Evidence for the formation of Mn2(CO)9(CS)

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*Cp*PPh$_2$), 72.4 (d, J = 3 Hz, *Cp*PPh$_2$), 70.6 (Cp). ^{31}P NMR ($CDCl_3$): δ 12.8. IR (CH_2Cl_2): $\nu_{C=O}$ 1682 cm^{-1}. Anal. Calcd for $C_{23}H_{19}FeOP$: C, 69.37; H, 4.81. Found: C, 69.30; H, 4.86.

***N*-[(1*R*)-(+)-1-Phenylethyl][1′-(diphenylphosphino)-1-ferrocenyl]methylimine (6).** A benzene (20 mL) solution containing **5** (0.50 g, 1.3 mmol), (*R*)-methylbenzylamine (0.16 g, 1.3 mmol), and camphorsulfonic acid (5 mg) was heated at 40 °C for 2 h. The solvent was removed under reduced pressure to afford crude **6** as an orange oil. This product was used in the preparation of 7 below. ^{1}H NMR ($CDCl_3$): δ 7.88 (s, 1 H, C*H*=N), 7.42–7.26 (m, 15 H, phenyls), 4.63 (q, J = 1.6 Hz, 1 H, Cp), 4.57 (q, J = 1.7 Hz, 1 H, Cp), 4.32–4.24 (m, 5 H, Cp and C*H*Me), 4.06–4.02 (m, 2 H, Cp), 1.50 (d, J = 6.6 Hz, 3 H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 159.2 (*C*H=N), 145.2 (ipso phenyl from amine), 138.8 (d, J = 8 Hz, doubled due to chiral environment, ipso carbon of P*Ph*), 133.4 (d, J = 19 Hz), 128.8 (Ph), 128.2 (Ph), 128.2 (d, J = 13 Hz, P*Ph*), 126.6 (Ph), 126.5 (Ph), 81.2 (ipso Cp carbon), 73.8 (d, J = 15 Hz, CpPPh$_2$), 73.7 (d, J = 15 Hz, CpPPh$_2$), 71.9 (apparent triplet, J = 3 Hz, Cp), 71.6 (*C*HCH$_3$), 69.9 (Cp), 69.3 (d, J = 9 Hz), 24.2 (*C*H$_3$). ^{31}P NMR ($CDCl_3$): δ 12.0.

1′-(Diphenylphosphino)-1-[((*R*)-methylbenzylamino)methyl]ferrocene (7). To a THF solution (10 mL) chilled to 0 °C containing $LiAlH_4$ (0.10 g, 2.6 mmol) was added a THF solution (5 mL) containing **6** (0.48 g, 0.96 mmol) in one portion. The cooling bath was removed and the mixture allowed to react for 2 h. The mixture was quenched (0.1 g of H_2O, 0.1 g of 10% NaOH, 0.3 g of H_2O), dried over K_2CO_3, and filtered, and the solvent removed under reduced pressure. The crude product was subjected to column chromatography with use of gradient elution (0% to 5% MeOH in CH_2Cl_2). The major yellow band was collected and the solvent removed to afford **7** as an orange oil (0.40 g, 83%). ^{1}H NMR ($CDCl_3$): δ 7.32–7.25 (m, 15 H, phenyls), 4.26 (t, J = 1.8 Hz, 2 H, Cp), 4.06 (t, J = 1.8 Hz, 2 H, Cp), 4.04–3.96 (m, 4 H, Cp), 3.73 (q, J = 6.6 Hz, 1 H, C*H*CH$_3$), 3.20 (d, J = 13 Hz, 1 H, C*H*$_2$), 3.15 (d, J = 13 Hz, 1 H, C*H*$_2$), 1.53–1.42 (br s, 1 H, N*H*), 1.31 (d, J = 6.6 Hz, 3 H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 145.9 (ipso phenyl, amine), 139.1, 139.0 (d's, J = 10 Hz, ipso P*Ph*$_2$, doubled due to the chiral environment), 133.4 (d's, J = 20 Hz, 0.01 ppm difference for d's), 128.5 (doubling observed), 128.1 (d's, J = 7 Hz, doubling observed), 126.9, 126.7 (phenyl C's of amine), 87.8 (ipso of *Cp*CH$_2$NHR*), 75.9 (ipso of *Cp*PPh$_2$), 73.2 (d, J = 14 Hz, *Cp*PPh$_2$), 71.3 (d, J = 4 Hz, *Cp*PPh$_2$), 69.5, 69.2, 69.0, 68.9 (*Cp*CH$_2$NHR*), 57.6 (benzylic *C*H), 46.2 (CH$_2$), 24.6 (CH$_3$). ^{31}P NMR ($CDCl_3$): δ 11.6. Anal. Calcd for $C_{31}H_{30}FeNP$: C, 73.97; H, 6.01. Found: C, 74.20; H, 6.18.

