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Oxidative Addition of Diphenyl Disulfide/Thiophenol to $[Mn(CO)_5]^-$: Crystal Structure of *cis*-$[Mn(CO)_4(SPh)_2]^-$

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Oxidative addition of diphenyl disulfide to the coordinatively unsaturated $[Mn(CO)_5]^-$ led to the formation of low-spin, six-coordinate *cis*-$[Mn(CO)_4(SPh)_2]^-$. The complex *cis*-[PPN]$[Mn(CO)_4(SPh)_2]$ crystallized in monoclinic space group $P2_1/c$ with $a = 9.965(2)$ Å, $b = 24.604(5)$ Å, $c = 19.291(4)$ Å, $\beta = 100.05(2)°$, $V = 4657(2)$ Å^3, and $Z = 4$; final $R = 0.036$ and $R_w = 0.039$. Thermal transformation of *cis*-$[Mn(CO)_4(SPh)_2]^-$ to $[(CO)_3Mn(\mu\text{-}SPh)_3Mn(CO)_3]^-$ was completed overnight in THF at room temperature. Additionally, reaction of $[Mn(CO)_5]^-$ and PhSH in 1:2 mole ratio also led to *cis*-[PPN]$[Mn(CO)_4(SPh)_2]$. Presumably, oxidative addition of PhSH to $[Mn(CO)_5]^-$ was followed by a Lewis acid-base reaction to form *cis*-$[Mn(CO)_4(SPh)_2]^-$ with evolution of H_2.

INTRODUCTION

As part of our recent investigations of oxidative addition of RE-ER (E = Te, Se; R = Ph, alkyl) to anionic metal carbonyl fragments, we have synthesized, characterized, and studied two series of transition-metal-terminal-chalcogenolate complexes, namely, the iron(II)-chalcogenolate and manganese(I)-chalcogenolate derivatives, *fac*-$[Fe(CO)_3(EPh)_3]^-$ and *cis*-$[Mn(CO)_4(ER)_2]^-$ (E = Te, Se; R = Ph, alkyl).[1,2] For the purposes of comparison with these studies on the factors controlling the activation of diorganyl dichalcogenides in the reaction of diorganyl dichalcogenides and anionic metal carbonyl fragments, we have sought to investigate the reactions of these anionic metal carbonyls and diorganyl disulfides/thiophenol. In this paper, we describe the synthesis of *cis*-$[Mn(CO)_4(SPh)_2]^-$, in order to clarify the possible reaction pathway in these related reaction systems.

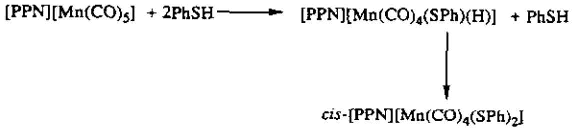
RESULTS AND DISCUSSION

The use of dialkyl dichalcogenides as reagents for the synthesis of metal-chalcogenolate species is well established.[1-3] In addition to *cis*-$[Mn(CO)_4(SPh)_2]^-$, the reactions between R_2E_2 (E = Te, Se; R = Ph, alkyl) and $[Mn(CO)_5]^-$ have been employed previously in the syntheses of the *cis*-$[Mn(CO)_4(EPh)_2]^-$ complexes.[2] Diphenyl disulfide reacts cleanly with anionic $[Mn(CO)_5]^-$ in dry THF to yield low-spin, six-coordinate *cis*-$[Mn(CO)_4(SPh)_2]^-$ which can be isolated in 98% yield after removal of solvent and recrystallization with THF and hexane (eq. 1). This result shows that $[Mn(CO)_5]^-$ promoted the oxidative addition of diphenyl disulfide, although cleavage of S-S bond by nucleophiles is a well-known phenomenon which results in displacement of the group RS^-.[4] This is in contrast to the formation of neutral $Mn(CO)_5(SPh)$ species reported by Treichel and coworkers for reaction of $(PhS)_2$ and $[Mn(CO)_5]^-$ at -26 °C.[5] An atmosphere of CO did prevent oxidative addition of $(PhS)_2$ when we exposed the mixture of $[Mn(CO)_5]^-$ and $(PhS)_2$ to 1 atm of CO in THF at room temperature. The structure of *cis*-[PPN]$[Mn(CO)_4(SPh)_2]$ was confirmed by X-ray crystallography on a single crystal. The infrared spectrum of the title compound shows bands in the carbonyl stretching region at 2050 w, 1975 vs, 1954 m, 1908 m cm^{-1} in THF. This pattern is well documented for a *cis*-manganese(I)-diphenylchacogenolate complexes in THF at ambient temperature.[2] The yellow crystals *cis*-[PPN]$[Mn(CO)_4(SPh)_2]$ suitable for X-ray crystallography was obtained by diffusion of hexane into yellow THF solution under 1 atm of CO at -15 °C for 4 weeks (Fig. 1).

