Table VII. Selected Distances (Å) and Angles (deg)

Fe–P	2.258 (1)	Fe–cent[a]	1.768
Fe–C(1)	2.067 (4)	O(1)–C(3)	1.231 (5)
Fe–C(2)	2.181 (4)	C(1)–C(2)	1.431 (6)
Fe–C(4)	2.188 (4)	C(1)–C(5)	1.406 (6)
Fe–C(5)	2.066 (4)	C(2)–C(3)	1.492 (6)
Fe–C(9)	1.765 (5)	C(3)–C(4)	1.496 (6)
Fe–C(10)	1.757 (5)	C(4)–C(5)	1.416 (6)
P–Fe–C(9)	92.2 (2)	C(5)–C(6)–C(7)	103.1 (4)
P–Fe–C(10)	94.3 (1)	C(1)–C(8)–C(7)	102.6 (3)
C(1)–C(2)–C(3)	106.9 (3)	O(1)–C(3)–C(2)	127.7 (4)
C(2)–C(3)–C(4)	104.8 (3)	C(1)–C(2)–C(11)	126.3 (4)
C(3)–C(4)–C(5)	107.2 (3)	C(3)–C(4)–C(21)	124.9 (4)
C(1)–C(5)–C(4)	110.1 (4)	Cent–Fe–P[a]	132.6
C(2)–C(1)–C(5)	109.4 (3)	Cent–Fe–C(9)[a]	116.9

[a] Cent is the calculated geometric center of C(1), C(2), C(4), and C(5).

Tricarbonyl(2,4-diphenyl-6-*syn*-hydroxy-6-*anti*-methylbicyclo[3.3.0]octa-1,4-dien-3-one)iron (39). To a solution of **38** (38 mg, 0.090 mmol) in 5 mL of THF cooled to −78 °C, 3.0 M MeMgBr (0.30 mL, 0.90 mmol) was added. The solution was stirred for 4 h, then quenched with saturated NH_4Cl solution, diluted with Et_2O, and washed twice with NaCl solution. The product was purified by flash chromatography giving **39** (39 mg, 97%). $R_f = 0.29$ (40% EtOAc/hexanes). Mp 210–1 °C. IR (CCl_4) 3363 (br), 2067, 2017, 1999, 1648 cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.34 (d, *J* = 1.6 Hz, 2 H), 8.31 (d, *J* = 1.1 Hz, 2 H), 7.99–7.29 (m, 6 H), 3.07 (dd, *J* 16.5, 7.7 Hz, 1 H), 2.92 (ddd, *J* = 16.5, 10.1, 6.8 Hz, 1 H), 2.50–2.31 (m, 2 H, H7), 2.44 (s, 1 H, –OH), 1.66 (s, 3 H, –Me) ^{13}C NMR ($CDCl_3$) δ 208.2 ($Fe(CO)_3$), 171.1 (C3), 131.8, 129.2, 128.7, 128.4, 128.2, 127.9, 109.3, 104.4, 103.3, 78.5, 77.7 (C7), 43.0 (MeO), 26.4 (C7), 25.4 (C8). HRMS calculated for $C_{24}H_{18}O_5Fe$ (M): 442.0504. Found: 442.0500; *m/e* (%) 442 (1), 358 (37), 286 (100).

X-ray Diffraction Analysis of 25. Crystals formed in a concentrated solution of **25** in CH_2Cl_2, to which hexane was added, after storage at −20 °C for 1 day. A single crystal was mounted on the end of a glass fiber using epoxy. Details of the crystal data collection, solution, and refinement[27] of the structure are summarized in Table V. The refined atomic coordinates are listed in Table VI. Atomic scattering factors and corrections for anomolous dispersion were taken from the usual source.[28]

Acknowledgment. We are grateful to the National Science Foundation (CHE 89-21944) for financial support. R.A.D. thanks BP America for financial support.

Supplementary Material Available: Tables of anisotropic thermal parameters (U_{ij}), bond lengths, bond angles, and calculated hydrogen atom positions (7 pages). Ordering information is given on any current masthead page.