1′-(Tri-*n*-butylstannyl)-1-ferrocenecarboxaldehyde (8). Compound 8 was prepared from **1** (2.07 g, 2.71 mmol) in a manner similar to that above (i.e. **5**). Purification was achieved by using column chromatography with gradient elution (0% to 5% ethyl acetate in hexane) to afford **8** as a red oil (1.10 g, 82%). ^{1}H NMR ($CDCl_3$): δ 9.95 (s, 1 H, C*H*O), 4.74 (t, J = 1.8 Hz, 2 H, Cp), 4.53 (t, J = 1.8 Hz, 2 H, Cp), 4.48 (t, J = 1.6 Hz, 2 H, Cp), 4.10 (t, J = 1.6 Hz, 2 H, Cp), 1.60–1.51 (m, 6 H, C*H*$_2$), 1.39–1.32 (m, 6 H, C*H*$_2$), 1.06–1.01 (m, 6 H, C*H*$_2$), 0.92 (t, J = 7.2 Hz, 9 H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 193.4 (C=O), 75.9 (Cp), 73.2 (Cp), 72.1 (Cp), 69.5 (Cp), 29.1 (CH$_2$), 27.4 (CH$_2$), 13.7 (CH$_2$), 10.2 (CH$_3$). Anal. Calcd for $C_{23}H_{36}FeOSn$: C, 54.91; H, 7.21. Found: C, 54.98; H, 7.24.

1′-(Tri-*n*-butylstannyl)-1-[(dimethylamino)methyl]ferrocene (9). A methanol solution (20 mL) containing camphorsulfonic acid (0.45 g, 1.9 mmol) was saturated with dimethylamine while being chilled in an ice bath. A methanol solution containing 8 (1.07 g, 2.13 mmol) was transferred to the amine/methanol mixture and stirred for 2 min; then $NaBH_3CN$ (0.50 g, 7.6 mmol) was added in one portion. The cooling bath was removed and the mixture stirred for an additional 30 min. The mixture was diluted with ether (100 mL) and washed with water (3 × 100 mL), brine (100 mL), and then dried over K_2CO_3. The solvent was removed and the crude product purified by chromatography employing gradient elution (0 to 15% ethyl acetate in hexane). The third yellow band was collected to afford pure **9** (0.70 g, 62%). ^{1}H NMR ($CDCl_3$): δ 4.27 (t, J = 1.7 Hz, 2 H, Cp), 4.11 (t, J = 1.8 Hz, 2 H, Cp), 4.04 (t, J = 1.8 Hz, 2 H, Cp), 3.95 (t, J = 1.7 Hz, 2 H, Cp), 3.27 (s, 2 H, C*H*$_2$), 2.16 (s, 6 H, NC*H*$_3$), 1.60–1.51 (m, 6 H, C*H*$_2$), 1.39–1.32 (m, 6 H, C*H*$_2$), 1.05–1.01 (m, 6 H, C*H*$_2$), 0.92 (t, J = 7.2 Hz, 9 H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 83.1 (ipso *Cp*CH$_2$), 74.9 (Cp), 71.0 (w satellites, *Cp*Sn), 70.0 (*Cp*CH$_2$), 68.9 (ipso *Cp*Sn), 68.0 (*Cp*CH$_2$), 59.4 (Cp*C*H$_2$), 44.8 (N*C*H$_3$), 29.2 (CH$_2$), 27.4 (CH$_2$), 13.7 (CH$_2$), 10.3 (CH$_3$). Anal. Calcd for $C_{25}H_{43}FeNSn$: C, 56.43; H, 8.15. Found: C, 56.37; H, 8.25.

