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# Mixed-Valence Manganese Carbonyl Complexes with Supersilyl Thiolate Ligands: [(OC)$_4$Mn($\mu$-SSi*t*Bu$_3$)$_2$Mn(THF)X] (X = Br, SSi*t*Bu$_3$) and Na(THF)$_6$[(OC)$_3$Mn($\mu$-SSi*t*Bu$_3$)$_3$MnSSi*t*Bu$_3$]

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The manganese carbonyl thiolates [(OC)$_4$Mn($\mu$-SSi*t*Bu$_3$)$_2$Na(THF)$_2$], [(OC)$_4$Mn($\mu$-SSi*t*Bu$_3$)$_2$Mn(THF)Br], [(OC)$_4$Mn($\mu$-SSi*t*Bu$_3$)$_2$Mn(THF)SSi*t*Bu$_3$], and Na(THF)$_6$[(OC)$_3$Mn($\mu$-SSi*t*Bu$_3$)$_3$MnSSi*t*Bu$_3$] can be prepared from the precursors Na(THF)$_2$SSi*t*Bu$_3$ and [Mn(CO)$_5$Br]. When [Mn(CO)$_5$Br] is treated with 1 or 2 equiv of Na(THF)$_2$SSi*t*Bu$_3$, the 1:2 substitution product [(OC)$_4$Mn($\mu$-SSi*t*Bu$_3$)$_2$Na(THF)$_2$] (monoclinic, $P2_1/c$) is formed quickly. When additional amounts of [Mn(CO)$_5$Br] are present (as in the 1:1 reaction) or are subsequently added to the reaction mixture, the dinuclear Mn(I)Mn(II) complex [(OC)$_4$Mn($\mu$-SSi*t*Bu$_3$)$_2$Mn(THF)Br] (monoclinic, $P2_1/n$) can be obtained along with [Mn$_2$(CO)$_{10}$]. Treatment of [(OC)$_4$Mn($\mu$-SSi*t*Bu$_3$)$_2$Mn(THF)Br] with 1 equiv of Na(THF)$_2$SSi*t*Bu$_3$ gives the mixed-valence dinuclear manganese thiolate complex [(OC)$_4$Mn($\mu$-SSi*t*Bu$_3$)$_2$Mn(THF)SSi*t*Bu$_3$] (monoclinic, $C2/c$). Cocrystals of the Mn(I)Mn(II) species Na(THF)$_6$[(OC)$_3$Mn($\mu$-SSi*t*Bu$_3$)$_3$MnSSi*t*Bu$_3$] with the trisulfane *t*Bu$_3$Si-SSS-Si*t*Bu$_3$ (trigonal, $R\bar{3}$) are obtained by the reaction of [Mn(CO)$_5$Br] with 2 equiv of Na(THF)$_2$SSi*t*Bu$_3$. The complex anion [(OC)$_3$Mn($\mu$-SSi*t*Bu$_3$)$_3$MnSSi*t*Bu$_3$]$^-$ contains a terminal thiolate ligand with a linear Mn−S−Si unit.

## Introduction

In a number of recent studies, bulk silyl chalcogenolate ligands of the type ESiR$_3^-$ (E = O, S, Se, Te) have been used to stabilize transition-metal centers.[1,2] In macromolecular chemistry, silyl chalcogenolates have also found application. Cyclic thiolates of the general form [M(SSi*t*Bu$_3$)X]$_n$ (M = Fe, Co, Ni; X = Cl, Br, I; $n$ = 12, 14) can be prepared by heating solvated monomeric or dimeric precursors under vacuum.[3] Disilyl chalcogenides (Me$_3$Si)$_2$E (E = S, Se) have been employed in the synthesis of polynuclear metal clusters, driven by the release of Me$_3$SiX when (Me$_3$Si)$_2$E is treated with metal halides MX$_n$.[4] Structural studies of the phosphanediides [M$_2$PSi*t*Bu$_3$], which are isoelectronic with tri-*tert*-butylsilyl (supersilyl) thiolates, also reveal metal−metal interactions.[5] It is interesting to note that in [Ag$_2$PSi*t*Bu$_3$]$_8$ the Ag atoms feature an Ag$_{16}$ cluster.[5] The polyhedron formed by that cluster belongs to the family of the Johnson polyhedra and is a Square gyrobicupola (J29).