OM9204090

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Coordination and Reactivity of 3,3-Dimethylthietane in Dimanganese Carbonyl Cluster Complexes

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The complex $Mn_2(CO)_9(\overline{SCH_2CMe_2C}H_2)$ (**1**) was obtained from the reaction of $Mn_2(CO)_9(NCMe)$ with 3,3-dimethylthietane (3,3-DMT) at 40 °C. Reaction of **1** with Me_3NO resulted in decarbonylation and the formation of the complex $Mn_2(CO)_8[\mu\text{-}\overline{SCH_2CMe_2C}H_2]$ (**2**). Complex **2** was characterized by single-crystal X-ray diffraction analyses and was found to contain a 3,3-DMT ligand bridging the two mutually bonded manganese metal atoms by using both lone pairs of electrons on the sulfur atom, Mn–Mn = 2.8243 (9) Å. Complex **2** reacted with HCl at 25 °C to yield the complex $[Mn(CO)_3(\overline{SCH_2CMe_2C}H_2)(\mu\text{-Cl})]_2$ (**3**) in 84% yield and $HMn(CO)_5$. The structure of complex **3** was determined by single-crystal X-ray diffraction analyses. In the solid state the molecule contains two manganese atoms bridged by two chlorine atoms, Mn···Mn = 3.578 (1) Å. There are two 3,3-DMT ligands terminally coordinated in axial sites one on each metal atom with an overall trans geometry. IR and ^1H NMR spectra of **3** indicate that it exists in solution as a mixture of isomers. For **1**: space group = *Pbca*, $a = 12.018$ (2) Å, $b = 17.135$ (2) Å, $c = 16.669$ (2) Å, $Z = 8$, 1432 reflections, $R = 0.026$. For **2**: space group = $P2_1/c$, $a = 10.984$ (2) Å, $b = 9.052$ (2) Å, $c = 11.884$ (2) Å, $\beta = 90.94$ (1)°, $Z = 2$, 1298 reflections, $R = 0.023$.

Introduction

Recently we have been studying the ring-opening transformations of thietane ligands on metal cluster carbonyl complexes. A number of ring-opening processes have now been identified.[1-8]

Thermal transformations result in the insertion of a metal atom into one of the carbon–sulfur bonds to yield the formation of a thiametallacycle (e.g., eq 1).[1-3] Similar results are achieved by photochemical stimulation (e.g. eq 2).[4,5]

We have also shown that the bridging thietane ligands undergo facile ring opening by nucleophilic addition in the

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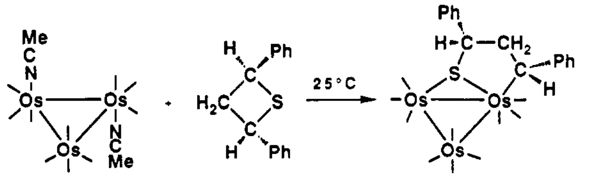
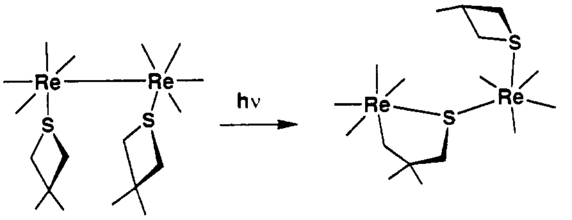
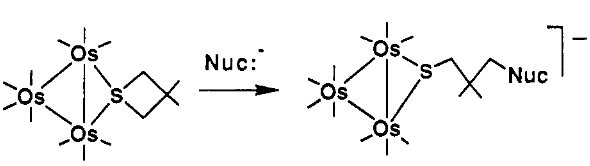


(1)



(2)

complexes $Os_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$,[6] $Os_3(CO)_9[\mu\text{-}\overline{SCH_2CMe_2CH_2}](\mu_3\text{-}S)$,[7] and $Os_4(CO)_{13}[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$,[8] and $Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2CH_2}](\mu\text{-}H)_3$[9] to yield clusters which contain bridging thiolato ligands (e.g. eq 3). The carbon–sulfur bond cleavage mechanism has been shown to occur by a backside nucleophilic attack at the carbon atom and is accompanied by an inversion of configuration at that site.[6] We have also reported the first example of a facile, head-to-tail ring-opening oligomerization of 3,3-dimethylthietane, 3,3-DMT, through a process that is initiated by a bridging coordination of the first 3,3-DMT molecule to the triosmium cluster.[10] Herein, we report the synthesis and characterization of the dimanganese complexes $Mn_2(CO)_9(\overline{SCH_2CMe_2CH_2})$ (1) and $Mn_2(CO)_8[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$ (2) and the results of a study of the reaction of 2 with HCl.