1′-(Diphenylphosphino)-1-[(dimethylamino)methyl]ferrocene (10). A THF solution (10 mL) of **9** (0.50 g) maintained at −78 °C was treated with *n*-BuLi and allowed to react for an additional 30 min. Ph_2PCl was added to the mixture and the cooling bath removed. The mixture was diluted with ether and an aqueous workup applied. Final purification was achieved by column chromatography on alumina with CH_2Cl_2/MeOH as eluant (gradient elution) to afford analytically pure **10** as an orange solid (0.35 g, 86%, mp 106–108 °C). ^{1}H NMR ($CDCl_3$): δ 7.40–7.27 (m, 10 H, phenyls), 4.32 (t, J = 1.7 Hz, 2 H, Cp), 4.10 (t, J = 1.7 Hz, 2 H, Cp), 4.05 (q, J = 1.8 Hz, 2 H, Cp), 4.02 (t, J = 1.8 Hz, 2 H, Cp), 2.98 (s, 2 H, C*H*$_2$NMe$_2$), 2.10 (s, 6 H, NC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 139.2 (d, J = 10 Hz, ipso P*Ph*), 133.4 (d, J = 20 Hz, phenyl), 128.5 (phenyl), 128.1 (d, J = 7 Hz), 84.0 (ipso *Cp*CH$_2$), 73.3 (d, J = 15 Hz, *Cp*PPh$_2$), 71.3 (d, J = 4 Hz, *Cp*PPh$_2$), 71.2 (*Cp*CH$_2$, 69.3 (*Cp*CH$_2$), 58.5 (CH$_2$), 44.7 (CH$_3$). ^{31}P NMR ($CDCl_3$): δ 11.8. Anal. Calcd for $C_{25}H_{26}FeNP$: C, 70.27; H, 6.13. Found: C, 70.00; H, 6.21.

Transmetalation Study of 1,1′-Bis(tri-*n*-butylstannyl)ferrocene with More Than 1 Equiv of *n*-BuLi. A THF solution (20 mL) of **1** (0.98 g, 1.3 mmol) was treated with *n*-BuLi (3.9 mmol) and allowed to react at −78 °C for 1 h. The mixture was quenched with an excess of methanol (20 molar equiv), and solvents were removed under reduced pressure. The product ratio (ferrocene/1-(tri-*n*-butylstannyl)ferrocene[12]) was determined by NMR spectroscopy.

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Registry No. 1, 12291-11-1; 3, 124944-39-4; 5, 124944-40-7; 6, 124944-41-8; 7, 124944-42-9; 8, 124944-43-0; 9, 124944-44-1; 10, 124944-45-2; DMF, 68-12-2; $(C_5H_4Li)_2Fe$, 32677-77-3; Bu_3SnCl, 1461-22-9; Ph_2PCl, 1079-66-9; (*R*)-methylbenzylamine, 3886-69-9; dimethylamine, 124-40-3.

Evidence for the Formation of $Mn_2(CO)_9(CS)$

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Summary: The reaction of $[Mn(CO)_5]^-$ with $SCCl_2$ in pentane at room temperature produces minor amounts of a mixture of $Mn_2(CO)_9CS$ and $Mn_2(CO)_{10}$, isolated from the solution. The main reaction product, which is insoluble in pentane, consists of a CO- and Cl-containing ionic material. In the presence of 18-crown-6, $[K(18\text{-crown-}6)][Mn(CO)_4Cl_2]$ is formed exclusively. The thiocarbonyl derivative, which could not be separated from $Mn_2(CO)_{10}$, was identified and characterized by mass, IR, and ^{55}Mn NMR spectroscopic methods, which also showed that

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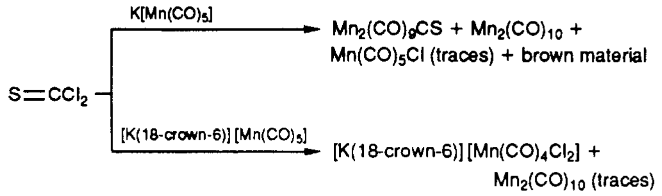
Scheme I



$Mn_2(CO)_9CS$ exists as a mixture of the cis and trans isomers. Further, the formation of $Mn_2(CO)_9CS$ was demonstrated by reactions with PPh_3 and Br_2.