$$\begin{tikzcd}[PPN][Mn(CO)_5] + PhSSPh \arrow[r] & cis\text{-}[PPN][Mn(CO)_4(SPh)_2] \arrow[d] \\ & [PPN][(CO)_3Mn(\mu\text{-}SPh)_3Mn(CO)_3]\end{tikzcd} \quad (1)$$

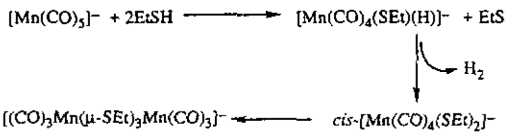
Upon stirring for extended periods at room temperature, a THF solution of *cis*-$[Mn(CO)_4(SPh)_2]^-$ turned orange. This transformation occurred quickly at ambient temperature over 8 hours, during which period no intermediate was detected. IR ν co and ^{1}H NMR spectra revealed the orange compound to be a well-known benzenethiolate-triply-bridged dimer of composition [PPN][$(CO)_3Mn(\mu\text{-}SPh)_3Mn(CO)_3$] (ν co (THF): 1906 vs, 1986 s cm^{-1}) (eq. 1).[5,6]

As illustrated in eq. 2, treatment of [PPN][$Mn(CO)_5$] with PhSH in 1:2 ([$Mn(CO)_5$]$^-$: PhSH) molar ratio in THF at ambient temperature also leads to formation of *cis*-[$Mn(CO)_4(SPh)_2$]$^-$ instead of formation of the neutral unstable $PhSMn(CO)_5$ via reaction of $HMn(CO)_5$ and PhSH.[7] This reaction is rapid at room temperature and is complete within 6 h. The proposed reaction sequence appears in eq. 2. It is likely that oxidative addition of PhS-H to [$Mn(CO)_5$]$^-$ is followed by a Lewis acid-base reactions to form *cis*-[$Mn(CO)_4(SPh)_2$]$^-$ with evolution of H_2 gas which was identified by gas chromatography. However, the presumed intermediate [$Mn(CO)_4(H)(SPh)$]$^-$ was not observed spectrally even at -40 °C. When the same reactions were carried out in a 1:1 molar ratio under similar experimental conditions. Two species of the nearly equal amounts, the product *cis*-[PPN][$Mn(CO)_4(SPh)_2$] and the unreacted [PPN][$Mn(CO)_5$], were present according to IR spectra.



(2)

We also sought to answer how strongly the nature of the Mn(I)-thiolate product depends on the substituents by conducting a similar reaction in which we used EtSH in place of PhSH. The reaction sequences shown in (2) with thiophenol appears to be generalizable to other alkylthiols. Reaction of [$Mn(CO)_5$]$^-$ and EtSH was much slower, but definite formation of [$(CO)_3Mn(\mu\text{-}SEt)_3Mn(CO)_3$]$^-$ was shown by IR and ^{1}H NMR. The formation of final product [$(CO)_3Mn(\mu\text{-}SEt)_3Mn(CO)_3$]$^-$ indicated that the reaction pathway as shown eq. 3.



(3)

The dropwise addition of $(PhSe)_2$ and $(PhTe)_2$ to a solution of *cis*-[$Mn(CO)_4(SPh)_2$]$^-$ at ambient temperature for 2 h led to the formation of *cis*-[$Mn(CO)_4(SePh)_2$]$^-$ and *cis*-[$Mn(CO)_4(TePh)_2$]$^-$ along with $(PhS)_2$, as identified by gas chromatography. The reaction presumably proceeded by reductive elimination followed by oxidative addition. These results show the relative order of thermal stability of the series of anionic manganes(I)-chalcogenolate complexes being *cis*-[$Mn(CO)_4(TePh)_2$]$^-$ > *cis*-[$Mn(CO)_4(SePh)_2$]$^-$ > *cis*-[$Mn(CO)_4(SPh)_2$]$^-$.