(3)

Experimental Section

General Data. Reagent grade solvents were stored over 4-Å molecular sieves. The compounds $Mn_2(CO)_9(NCMe)$[11] and 3,3-dimethylthietane[12] were prepared by the published procedures. Trimethylamine *N*-oxide dihydrate (Aldrich) was dehydrated by using a Dean–Stark apparatus with benzene as the solvent prior to use. All reactions were performed under a nitrogen atmosphere unless specified otherwise. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ^1H NMR spectra were run on either a Bruker AM-300 or AM-500 spectrometer operating at 300 or 500 MHz, respectively. Chromatographic separations were performed in air on Analtech 250-μm $F_{25}34$ silica gel HLF Uniplates. Silica gel (70–230 mesh, 60 (Å) was purchased from Aldrich. Mass spectra were obtained on a VG model 70SQ spectrometer using electron impact ionization. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Preparation of $Mn_2(CO)_9(\overline{SCH_2CMe_2CH_2})$ (1). A 734.8-mg amount (1.82 mmol) of $Mn_2(CO)_9(NCCH_3)$ was dissolved in 80 mL of CH_2Cl_2. A 240-μL amount (2.21 mmol) of 3,3-dimethylthietane was added to the solution. The mixture was heated to reflux for 2.5 h. The solvent was removed by rotary evaporation. The residue was dissolved in a minimum of CH_2Cl_2 and transferred to silica gel TLC plates. Elution with a hexane/CH_2Cl_2 9/1 solvent mixture yielded $Mn_2(CO)_9(\overline{SCH_2CMe_2CH_2})$ (1) 677.0 mg, 80% as a bright yellow band. For 1: IR (ν(CO) cm^{-1} in hexane) 2089 (m), 2018 (s), 2007 (m), 1989 (vs), 1977 (m), 1966 (m), 1937 (m). ^1H NMR (δ in $CDCl_3$) 3.21 (s, 4 H), 1.35 (s, 6 H). Mass spectral analysis (70 eV, 90 °C) m/z for $^{55}Mn = 464 - 28x$, $x = 0$–9 $\{[M]^+ - x(CO)\}$. Anal. Calcd for 1: C, 36.22; H, 2.17. Found: C, 36.09; H, 2.19.

Table I. Crystal Data for Compounds 2 and 3

	2	3
empirical formula	$Mn_2SO_8C_{13}H_{10}$	$Mn_2Cl_2S_2O_6C_{16}H_{20}$
formula wt	436.15	553.23
cryst syst	orthorhombic	monoclinic
lattice parameters		
a (Å)	12.018 (2)	10.984 (2)
b (Å)	17.135 (2)	9.052 (2)
c (Å)	16.669 (2)	11.884 (2)
β (deg)		90.94 (1)
V (Å^3)	3433 (1)	1181.5 (3)
space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
Z value	8	2
D_{calc} (g/cm^3)	1.69	1.55
μ (Mo Kα) (cm^{-1})	20	20
$2\theta_{max}$ (deg)	43.2	45.0
no. of obsns ($I > 3\sigma(I)$)	1432	1298
no. of variables	217	167
residuals: R, R_w	0.026, 0.027	0.023, 0.026
goodness-of-fit indicator	1.45	1.43
max shift in final cycle	0.00	0.05
largest peak in final diff map, e$^-$/Å^3	0.19	0.16
absorption correction	empirical	empirical

Reaction of 1 with Me_3NO. A 102.2-mg amount (0.220 mmol) of 1 was dissolved in 15 mL of CH_2Cl_2. A solution containing 20.0 mg (0.27 mmol) of Me_3NO dissolved in 5 mL of CH_2Cl_2 was added dropwise over 5 min. The mixture was stirred for an additional 30 min at 25 °C. The solvent was then removed by rotary evaporation. The residue was dissolved in a minimum CH_2Cl_2 and transferred to silica gel TLC plates. Elution with a hexane/CH_2Cl_2 7/3 solvent mixture yielded 58.1 mg of unreacted 1 and 11.2 mg of $Mn_2(CO)_8(\mu\text{-}\overline{SCH_2CMe_2CH_2})$ (2), 27%, as an orange band. For 2: IR (ν(CO) cm^{-1} in hexane) 2073 (m), 2015 (s), 1993 (m), 1983 (vs), 1952 (m), 1940 (m). ^1H NMR (δ in $CDCl_3$) 3.52 (s, 4 H), 1.56 (s, 6 H). Mass spectral analysis (70 eV, 120 °C) m/z for $^{55}Mn = 436 - 28x$, $x = 0$–8 $\{[M]^+ - x(CO)\}$. Anal. Calcd for 2: C, 35.80; H, 2.31. Found: C, 35.59; H, 2.24.