Although the number of thiocarbonyl complexes has increased enormously in the course of the last few years, thiocarbonyl derivatives of binary carbonyl complexes of the type $M_x(CO)_y$, in which one or more CO groups are replaced by the homologous CS ligand, have been limited to $M(CO)_5CS$ (M = Cr, Mo, W)[2] and $Fe(CO)_4CS$;[3] no example of a binuclear or oligonuclear complex has been described. The four compounds were prepared from the corresponding carbonyl dianions and thiophosgene. The unstable species $Ni(CS)_4$ was identified by mass spectroscopy.[4] The development in the field of transition-metal thiocarbonyl compounds including seleno- and tellurocarbonyl analogues has been summarized in several review articles.[5-8]

In this paper, we describe the formation of $Mn_2(CO)_9CS$, the first thiocarbonyl derivative of zerovalent manganese, and the characterization of this complex by spectroscopy and chemical reactions.[9]

Results and Discussion

When $K[Mn(CO)_5]$ is allowed to react with $SCCl_2$ in pentane, a yellow solution is produced along with a dark brown solid as the main reaction product. From the solution a mixture of $Mn_2(CO)_9CS$ and $Mn_2(CO)_{10}$ can be isolated with an overall yield of about 14%. The dark brown solid is insoluble in pentane and other nonpolar solvents but soluble in THF. The nature of this material is as yet unclear. The IR spectrum exhibits no bands in the region of a terminal or bridging CS ligand. Some $Mn(CO)_5Cl$ can be separated from this material by sublimation.

When the reaction is carried out in the presence of 18-crown-6, the pentane-insoluble material is identified as $[K(18\text{-crown-}6)][Mn(CO)_4Cl_2]$ and is obtained in nearly 100% yield; only traces of $Mn_2(CO)_{10}$ and no CS-containing material are formed in this case (Scheme I). The IR bands of the $[Mn(CO)_4Cl_2]^-$ anion in the ν(CO) and δ(CO) region are not identical with the bands of the insoluble material formed in the absence of 18-crown-6. The latter is probably a mixture of oligomeric Cl- and CO-containing ionic species; $K[Mn(CO)_4Cl_2]$ is presumably present only as a minor component.

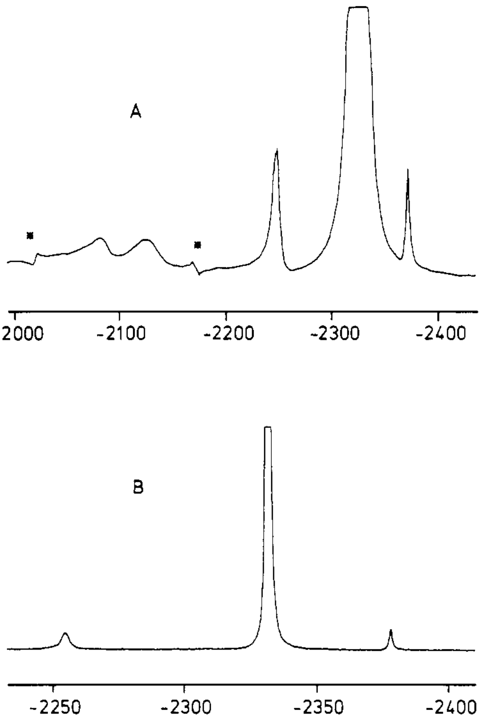
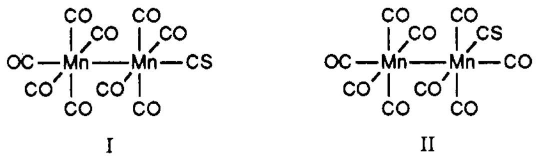


Figure 1. 89.28-MHz ^{55}Mn NMR spectrum of a mixture of $Mn_2(CO)_{10}$ (main signal) and $Mn_2(CO)_9CS$, isomers I and II (0.11 M in THF/THF-d_8): (A) sweep width 125 kHz, time domain 1024K, pulse width 10 μs, relaxation delay 0.5 s (the two peaks indicated with asterisks are due to the scanning technique); (B) section close to the main signal, resolution enhanced, sweep width 45.5 kHz, time domain 8200K.