The molecular structure of *cis*-[$Mn(CO)_4(SPh)_2$]$^-$ was determined by X-ray diffraction, as illustrated in Fig. 1. The coordination geometry around Mn(I) atom in *cis*-[$Mn(CO)_4(SPh)_2$]$^-$ is a distorted octahedral fashion with a bond angle of 81.64(5)° for S(1)-Mn-S(2), comparable to the larger E-Mn-E bond angles (83.0(1)° for *cis*-[$Mn(CO)_4(SePh)_2$]$^-$ and 82.79(4)° for *cis*-[$Mn(CO)_4(TePh)_2$]$^-$) (Table 1). The average Mn(I)-S distance 2.398(1) Å in the title complex is significantly shorter than the reported Mn(II)-SPh bond 2.442(3) Å (average) in the [$Mn(SPh)_4$]$^{2-}$.[8] The difference between the Mn(I)-S and Mn(I)-Se lengths is approximately 0.13 Å, which is consistent with the difference in the covalent radii of S (1.04 Å) and Se (1.17 Å) (Table 1). We also noticed that the shortening of M-S bonds resulting from the M-S dπ-pπ bonding has been analyzed by Chisholm *et al.* and Ashby recently.[9,10] The sum of the covalent radii of C (0.77 Å) and S (1.04 Å) is about 0.05 Å longer than the observed S-C distance (1.764(4) Å) in *cis*-[$Mn(CO)_4(SPh)_2$]$^-$ which indicates the importance of a conjugation interaction between the aryl π-system and the S 3p lone pair.[10,11] Also, the S-C lengths of the title compound are shorter by 0.197 Å (average) than the Se-C lengths of the corresponding complex (Table 1).

Another feature of interest in the structure of *cis*-[$Mn(CO)_4(SPh)_2$]$^-$ centers on the Mn-S-C bond angles, the

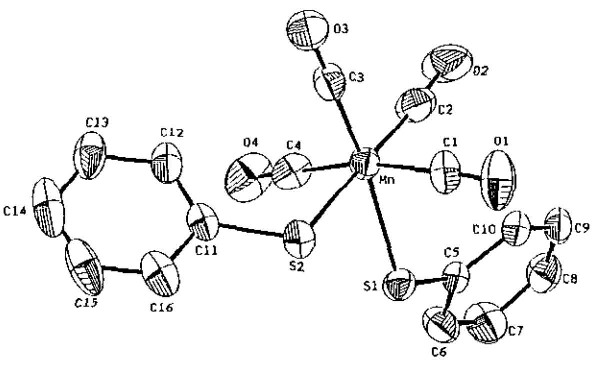


Fig. 1. ORTEP drawing and labeling scheme of the *cis*-[$Mn(CO)_4(SPh)_2$]$^-$ anion with thermal ellipsoids drawn at the 50% probability level.

Table 1. Comparisons of Bond Lengths (Å) and Angles (deg) in *cis*-$[Mn(CO)_4(EPh)_2]^-$

E	Mn-E_{av}	E_{av}-C_{av}	E-Mn-E	Mn-E-C_{av}	ref.
S	2.398(1)	1.764(4)	81.64(5)	113.2(2)	this work
Se	2.527(4)	1.96(2)	83.0(1)	104.9(6)	2b
Te	2.674(1)	2.130(6)	82.79(4)	106.7(2)	2a

average Mn-S-C bond angle (113.2(2)°) in this title complex falls within the range of 106° and 116° observed in the distribution of M-S-C bond angles of metal-terminal-benzenethiolate complexes (a mean value of 110.8(3.4)°).[10,12]