Reaction of 2 with HCl. A 26.4-mg amount (0.057 mmol) of 2 was dissolved in 20 mL of hexane. Aqueous 6 M HCl (1 mL) was added. The mixture was stirred at 25 °C for 17 h. An IR spectrum of the reaction solution showed absorptions at 2100 (w), 2056 (m), 2046 (w), 2022 (s), 2016 (vs), 2009 (m), 2000 (w), 1984 (w), 1967 (m), and 1959 (w). The two absorptions at 2016 (vs) and 2007 (s) are characteristic of $HMn(CO)_5$.[13] The solvent was removed by rotary evaporation and the residue was purified by recrystallization from hexane at 5 °C to yield 14.1 mg of yellow $[Mn(CO)_3(\overline{SCH_2CMe_2CH_2})(\mu\text{-}Cl)]_2$, *trans*-3, 84%. For 3: IR (ν(CO) cm^{-1} in hexane) 2053 (m), 2045 (m), 2034 (s), 1977 (w), 1969 (w), 1955 (s), 1944 (m), 1931 (vs). Upon dissolution in chloroform the spectrum changed dramatically. After 15 min the following absorptions were observed: 2102 (w), 2028 (vs), 2016 (sh), 1965 (m). When the solvent was removed and the residue was redissolved in hexane, the following absorptions were observed: 2100 (w), 2022 (vs), 2012 (w), 1967 (m), 1959 (m), 1931 (w), but over a period of 1–2 h the absorptions of *trans*-3 reappeared, although a complete conversion back to *trans*-3 did not occur. ^1H NMR (δ in C_6D_6): 2.99 (s), 2.89 (br, s), 2.81 (br, s), 0.89 (s), 0.84 (s) relative intensities: approximately 5:1:1:4:1. ^1H NMR (δ in $CDCl_3$): 3.76 (s), 3.48 (s), 3.37 (s), 3.34 (br, s), 3.18 (br, s), 1.64 (s), 1.48 (s), 1.46 (sh), 1.36 (s) relative intensities: approximately 3:3:1:1:1:2:2:1:3. The resonances in NMR samples of 3 quickly broadened over a short period of time. This effect could be slowed to a few hours if the samples were prepared under nitrogen by using carefully degassed solvents. The broadening

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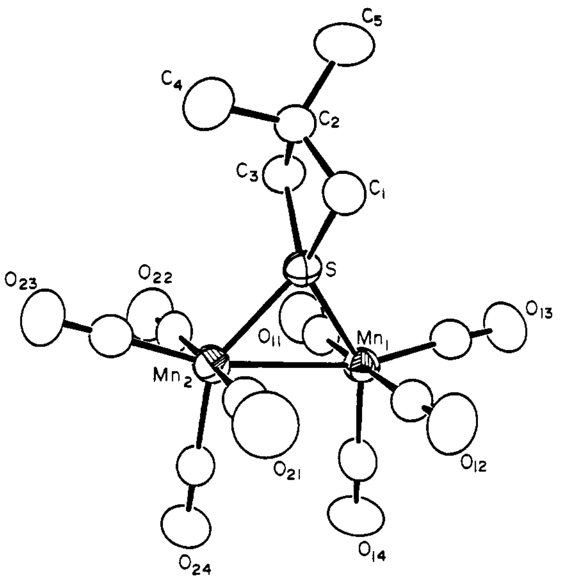

Figure 1. ORTEP diagram of $Mn_2(CO)_8[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$ (2) showing 50% probability thermal ellipsoids.

is believed to be due to the formation of small amounts of paramagnetic decomposition products. Anal. Calcd for **3**: C, 34.74; H, 3.64. Found: C, 34.32; H, 3.46.

Crystallographic Analyses. Red crystals of **2** were grown from solution in benzene solvent at 5 °C. Yellow crystals of **3** were grown from solution in hexane solvent at 5 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation. The unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6S automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of these analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[14a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[14b] Lorentz polarization (Lp) and absorption corrections were applied in each analysis. Full-matrix least-squares refinements minimized the function

$$\sum_{hkl} w(|F_o| - |F_c|)^2$$

where

$$w = 1/\sigma(F)^2, \quad \sigma(F) = \sigma(F_o^2)/2F_o$$

$$\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$$

Compound **2** crystallized in orthorhombic crystal system. The space group *Pbca* was identified uniquely based on the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound **3** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified uniquely based on the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located crystallographically and successfully refined using isotropic thermal parameters.

