, Tuscon, AZ. All infrared solution spectra were obtained on a Mattson Cygnus 25 FTIR spectrometer using 0.1- or 0.5-mm potassium bromide cells. NMR spectra were obtained on a JEOL FX90Q (^{1}H) or a Bruker WM360 (^{1}H, ^{13}C) spectrometer and are reported as positive downfield from TMS. Chromatographic separations were performed by using untreated silica gel (60–200 mesh).

EI mass spectra were recorded on a VG TRIO 1 instrument using the VG LAB BASE data system operating with a 70-eV electron beam and a 150-μA trap current. All other spectra including the **2a** decomposition studies were recorded on a VG ZAB-HF in the fast atom bombardment (FAB) ionization mode. The FAB ion source used was the standard VG Analytical, Inc., system equipped with a saddle field atom gun. Xenon was used for the bombarding fast atom beam; typical operating conditions were beam energies of 8 keV and neutral beam currents equivalent to 1.5 mA supplied by an ION TECH (Model B 50) current and voltage regulator/meter.

Materials. **1a**,[7b,c] **1b**,[16] **3a**,[17] and **3b**[17] were prepared by published procedures. Me_3NO was purchased from Eastman Kodak Co. as the dihydrate and dried by removing the water as an azeotrope with benzene.

Synthesis of KS_2CH.[18] To a solution of $KB(O^iPr)_3H$[19] (50 mmol) in THF (30 mL) was added CS_2 (4.0 g, 53 mmol) via syringe. The solution turned from clear to orange initially, and yellow-orange solids eventually precipitated from the solution. The solution was stirred for 1 h, after which it was concentrated and the solids were filtered from the solution. Recrystallization of the solids from ethanol produced 2.4 g (41% yield) of yellow crystals of KS_2CH. KS_2CD was prepared similarly by using $KB(O^iPr)_3D$.

Synthesis of 2a. **1a** (0.5 g, 1.8 mmol) and CS_2 (1 mL) in CH_2Cl_2 (30 mL) were stirred at room temperature for 30 min, during which the solution turned from yellow to red. The solution was then filtered, the solvent was removed by vacuum, and the product was recrystallized from acetone/hexane, producing 0.48 g (75% yield) of rust red crystals. ^{1}H NMR ($(CD_3)_2CO$): δ 2.25 (s, 18 H, CH_3), 11.44 (s, 1 H, SC(S)H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 210 K): δ 224.1 (s, CO), 108.2 (s, C_6Me_6), 16.5 (s, CH_3). IR (THF): ν(CO) 1969, 1921 cm^{-1}; ν(CS) 1245, 1011, and 647 cm^{-1}. See Table I for mass spectral data. Anal. Calcd for $C_{15}H_{19}O_2S_2Mn$: C, 51.42; H, 5.47. Found: C, 50.95; H, 5.23.

Alternate Method. To a mixture of **3a** (0.5 g, 1.12 mmol) and Me_3NO (0.13 g, 1.73 mmol) was added THF (50 mL) with stirring for 30 min at 0 °C, turning the solution from yellow to purple. To this was added a 10-mL THF solution of KSC(S)H (0.17 g, 1.46 mmol). The resultant solution was stirred for an additional 30 min at room temperature, followed by filtration and elution from a column of silica with acetone/hexane. Recrystallization from acetone/hexane produced 0.28 g (70% yield) of rust red crystals. $(\eta^6\text{-}C_6Me_6)Mn(CO)_2SC(S)D$ was prepared in a similar manner by using KSC(S)D.

Synthesis of 2b. To **3b** (0.362 g, 1.0 mmol) and Me_3NO (0.075 g, 1.0 mmol) was added 50 mL of THF at 0 °C, resulting in a purple solution. After 30 min of stirring, a 10-mL THF solution of KSC(S)H (0.116 g, 1.0 mmol) was added, followed by an additional 1 h of stirring at 0 °C. Upon concentration of the solvent followed by addition of hexane and cooling to −20 °C, 0.16 g (60% yield) of red crystals were obtained after filtration. ^{1}H NMR ($(CD_3)_2CO$): δ 6.19 (s, 6 H, C_6H_6), 11.68 (s, 1 H, SC(S)H). IR (THF): ν(CO) 1995, 1948 cm^{-1}; ν(CS) 1240, 992, and 625 cm^{-1}. Mass spectral data (FAB MS): parent ion at *m*/*z* 267, $(M + H)^+$. Instability of the product precluded elemental analysis.