Chart I



From the spectroscopic results, the content of $Mn_2(CO)_9CS$ in the mixture of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9CS$ has been estimated to be about 9%; this corresponds to about a 1.6% yield of the thiocarbonyl complex. Unfortunately, attempts to separate the two compounds chromatographically have thus far failed. Similar physical properties apparently prevent easy separation of the two complexes.

At present, nothing is known about the reaction mechanism. An electron transfer as the first step, generating the radical $[Mn(CO)_5]^\bullet$, can be proposed. Dimerization of this radical would explain the formation of $Mn_2(CO)_{10}$.

The presence of $Mn_2(CO)_9CS$ in the pentane-soluble material was evidenced by ^{55}Mn NMR, IR, and mass spectroscopy and by chemical reactions.

The IR spectrum of the $Mn_2(CO)_{10}/Mn_2(CO)_9CS$ mixture in a Nujol mull exhibits the characteristic pattern of $Mn_2(CO)_{10}$ in the ν(CO) region. However, at 1300 and 1280 cm^{-1}, two medium-strong bands appear, which are in the typical region for terminal CS groups. Additionally, the higher frequency band shows a shoulder at 1295 cm^{-1}. The expected ν(CO) bands for $Mn_2(CO)_9CS$ are covered by the strong bands of $Mn_2(CO)_{10}$, the major component.

$Mn_2(CO)_9CS$ was also detected by ^{55}Mn NMR spectroscopy. Besides the main signal for $Mn_2(CO)_{10}$ (−2326 ppm relative to $KMnO_4$ in H_2O), the spectrum exhibits four additional signals with lower intensities as shown in

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Table I. Mass Spectrum of the $Mn_2(CO)_{10}/Mn_2(CO)_9CS$ Mixture

ion ($Mn_2(CO)_{10}$)	*m/z* (rel intens)	ion ($Mn_2(CO)_9CS$)	*m/z* (rel intens)
	FI Mode		
$Mn_2(CO)_{10}$	390 (100)	$Mn_2(CO)_9CS$	406 (18)
	EI Mode		
$Mn_2(CO)_{10}$	390 (23.4)	$Mn_2(CO)_9CS$	
$Mn_2(CO)_9$		$Mn_2(CO)_8CS$	
$Mn_2(CO)_8$		$Mn_2(CO)_7CS$	
$Mn_2(CO)_7$		$Mn_2(CO)_6CS$	
$Mn_2(CO)_6$		$Mn_2(CO)_5CS$	
$Mn_2(CO)_5$	250 (39.8)	$Mn_2(CO)_4CS$	266 (1.7)
$Mn_2(CO)_4$	222 (94.4)	$Mn_2(CO)_3CS$	238 (1.6)
$Mn_2(CO)_3$	194 (40.6)	$Mn_2(CO)_2CS$	210 (2.0)
$Mn_2(CO)_2$	166 (40.2)	$Mn_2(CO)CS$	182 (1.7)
Mn_2CO	138 (13.1)	Mn_2CS	154 (3.3)
Mn_2	110 (100)		

Figure 1. Two of these are relatively sharp and close to the signal for $Mn_2(CO)_{10}$ (−2372 and −2248 ppm) with relative intensities of 1:2. The other two signals are broader and located at −2082 and −2125 ppm. The two sharp high-field signals can be attributed to the $Mn(CO)_5$ moieties, while the signals at lower field should correspond to the $Mn(CO)_4CS$ groups. The four signals and the appearance of two ν(CS) bands in the IR spectrum can be explained by the formation of two isomers that have the CS ligand either in an axial (trans to a $Mn(CO)_5$ group, isomer I) or in an equatorial (trans to a CO group, isomer II) position (Chart I). From the relative intensities, it follows that the pair of peaks at −2372 and −2082 ppm belongs to the minor isomer and the resonances at −2248 and −2125 ppm to the major isomer.