Table II. Positional Parameters and *B*(eq) Values (Å²) for $Mn_2(CO)_8(SCH_2CMe_2CH_2)$, 2

atom	*x*	*y*	*z*	*B*(eq)
Mn(1)	0.35262 (05)	0.21509 (03)	0.14964 (04)	3.04 (3)
Mn(2)	0.36036 (05)	0.33608 (03)	0.03472 (04)	3.14 (3)
S	0.36900 (08)	0.34225 (06)	0.16704 (06)	2.90 (5)
O(11)	0.5991 (03)	0.19576 (19)	0.1515 (02)	5.9 (2)
O(12)	0.1055 (03)	0.22775 (19)	0.1588 (02)	5.5 (2)
O(13)	0.3439 (03)	0.12505 (19)	0.29946 (19)	5.4 (2)
O(14)	0.3358 (03)	0.08161 (19)	0.0371 (02)	6.5 (2)
O(21)	0.1154 (03)	0.3631 (02)	0.0327 (02)	6.3 (2)
O(22)	0.6077 (03)	0.32931 (19)	0.0227 (02)	6.0 (2)
O(23)	0.3785 (03)	0.48644 (17)	−0.04995 (20)	5.6 (2)
O(24)	0.3446 (03)	0.22248 (17)	−0.09865 (19)	5.7 (2)
C(1)	0.2876 (03)	0.4059 (02)	0.2338 (03)	3.5 (2)
C(2)	0.3916 (04)	0.4557 (02)	0.2517 (03)	3.6 (2)
C(3)	0.4770 (03)	0.3935 (02)	0.2243 (03)	3.7 (2)
C(4)	0.3958 (04)	0.5274 (03)	0.1977 (03)	5.0 (3)
C(5)	0.4038 (05)	0.4790 (03)	0.3393 (03)	6.1 (3)
C(11)	0.5047 (04)	0.2044 (02)	0.1485 (03)	4.0 (2)
C(12)	0.2006 (04)	0.2239 (02)	0.1528 (03)	3.7 (2)
C(13)	0.3478 (04)	0.1623 (02)	0.2427 (03)	3.8 (2)
C(14)	0.3414 (04)	0.1337 (03)	0.0798 (03)	4.1 (2)
C(21)	0.2083 (04)	0.3501 (03)	0.0349 (03)	4.0 (2)
C(22)	0.5127 (04)	0.3301 (02)	0.0291 (03)	3.9 (2)
C(23)	0.3714 (04)	0.4284 (03)	−0.0165 (03)	3.8 (2)
C(24)	0.3498 (04)	0.2665 (02)	−0.0472 (03)	3.8 (2)

Table III. Intramolecular Distances for 2[a]

atom	atom	dist	atom	atom	dist
Mn(1)	Mn(2)	2.8243 (9)	Mn(2)	C(22)	1.837 (5)
Mn(1)	S	2.207 (1)	Mn(2)	C(23)	1.803 (5)
Mn(1)	C(11)	1.837 (5)	Mn(2)	C(24)	1.818 (5)
Mn(1)	C(12)	1.834 (5)	S	C(1)	1.841 (4)
Mn(1)	C(13)	1.796 (5)	S	C(3)	1.835 (4)
Mn(1)	C(14)	1.821 (5)	C(1)	C(2)	1.543 (5)
Mn(2)	S	2.211 (1)	C(2)	C(3)	1.549 (5)
Mn(2)	C(21)	1.843 (5)	O	C(av)	1.144 (5)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Results

The reaction of $Mn_2(CO)_9(NCMe)$ with 3,3-DMT produced complex **1** in 80% yield by simple ligand substitution. Complex **1** was characterized by IR, ^1H NMR, and mass spectroscopies and elemental analysis. On the basis of spectroscopic evidence, we believe the structure of **1** to be the mono-substituted 3,3-DMT derivative of $Mn_2(CO)_{10}$, $Mn_2(CO)_9(\overline{SCH_2CMe_2CH_2})$, analogous to the known compound $Re_2(CO)_9(\overline{SCH_2CMe_2CH_2})$ that has been characterized crystallographically and has the 3,3-DMT ligand coordinated in an equatorial site (cis) to the metal–metal bond.[4] Treatment of **1** with Me_3NO yielded the complex $Mn_2(CO)_8[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$, **2**, in 27% yield. The molecular structure of this complex was established by single-crystal X-ray analysis. An ORTEP drawing of the molecular structure of **2** is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV. This molecule consists of two metal atoms with four terminal carbonyl ligands coordinated to each metal atom. The two manganese atoms are bridged by the sulfur atom of the 3,3-DMT ligand by the coordination of both lone pairs of electrons on the sulfur atom, one to each metal atom. This is the first example of a thietane ligand bridging two metal atoms from the first transition series. The Mn–S distances are 2.207 (1) and 2.211 (1) Å. The

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(14) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *Ibid.* Table 2.3.1, pp 149–150.