EXPERIMENTAL SECTION

Manipulations, reactions and transfer of samples were conducted under nitrogen by standard Schlenk techniques or in a glovebox (Ar gas). Solvents were distilled under nitrogen from appropriate drying agents (diethyl ether from CaH_2; acetonitrile from CaH_2/P_2O_5; hexane and tetrahydrofuran (THF) from Na/benzophenone) and stored in dried, N_2-filled flasks over 4 Å molecular sieves. A nitrogen purge was used on these solvents before use and transfer to reaction vessels was via stainless-steel cannula under N_2 at a positive pressure. The reagents manganese decacarbonyl, diphenyl disulfide, bis(triphenylphosphoranylidene)ammonium chloride, thiophenol, ethylthiol (Aldrich) were used as received. Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-7 FTIR) with sealed solution cells (0.1 mm) and KBr windows. In NMR spectra (recorded on a Bruker AC 200 spectrometer), chemical shifts of ^1H and ^{13}C are relative to tetramethylsilane. UV-visible spectra were recorded on a GBC 918 spectrophotometer. Gas chromatography was carried out on a Shimadzu GC-3BT, and Shimadzu R-11 recorder. Analyses made use of thermal conductivity detector (TCD) and a flame-ionizing detector (FID); nitrogen was the carrier gas, the column was OV-17 (5%) on Chromosorb W, 80/100 mesh, 6 ft × 1/8 in. stainless steel tubing. Analyses of carbon, hydrogen and nitrogen were obtained with a CHN analyzer (Heraeus).

Reaction of $[PPN][Mn(CO)_5]$ and $(PhS)_2$

$[PPN][Mn(CO)_5]$ (0.5 mmol, 0.367 g)[2] dissolved in THF (3 mL) was stirred under N_2, and diphenyl disulfide (0.5 mmol, 0.109 g) in THF solution was added to the $[PPN][Mn(CO)_5]$ solution by cannula under positive N_2 gas at 15 °C. A vigorous reaction occurred immediately with evolution of CO gas. After stirring of the reaction solution for 15 min, hexane was added to precipitate the yellow solid. The product was isolated by removing the solvent and recrystallizing the residue in THF-hexane. The yield was 0.453 g (98%) of a yellow solid *cis*-$[PPN][Mn(CO)_4(SPh)_2]$. Diffusion of hexane into THF *cis*-$[PPN][Mn(CO)_4(SPh)_2]$ solution under CO atmosphere at -15 °C led to formation of yellow crystal *cis*-$[PPN][Mn(CO)_4(SPh)_2]$ suitable for X-ray crystallography. IR (ν co) (THF): 2050 w, 1975 vs, 1954 m, 1908 m cm^{-1}. ^1H NMR (CD_3CN): δ 6.86-7.70 (m) (Ph) ppm. Absorption spectrum (THF) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 411 (1,416), 335 (4,697), 293 (13,320). Anal. calcd for $C_{52}H_{40}O_4NP_2S_2Mn$: N, 1.52; C, 67.60; H, 4.36. Found: N, 1.67; C, 67.93; H, 4.41. However, *cis*-$[PPN][Mn(CO)_4(SPh)_2]$ THF solution was stirred at ambient temperature overnight; the IR spectrum revealed that the *cis*-$[PPN][Mn(CO)_4(SPh)_2]$ converted to the well-known $[(CO)_3Mn(\mu\text{-}SPh)_3Mn(CO)_3]^-$,[5,6] and [PPN][SPh]. The solution was then filtered to remove [PPN][SPh] after addition of diethyl ether, and the orange solid $[PPN][(CO)_3Mn(\mu\text{-}SPh)_3Mn(CO)_3]$ was isolated on addition of hexane. IR (ν co) (THF): 1906 vs, 1986 s cm^{-1}.

Reaction of $[PPN][Mn(CO)_5]$ and PhSH

A portion (44 μL, 0.4 mmol) of PhSH was syringed into $[PPN][Mn(CO)_5]$ (0.2 mmol, 0.147 g) in THF (2 mL) at ambient temperature. The reaction mixture was stirred for 6 h at room temperature, yielding a yellow solution with IR ν co (THF) 2050 w, 1975 vs, 1954 m, 1908 m cm^{-1}, consistent with the formation of *cis*-$[PPN][Mn(CO)_4(SPh)_2]$ and H_2 gas identified by gas chromatography.