Shielding variations of a metal nucleus in a series of similar complexes are mainly influenced by the overall ligand strength, such that a ligand weaker than CO induces deshielding of the metal nucleus.[10] This has been shown, inter alia, for the $\delta(^{55}Mn)$ values of $Mn_2(CO)_9PPh_2Et$.[11] From various spectroscopic studies and theoretical considerations it was deduced that the electron-withdrawing capacity increases on going from CO to CS,[12] but CS is also a better σ-donor ligand than CO. From the $\delta(^{55}Mn)$ value for $Mn_2(CO)_9CS$ it is clear that, in a magnetochemical series of ligand strength, thiocarbonyl is an overall weaker ligand than CO in this Mn(0) complex. To assign the pairs of signals to the two isomers, one can use relaxation arguments: Isomer I, the trans isomer, with CS in the axial position, gives rise to a field gradient at the ^{55}Mn nucleus that is more than twice that of the cis isomer II.[13] Hence, coupling of the field gradient with the quadrupole moment, *Q*, of the ^{55}Mn nucleus (nuclear spin $^5/_2$, $Q = 0.33 \times 10^{-28}$ m^2) is more effective and relaxation times are expected to be shorter in the trans isomer. The broader lines at −2248 and −2125 ppm are therefore assigned to isomer I.

From the relative intensities of all the signals, a $Mn_2(CO)_{10}$:$Mn_2(CO)_9CS$ ratio of about 11:1 was estimated.

The ^{13}C NMR spectrum of the $Mn_2(CO)_{10}/Mn_2(CO)_9CS$ mixture in toluene-d_8 shows only the broad signals of the carbonyl groups at about 218 and 221 ppm. The broadening of the signals, which arises from the large quadrupole moment of manganese, prevents detection of the signal of the CS carbon atom.

The presence of the thiocarbonyl complex is also suggested by mass spectroscopic studies. In the electron impact (EI) mode, the mass spectrum of the mixture exhibits low-intensity peaks for the corresponding thiocarbonyl fragments in addition to the peaks for $Mn_2(CO)_{10}$ but no molecular ion for $Mn_2(CO)_9CS$. Similar to the fragmentation of $Mn_2(CO)_{10}$, the first four peaks of the fragmentation pattern of $Mn_2(CO)_9CS$, resulting from successive loss of carbon monoxide, are absent. The fragments and relative intensities are collected in Table I. In the field ionization (FI) mode, however, the molecular ion of $Mn_2(CO)_9CS$ at $m/z = 406$ is observed at 18% intensity, relative to the molecular ion of $Mn_2(CO)_{10}$ at $m/z = 390$ (100%). Attempts to obtain a high-resolution mass spectrum from the CS-containing peaks have failed because of the low intensities of these peaks. From the mass spectroscopic results it can be deduced that the $Mn_2(CO)_9CS$ component in the mixture constitutes 5–10% of the whole material. No ion with two or more CS groups was detected.

The formation of $Mn_2(CO)_9CS$ is also suggested by chemical methods. The $Mn_2(CO)_{10}/Mn_2(CO)_9CS$ mixture was treated with $PPh_3/ONMe_3$ according to the method for the preparation of monosubstituted derivatives of $Mn_2(CO)_{10}$.[14] The IR spectrum of the product is identical with that of an authentic $Mn_2(CO)_9PPh_3$ sample, but it contains an additional weak band at 1265 cm^{-1}. This band can probably be assigned to the ν(CS) vibration of a $Mn_2(CO)_8(CS)PPh_3$ species, present in low concentrations. Shifts of ν(CS) bands to lower frequencies upon replacement of CO by a phosphine group are typical and reflect the greater electron-donating capacity of the phosphine ligand.

Similarly, oxidation of the $Mn_2(CO)_{10}/Mn_2(CO)_9CS$ mixture with Br_2 gives a material that is identical with $Mn(CO)_5Br$ in its IR spectrum. A medium-weak band at 1320 cm^{-1}, however, not found in $Mn(CO)_5Br$ suggests the presence of small amounts of $Mn(CO)_4(CS)Br$ in the reaction product. Sublimation of the oxidation product does not markedly change the relative intensity of the ν(CS) band.