Another approach to complexes with chalcogen coordination is to start from materials which after salt metathesis leave the possibility of further manipulation. For example, in [Mn(CO)$_5$Br] the bromo ligand could be exchanged for a chalcogenolate, leaving unreacted CO ligands. Up to now manganese dinuclear carbonyl thiolate complexes of the type [(OC)$_4$Mn($\mu$-SR)$_2$Mn(CO)$_4$], [Mn($\mu_3$-SR)(CO)$_3$]$_4$, and [(OC)$_3$Mn($\mu$-SR)$_3$Mn(CO)$_6$]$^-$ are known and have been structurally characterized (Scheme 1).[6–8] Only with pentafluorobenzenethiol was it possible to isolate and characterize a mononuclear pentacarbonyl complex of the type [Mn(CO)$_5$SR] (R = C$_6$F$_5$).[9,10] It is interesting to note that treatment of [Mn(CO)$_5$Br] with organic thiolates SR$^-$ normally affords tetrameric species, [Mn($\mu_3$-SR)(CO)$_3$]$_4$, rather than mononuclear complexes [Mn(CO)$_5$SR]. The tricarbonylmanganese(I) organylthiolates [Mn($\mu$-SR)(CO)$_3$]$_n$ (R = *n*Bu, Ph) were originally reported to be trimeric ($n$ = 3), and a structure involving a triangular metal atom cluster was proposed.[10] However, subsequent mass spectral studies indicated that, in the vapor phase, a tetrameric formulation rather than a trimeric one is more correct.[11] In addition, the results of the X-ray structure analysis of tricarbonylmanganese(I) benzenethiolate confirm the tetrameric nature of this type of manganese carbonyl complex.[7,12,13]

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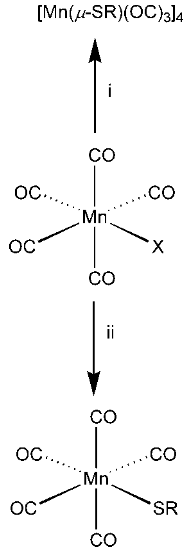
**Scheme 1. Synthesis of [Mn(CO)$_5$SR] and of [Mn($\mu_3$-SR)(CO)$_3$]$_4$$^a$**

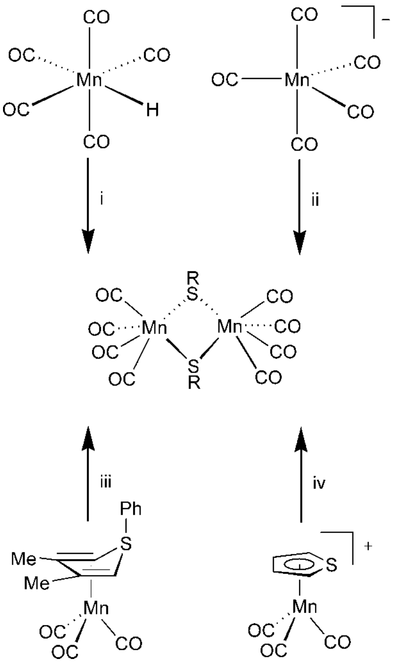


$^a$ Legend: (i) +SR$^-$ (e.g. R = Me, Et, Ph, Tol), −Br$^-$ (X = Br); (ii) +HSR (R = $C_6F_5$), −$H_2$ (X = H).

Dinuclear complexes of the type [(OC)$_4$Mn($\mu$-SR)$_2$Mn(CO)$_4$] were prepared (i) by oxidation of the pentacarbonyl anion [Mn(CO)$_5$]$^-$ with disulfides RSSR,[14,15] (ii) by treating the hydrido complex H[Mn(CO)$_5$] with thiols HSR.[9,10] (iii) by hydrogenation of [(1-phenylthiophene)Mn(CO)$_3$],[12] or (iv) by reaction of the [(thiophene)Mn(CO)$_3$]$^+$ cation with thiolates SR$^-$,[6] as shown in Scheme 2. However, the formation of [(OC)$_4$Mn($\mu$-SR)$_2$Mn(CO)$_4$] thereby must be complicated, since each Mn center has three or five CO ligands in the beginning when it is used as starting material but the reaction product possesses four CO ligands.