Table IV. Intramolecular Bond Angles for 2[a]

atom	atom	atom	angle
Mn(2)	Mn(1)	S	50.31 (3)
S	Mn(1)	C(11)	90.6 (1)
S	Mn(1)	C(12)	90.2 (1)
S	Mn(1)	C(13)	112.8 (1)
S	Mn(1)	C(14)	147.8 (1)
Mn(1)	Mn(2)	S	50.20 (3)
S	Mn(2)	C(21)	92.2 (1)
S	Mn(2)	C(22)	90.4 (2)
S	Mn(2)	C(23)	115.3 (1)
S	Mn(2)	C(24)	141.7 (1)
Mn(1)	S	Mn(2)	79.48 (4)
Mn(1)	S	C(1)	128.1 (1)
Mn(1)	S	C(3)	127.2 (1)
Mn(2)	S	C(1)	127.4 (1)
Mn(2)	S	C(3)	125.1 (1)
C(1)	S	C(3)	77.2 (2)
S	C(1)	C(2)	90.8 (2)
C(1)	C(2)	C(3)	95.7 (3)
S	C(3)	C(2)	90.8 (3)
Mn	C	O(av)	177.2 (4)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

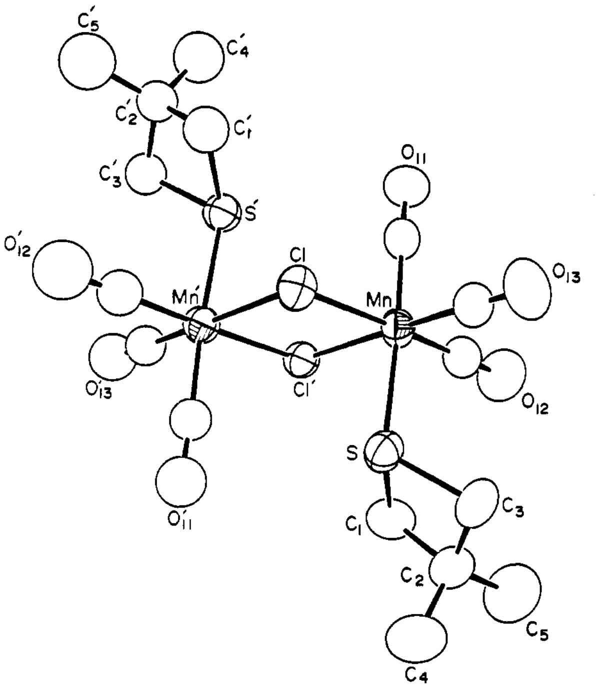


Figure 2. ORTEP diagram of $[\mathrm{Mn(CO)_3(\overline{SCH_2CMe_2C}H_2)}(\mu\text{-}\mathrm{Cl})]_2$ (*trans*-**3**) showing 50% probability thermal ellipsoids.

Mn–S–Mn angle at the sulfur atom is small, 79.48 (4)°, but is similar to that found in $\mathrm{Os_3(CO)_{10}}[\mu\text{-}\mathrm{\overline{SCH_2CMe_2C}H_2}]$, 73.1°. Both are much smaller than that is $\mathrm{Os_3(CO)_9}[\mu\text{-}\mathrm{\overline{SCH_2CMe_2C}H_2}](\mu_3\text{-}\mathrm{S})$, 104.3 (1)°, where the sulfur-bridged metal atoms are not mutually bonded. The thietane ring is slightly puckered; the C–S–C, C–C–C dihedral angle is 24.7°, as observed for other bridging thietane ligands.[7-10] The Mn–Mn bond distance of 2.8243 (9) Å is significantly shorter than that found in $\mathrm{Mn_2(CO)_{10}}$, 2.9038 (6) Å, which is believed to contain a Mn–Mn single bond.[15] The shortness of the Mn–Mn bond in **2** can be attributed to the bridging DMT ligand. Each metal atom in **2** will have an 18-electron configuration in the presence of a Mn–Mn single bond.

Table V. Positional Parameters and *B*(eq) Values (Å²) for $[\mathrm{MnCl(CO)_3(SCH_2CMe_2CH_2)}]_2$, 3

atom	*x*	*y*	*z*	*B*(eq)
Mn	0.37085 (4)	0.42707 (5)	0.42504 (3)	3.51 (2)
Cl	0.44044 (6)	0.45488 (8)	0.61767 (6)	3.81 (3)
S	0.29608 (7)	0.66992 (8)	0.44118 (6)	4.07 (4)
O(11)	0.4740 (2)	0.1259 (3)	0.4128 (2)	5.9 (1)
O(12)	0.2874 (3)	0.4050 (3)	0.1901 (2)	7.8 (2)
O(13)	0.1384 (2)	0.3057 (3)	0.4980 (2)	7.0 (1)
C(1)	0.3119 (3)	0.7847 (4)	0.3153 (4)	5.3 (2)
C(2)	0.1757 (3)	0.8255 (3)	0.3168 (3)	4.5 (2)
C(3)	0.1391 (3)	0.6951 (4)	0.3917 (3)	4.9 (2)
C(4)	0.1569 (5)	0.9712 (5)	0.3762 (5)	7.6 (3)
C(5)	0.1144 (6)	0.8273 (7)	0.2025 (4)	8.2 (3)
C(11)	0.4363 (3)	0.2423 (4)	0.4190 (3)	4.2 (1)
C(12)	0.3218 (3)	0.4131 (3)	0.2813 (3)	4.9 (2)
C(13)	0.2297 (3)	0.3526 (3)	0.4698 (3)	4.6 (2)