In the mass spectrum of the proposed $Mn(CO)_5Br/Mn(CO)_4(CS)Br$ mixture, fragments with the CS ligand are detected. Low-intensity peaks are recorded for the fragments $Mn(CO)_2(CS)Br$ ($m/z = 236$), $Mn(CO)(CS)Br$ ($m/z = 208$), and $Mn(CS)Br$ ($m/z = 180$) along with peaks derived from the loss of Br and CO from the molecular ion of $Mn(CO)_4(CS)Br$ belonging to the fragments $Mn(CO)_4(CS)$ ($m/z = 211$), $Mn(CO)_3(CS)$ ($m/z = 183$), and $Mn(CO)(CS)$ ($m/z = 127$). All peaks of the thiocarbonyl derivatives appear in intensities of about 1.5–3% relative to the peaks of the corresponding carbonyl derivatives.

No CS-containing product was obtained by reduction of the $Mn_2(CO)_{10}/Mn_2(CO)_9CS$ mixture with K/Na alloy; $[Mn(CO)_5]^-$ was exclusively formed. No reaction was observed with $[NEt_4]I$ at room temperature, which was successfully used for the separation of $W(CO)_6/W(CO)_5CS$ mixtures.[15]

The spectroscopic results suggest clearly that, under the conditions applied, $Mn_2(CO)_9CS$ is one of the reaction products of thiophosgene with $[Mn(CO)_5]^-$. Our efforts are now concentrated toward an increase of the yield of the title compound.

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Experimental Section

All procedures were performed under an atmosphere of dry N_2 with use of carefully dried solvents saturated with N_2. Column chromatography was performed by using Al_2O_3 (activity grade III). The ^{55}Mn NMR spectra were obtained on a Bruker ASM 360 spectrometer. IR spectra were recorded on a Perkin-Elmer 458 instrument. The electron injection (EI) and field ionization (FI) mass spectra were measured on CH7 MAT and Varian 711 instruments, respectively. $Mn_2(CO)_{10}$ was used as commercially obtained. $K[Mn(CO)_5]$ was prepared from $Mn_2(CO)_{10}$ with excess Na/K alloy in THF solution. Removal of the solvent in vacuo gave a greenish white powder that was used for the reaction.

Reaction of $K[Mn(CO)_5]$ with $Cl_2C{=}S$ in Pentane. A solution of 1 mL of $SCCl_2$ (excess) in pentane was added to a suspension of $K[Mn(CO)_5]$ (1.80 g, 7.7 mmol) in pentane with rapid stirring at 0 °C for about 10 min.[16] After the mixture was stirred for 30 min at room temperature, the reaction mixture was filtered and the dark brown filtrate evaporated to dryness. Sublimation of the orange yellow residue at 30–40 °C under high vacuum followed by chromatography on Al_2O_3 with pentane gave a yellow crystalline material (300–350 mg, 12–14%) that was shown by spectroscopic methods to be an approximately 9:1 mixture of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9(CS)$.

The dark brown material from the pentane filtrate exhibits IR bands at 2140 m, 2100 sh, 2030 vs, 1960 sh cm^{-1} in the ν(CO) region and 653 s cm^{-1} in the δ(CO) region.

Reaction of [K(18-crown-6)][$Mn(CO)_5$] with $Cl_2C{=}S$. To a suspension of $K[Mn(CO)_5]$ (1.76 g, 7.5 mmol) in pentane was added 18-crown-6 (1.98 g, 7.5 mmol) and the mixture stirred for 3 h at room temperature. Excess Cl_2CS was added and the pentane solution worked up in a manner similar to that described above. Only small amounts of $Mn_2(CO)_{10}$ were obtained from the pentane solution, and no CS-containing material could be detected by IR spectroscopy.

Recrystallization of the pentane-insoluble material from THF/pentane gave a yellow-green microcrystalline precipitate of [K(18-crown-6)][$Mn(CO)_4Cl_2$]. IR (Nujol): ν(CO) 2095 m, 2005 s, 1980 s, 1932 s cm^{-1}; δ(CO) 672 m, 644 m, 615 m cm^{-1}. The bands are identical with those of [$C(NMe_2)_3$][$Mn(CO)_4Cl_2$] obtained by an independent route.[17] Anal. Calcd for [K(18-crown-6)][$Mn(CO)_4Cl_2$]: C, 35.50; H, 4.47. Found: C, 34.97; H, 4.41.