Reaction of $[PPN][Mn(CO)_5]$ and EtSH

A portion (15.2 μL, 0.2 mmol) of EtSH was syringed into $[PPN][Mn(CO)_5]$ (0.1 mmol, 0.074 g) at ambient temperature. The reaction mixture was stirred for 7 days at room temperature, yielding an orange solution with IR ν co (THF) 1973 m, 1887 vs cm^{-1}, consistent with the formation of well-known $[PPN][(CO)_3Mn(\mu\text{-}SEt)_3Mn(CO)_3]$, light yellow precipitate [PPN][SEt], and H_2 gas identified by gas chromatography. The solution was filtered and hexane was added to precipitate the well-known $[PPN][(CO)_3Mn(\mu\text{-}SEt)_3Mn(CO)_3]$ orange solid.[5,6] IR (ν co) (THF): 1973 m, 1887 vs cm^{-1}. ^1H NMR (CD_3CN): δ 1.33 (t), 2.44 (q) ppm. ^{13}C NMR (CD_3CN): δ 27.6 (s), 18.5 (s) ppm.

Crystallography

The crystal data are summarized in Table 2. The crystal of *cis*-$[PPN][Mn(CO)_4(SPh)_2]$ moderately sensitive to air chosen for diffraction measurement was *ca.* 0.50 × 0.50 ×

Table 2. Crystallographic Data of Complex *cis*-[PPN][Mn(CO)$_4$(SPh)$_2$]

chem formula	$C_{52}H_{40}O_4NP_2MnS_2$
fw	923.89
cryst syst	Monoclinic
space group	$P2_1/c$
λ, Å (Mo K_α)	0.7107
a, Å	9.965(2)
b, Å	24.604(5)
c, Å	19.291(4)
β, deg	100.05(2)
V, $Å^3$	4657(2)
Z	4
d_{calcd}, g cm^{-3}	1.318
μ, cm^{-1}	4.575
T, °C	25
R^a	0.036
$R_w{}^b$	0.039

[a] $R = \Sigma|(F_o-F_c)|/\Sigma F_o$. [b] $R_w = [\Sigma(\omega(F_o-F_c)^2/\omega F_o{}^2]^{1/2}$

Table 3. Selected Bond Distances (Å) and Angles (deg) for *cis*-[PPN][Mn(CO)$_4$(SPh)$_2$]

S(1)-Mn	2.414(1)	Mn-C(1)	1.808(5)
S(2)-Mn	2.381(1)	Mn-C(2)	1.783(5)
S(1)-C(5)	1.762(4)	Mn-C(3)	1.784(4)
S(2)-C(11)	1.765(4)	Mn-C(4)	1.836(5)
S(1)-Mn-S(2)	81.64(5)	S(1)-Mn-C(1)	85.5(2)
Mn-S(1)-C(5)	112.0(1)	S(1)-Mn-C(2)	98.9(2)
Mn-S(2)-C(11)	114.4(2)	S(1)-Mn-C(3)	169.0(2)
C(2)-Mn-C(4)	88.8(2)	S(1)-Mn-C(4)	82.3(1)
C(2)-Mn-C(3)	92.1(2)	C(1)-Mn-C(4)	167.6(2)
C(1)-Mn-C(2)	91.1(2)	C(1)-Mn-C(3)	94.1(2)
C(3)-Mn-C(4)	98.3(2)		

0.50 mm. The crystal was mounted on a glass fiber and quickly coated in epoxy resin. The unit-cell parameters were obtained from 25 reflections with 2θ between 20.58° and 26.70°. Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated Mo K_α radiation employing the θ/2θ scan mode. A φ scan absorption correction was made.[13] Structural determinations were made using the NRCC-SDP-VAX package of programs.[14,15] Selected bond distances and angles is listed in Table 3.

ACKNOWLEDGMENT

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Supporting Information Available

Tables of crystal data and experimental conditions for the X-ray studies, atomic coordinates and B_{eq} values, bond lengths and angles, and anisotropic temperature factors for *cis*-[PPN][Mn(CO)$_4$(SPh)$_2$]. Ordering information is given on any current masthead page.

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Key Words

Manganese(I)-phenylthiolate derivatives.

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