Reaction of 2a and 4a. A solution of **4a** was prepared by the addition of Me_3NO (0.075 g, 1.0 mmol) to **3a** (0.446 g, 1.0 mmol) in 20 mL of THF at 0 °C followed by 30 min of stirring. To this purple solution was then added a 20-mL solution of **2a** (0.350 g, 1.0 mmol), followed by an additional 30 min of stirring at room temperature. The resulting red solution was evaporated to dryness under reduced pressure to give a red solid, which was redissolved in a minimal amount of CH_2Cl_2 and recrystallized with the addition of hexane and cooling to −20 °C, producing 0.65 g (85% yield) of **5**-PF_6. ^{1}H NMR ($(CD_3)_2CO$): δ 2.17 (s, 36 H, CH_3), 10.75 (s, 1 H, μ-SC(S)H). IR (THF): μ(CO) 1975, 1928 cm^{-1}. The mass spectral data are presented in Table I.

Reaction of 5-PF_6 and KS_2CH. To a CH_2Cl_2 (20 mL) solution of **5**-PF_6 (0.011 g, 0.014 mmol) was added an equal molar amount KS_2CH at room temperature. A gradual loss in the concentration of **5**-PF_6 and the formation of **2a** was observed spectroscopically (IR and ^{1}H NMR spectroscopy) over time, and the reaction was complete after 6 h of stirring at room temperature.

Reaction of 5-PF_6 and CH_3Li. To a stirred solution of **5**-PF_6 (0.012 g, 0.016 mmol) in THF (20 mL) was added an equal molar amount of CH_3Li via syringe. There was an immediate color change from red to orange, and IR data indicated the formation of **2a**, $(\eta^6\text{-}C_6Me_6)Mn(CO)_2CH_3$ (**8**), and $((\eta^6\text{-}C_6Me_6)Mn(CO)_2)_2$ (**9**).

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A Hydrogen-Bonding Mode in the Ion Association of the *d*-Tartrate Anion with the Λ-*ob*$_3$-Tris((1*R*,2*R*)-diaminocyclohexane)cobalt(III) Cation

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Introduction

It is well-known that oxo anions such as PO_4^{3-}, SO_4^{2-}, and SeO_3^{2-} form intimate ion pairs in solution with tris(diamine)metal complex cations with a *lel*$_3$ conformation.[1-3] This is because a set of three N–H groups on the triangular face of the *lel*$_3$ complex are disposed almost parallel to the C_3 axis so as to form triple linear hydrogen bonds to a set of three oxygen atoms of the oxo anions along the C_3 axis. Actually, such association modes have been found in the crystal structures of *lel*$_3$-$[Co(en)_3]_2[HPO_4]_3\cdot 9H_2O$[4] and *lel*$_3$-$[Co(en)_3][AsO_4]\cdot 3H_2O$[5] (en = 1,2-diaminoethane). In contrast, these oxo anions show a much weaker affinity for the *ob*$_3$ complexes[1,6-10] with a set of three N–H groups oblique to the C_3 axis, because the hydrogen bonds formed are inevitably bent and are thus weak.

In the course of our X-ray crystallographic study on ion-association modes of the *d*-(*R*,*R*)-tartrate dianion (abbreviated as the *d*-tart ion hereafter) with the *lel*$_3$-tris(diamine)cobalt(III) complex cations,[11-13] a common face-to-face contact mode has been found. In this contact mode, the three oxygen atoms, two alcoholic and one carboxylic, of the *d*-tart ion are nicely disposed among the three parallel N–H groups on the triangular face of the *lel*$_3$ complex to form three bifurcated hydrogen bonds to

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(1) *lel*$_3$ refers to a conformation in which each C–C bond in the three five-membered chelates lies parallel to the C_3 axis, while *ob*$_3$ refers to the one in which it lies oblique to this axis.

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