Reaction of the $Mn_2(CO)_{10}$/$Mn_2(CO)_9CS$ Mixture with PPh_3. The mixture of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9CS$ (120 mg) in toluene was stirred with PPh_3 (80 mg) in the presence of $ONMe_3$ (20 mg) for 3 h. The mixture was worked up as described for the preparation of $Mn_2(CO)_9P(C_6H_5)_3$.[14] The IR spectrum of this material showed an additional weak band at 1265 cm^{-1}, which was assigned to a CS-containing complex present in low yields.

Reaction of the $Mn_2(CO)_{10}$/$Mn_2(CO)_9CS$ Mixture with Br_2. A mixture of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9CS$ (270 mg) in CCl_4 solution was oxidized with Br_2 (120 mg, 0.75 mmol) according to the procedure outlined in ref 18. Evaporation of the solvent and sublimation of the residue gave a mixture of mainly $Mn(CO)_5Br$ and small amounts of $Mn(CO)_4(CS)Br$. IR (Nujol): ν(CS) 1320 cm^{-1}.

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(16) A lower yield of $Mn_2(CO)_9CS$ was observed by addition of stoichiometric amounts of Cl_2CS; the yields also decreased by use of THF as the solvent or by addition of Cl_2CS at −78 °C followed by warming the mixture to room temperature.

(17) Petz, W. Unpublished results.

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Structural Study of Disilanes Bridging Two [(η^5-C_5H_n)Fe(CO)$_2$] Groups (n = 5, 4) via Both Iron Atoms or via Both Cyclopentadienyl Ligands[1]

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Summary: The structures of two tetramethyldisilyl complexes of the (η^5-C_5H_n)Fe(CO)$_2$ (n = 5, 4) system have been determined by using X-ray diffraction methods, [(η^5-C_5H_5)Fe(CO)$_2$]$_2$Si$_2$Me$_4$ (I) and Si$_2$Me$_4$[(η^5-C_5H_4)Fe(CO)$_2$CH$_3$]$_2$ (II). The Si–Si bond length in I, where the two silicon atoms are attached to Fe atoms, is significantly longer than that in II, where the two iron-containing moieties are connected via the cyclopentadienyl rings. The two iron centers are conformationally trans with respect to the Si–Si bond in I but gauche in the case of II. ^{29}Si NMR data for the complexes reinforce the structural data indicating that the two metals activate the Si–Si bond in I.

The study of transition-metal–silicon complexes has been an active area of research since Piper, Lemal, and Wilkinson reported the first example, (η^5-C_5H_5)Fe(CO)$_2$SiMe$_3$, in 1956.[2] Such interest stems in part from the use of transition-metal complexes to catalyze reactions of organosilicon compounds, most notably hydrosilylation.[3,4] However, recently the use of transition-metal complexes to catalyze the formation and cleavage of silicon–silicon bonds has become a topic of considerable interest,[5-7] due to the upsurge in interest in polysilanes as photoresist, preceramic, and photoconducting materials.[8,9]

Oligo- and polysilyl derivatives of the (η^5-C_5H_5)Fe(CO)$_2$ system have been particularly interesting since they have been shown to exhibit a unique range of deoligomerizations,[10,11] molecular rearrangements,[12,13] and group migrations.[10,12] Furthermore, such chemistry is not always duplicated with other metal systems; for example, to date the complexes of Re(CO)$_5$ and (η^5-C_5H_5)Ru(CO)$_2$ have not exhibited a similar rich chemistry.[14]

The particular importance of the (η^5-C_5H_5)Fe(CO)$_2$ systems resulted in various spectroscopic investigations aimed at ascertaining the nature of the Fe–Si bond by such techniques as Mössbauer,[15] IR,[15] and ^{29}Si NMR spectroscopy.[16] From such studies it has been suggested that there is little significant retrodative π-bonding between the metal atom and the silicon atom in complexes of the type (η^5-C_5H_5)Fe(CO)$_2$SiR$_3$.

Structural analyses of such complexes are rare, due in part to the generally noncrystalline nature of the complexes. Drahnak et al. have reported the structures of two (η^5-C_5H_5)Fe(CO)$_2$ derivatives of cyclic silylcyclopentasilane,[17] and we have reported the structural analysis of the single-disilyl complex (η^5-C_5H_5)Fe(CO)$_2$SiMe$_2$SiPh$_3$.[18] This latter study established that the Si–Si bond was elongated with respect to that in Me$_3$SiSiPh$_3$[19] a situation

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