Table VI. Intramolecular Distances for 3[a]

atom	atom	dist	atom	atom	dist
Mn	Cl	2.4148 (9)	S	C(3)	1.827 (3)
Mn	Cl	2.3938 (8)	C(1)	C(2)	1.541 (4)
Mn	S	2.356 (1)	C(2)	C(3)	1.536 (4)
Mn	C(11)	1.823 (3)	C(2)	C(4)	1.512 (5)
Mn	C(12)	1.787 (4)	C(2)	C(5)	1.507 (5)
Mn	C(13)	1.780 (4)	Mn	Mn′	3.578 (1)
S	C(1)	1.832 (4)	O	C(av)	1.141 (4)

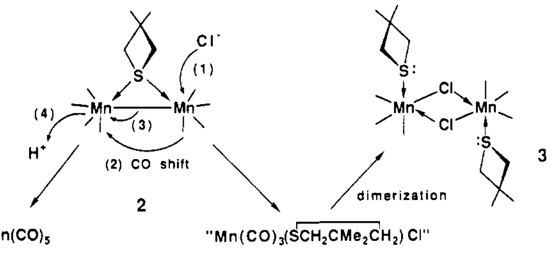
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table VII. Intramolecular Bond Angles for 3[a]

atom	atom	atom	angle
Cl	Mn	Cl	83.84 (3)
Cl	Mn	S	86.04 (3)
Cl	Mn	S	84.55 (3)
Mn	Cl	Mn	96.16 (3)
Mn	S	C(1)	115.2 (1)
Mn	S	C(3)	114.7 (1)
C(1)	S	C(3)	76.6 (2)
S	C(1)	C(2)	91.2 (2)
C(1)	C(2)	C(3)	94.9 (2)
S	C(3)	C(2)	91.6 (2)
Mn	C	O(av)	178.4 (3)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Compound **2** reacted with HCl in hexane at 25 °C to yield the complex $[\mathrm{MnCl(CO)_3(\overline{SCH_2CMe_2C}H_2)}]_2$ (*trans*-**3**, 84%, eq 4). Evidence for the coproduct $\mathrm{HMn(CO)_5}$ was obtained by IR spectroscopy of the reaction solutions, but this product was not isolated. Complex *trans*-**3** was characterized by IR, ¹H NMR, and a single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **3** is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected interatomic distances and angles are listed in Tables VI and VII. This complex contains two chlorine bridged metal atoms. The Mn–Cl bond distances are 2.4148 (9) and 2.3938 (8) Å. There is no metal–metal bond, Mn⋯Mn = 3.578 (1) Å. The Mn–Cl–Mn bond angle is 96.16 (3)°. The structure is related to the family of dihalo-bridged manganese carbo-



(4)

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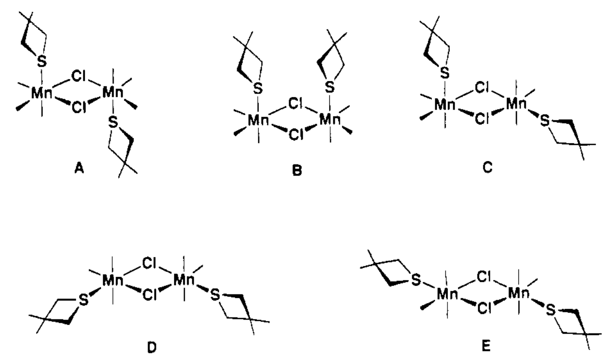

Figure 3. All nonequivalent geometric isomers of 3.

nyls, $[Mn(CO)_4(\mu\text{-}X)]_2$, X = Cl, Br, I. The bromo complex was structurally characterized by Dahl.[16] Each metal atom has one 3,3-DMT ligand and three CO ligands in terminal coordination sites. The Mn–S bond distance, 2.356 (1) Å, is significantly longer than that in **2**, where the 3,3-DMT ligand is in a bridging position. Overall, the molecule contains a center of symmetry (crystallographically imposed) which requires the molecule to have a geometry with *trans*-3,3-DMT ligands. Interestingly, when dissolved in the polar solvent chloroform, new absorptions appeared at 2102 (w), 2028 (vs), 2016 (sh), and 1965 (m) in a period of 5–10 min, and those observed in hexane were virtually absent. When the chloroform solvent was removed and the residue was redissolved in hexane, the absorptions of *trans*-**3** reappeared in the IR spectrum over 1–2 h, but complete conversion back to *trans*-**3** did not occur. Even in pure hexane solvent the absorptions of the new species appeared and grew to approximately 10–15% of the total intensity from solutions of pure *trans*-**3** over 2–3 h. Attempts to follow this transformation by ^1H NMR spectroscopy were unsuccessful. The ^1H NMR spectrum of **3** in $CDCl_3$ showed two sharp singlets at 3.76 and 3.48 ppm, one small singlet at 3.37 ppm, and two small broad singlets at 3.34 and 3.18 ppm in an approximately 3:3:1:1:1 relative ratio due to methylene protons. Three sharp singlets at 1.64, 1.48, and 1.36 ppm and a shoulder at 1.46 ppm were observed for the methyl protons in a relative ratio of 2:2:3:1. The ^1H NMR in benzene-d_6 showed one singlet at 2.99 ppm and two weaker broad singlets at 2.89 and 2.81 ppm in a 5:1:1 relative ratio due to the methylene protons. In addition, two singlets at 0.89 and 0.84 ppm with the relative intensities of 4:1 were observed for the methyl protons. Evidently, several slowly interconverting isomers are present in these solutions. The observation of sharp singlets for most of the methylene protons and singlets for averaged methyl resonances indicates that the 3,3-DMT ligands are rapidly inverting their configurations at the pyramidal sulfur atoms in most of the isomers;[17] however, broadness in a few of the resonances may be caused by an incomplete dynamical averaging at the inverting sulfur atom.

Discussion

The complex $Mn_2(CO)_8[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$ (**2**) containing a bridging 3,3-DMT ligand was prepared in a two-step reaction sequence via the isolable intermediate $Mn_2(CO)_9(\overline{SCH_2CMe_2CH_2})$ (**1**). In previous studies we showed that bridging thietane ligands in osmium complexes undergo facile ring-opening addition of Cl^- upon reaction with HCl or halide salts. In an effort to extend the scope of this ring-opening reaction to metal complexes of the first transition series, we have examined the reaction of **2** with HCl. However, we have found that the bridging thietane in **2** does not open in this reaction. Instead, chloride was added to one of the metal atoms. The reaction is proposed to occur as shown in the scheme. A multistep process involving (1) chloride addition, (2) a CO ligand shift accompanied by (3) a heterolytic cleavage of the metal–metal bond, and (4) protonation at the other metal atom would lead to formation of the $HMn(CO)_5$ and a 16-electron species "$Mn(CO)_3(\overline{SCh_2CMe_2CH_2})Cl$". The latter could combine with a similar species to yield the dimer **3** with bridging chloro ligands in which the metal atoms would have 18-electron configurations.

If the structure of **3** as found in the solid state (C_i symmetry) persists in solution, then only three of the six CO stretching vibrations would be IR active. Indeed, three strong absorptions were observed in the IR spectrum of **3** in hexane solvent, but several small absorptions were also seen. These small absorptions could be due to the formation of small amounts of conformational isomers formed by rotation of the thietane ligands about the Mn–S bonds.[18]

The dramatic changes in the IR spectrum observed when *trans*-**3** was dissolved in chloroform indicate the formation of still other species, presumably polar geometric isomer(s). These species could not be isolated and could be converted back to *trans*-**3** to a significant extent by removing the chloroform solvent and redissolving in hexane. The structures of all possible geometric isomers of **3** are shown in Figure 3. Isomer A is the one found in the solid state. Isomer E is considered unlikely for the new species in chloroform solvent since its structure is nonpolar. Isomers B–D are polar, and none can be ruled out by the data. Isomer B seems most attractive because CO ligands are not located opposite to one another in axial positions as found in A.

Conclusion

The reaction of Me_3NO with the complex $Mn_2(CO)_9(\overline{SCH_2CMe_2CH_2})$ resulted in the loss of one molecule of CO. As a result, the thietane ligand was converted to a bridging position to utilize both of its lone pairs of electrons in coordination. In contrast to the reactions of bridging 3,3-DMT ligands in other complexes, thietane ring opening did not occur in the reaction of **2** with HCl. Instead, the dimer **3** and $HMn(CO)_5$ were formed by HCl addition at the metal atoms.

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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

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