Chalcogenolates such as SSi*t*Bu$_3$$^-$ can donate a varying number of electrons when bound to a transition-metal center.[16,17] As pure $\sigma$ donors, they donate two electrons to a coordinated metal site. The free p orbital lone pairs, however, can both potentially donate in a $\pi$ fashion. This corresponds to four- or six-electron donation. The necessary prerequisite for six-electron donation is linear M−E−Si coordination. This coordination geometry can only be effectively induced by sterically hindered residues. These, by their very nature, have a large coordination cone angle (ca. 120° for OSi*t*Bu$_3$$^-$), making them comparable to Cp (cone angle ca. 130°) both in their electron donation (6e) and in their steric demands.[18] This sort of coordination and electron donation has rarely been observed for silyl chalcogenolates.[16,19] Due to the bulky residue Si*t*Bu$_3$ the formation of a linear Si−S−Mn unit is possible and thus six-electron donation is more likely. Such silyl chalcogenolates are thus, in a sense, isolobal with the cyclopentadienyl ligand.

**Scheme 2. Synthesis of Dinuclear Mn(I) Thiolates of the Type [(OC)$_4$Mn($\mu$-SR)$_2$Mn(CO)$_4$]$^a$**



$^a$ Legend: (i) +HSR (R = $C_6F_5$), −CO, −$H_2$; (ii) +RSSR (e.g. R = Me, Ph, $CF_3$), −CO; (iii) + $H_2$, −$H_2C{=}CMeMeC{=}CH_2$; (iv) +SR$^-$ (e.g. R = Me, Tol), −$C_4H_4S$.

In this paper, we describe the reaction of [Mn(CO)$_5$Br] with Na(THF)$_2$SSi*t*Bu$_3$ in a 1:1 and 1:2 stoichiometry, respectively. When the extremely bulky supersilyl thiolate is employed as a reaction partner of [Mn(CO)$_5$Br], some novel insight into the aggregation between thiolate ligands and Mn(I) centers can be expected.

## Results and Discussion

Surprisingly, the reaction of Na(THF)$_2$SSi*t*Bu$_3$ with [Mn(CO)$_5$Br], as shown in Scheme 3, is quite different from those between [Mn(CO)$_5$Br] and organyl thiolates. When [Mn(CO)$_5$Br] is treated with only 1 equiv of Na(THF)$_2$SSi*t*Bu$_3$, immediate gas evolution is observed, and the reaction mixture quickly becomes heterogeneous. After 2 h, NMR spectra ($^1$H, $^{13}$C, and $^{29}$Si) show that Na(THF)$_2$SSi*t*Bu$_3$ has been completely consumed, and the dominant signals can be assigned to the 1:2 product Na(THF)$_2$[(OC)$_4$Mn(SSi*t*Bu$_3$)$_2$] (**1**) (Scheme 3).

The thiolate complex **1**, however, reacts with the remaining 1 equiv of [Mn(CO)$_5$Br], and the new products [(OC)$_4$Mn($\mu$-SSi*t*Bu$_3$)$_2$Mn(THF)Br] (**2**) and [Mn$_2$(CO)$_{10}$] are formed. When the solvent is changed from THF to pentane, and the concentrated filtrate is left to stand for 2 weeks at −20 °C, orange crystals can be isolated. The solid-state structure, however, does not reveal the expected thiolate complex **2** but rather the Mn(I)Mn(II) complex [(OC)$_4$Mn($\mu$-SSi*t*Bu$_3$)$_2$Mn(THF)SSi*t*Bu$_3$] (**3**). However, the mixed-valence dinuclear manganese thiolate complex **2** was obtained when a purified sample of **1** was treated with 2 equiv of [Mn(CO)$_5$Br] (Scheme 3). Thereby [Mn$_2$(CO)$_{10}$] was obtained as a byproduct, which was identified in the IR spectrum, whereas the complex **2** was characterized by X-ray structure analysis. Apparently, due to the weak-field ligands THF and bromide, Mn(I) centers disproportionate in the presence of SSi*t*Bu$_3$$^-$ to [Mn$_2$(CO)$_{10}$] and Mn(II) (Scheme 3). However, **2** can be transformed easily with Na(THF)$_2$SSi*t*Bu$_3$ into **3**.

When [Mn(CO)$_5$Br] in THF is treated with 2 equiv of Na(THF)$_2$SSi*t*Bu$_3$, the reaction initially proceeds as described above using 1 equiv of thiolate. After 3 h, the thiolate

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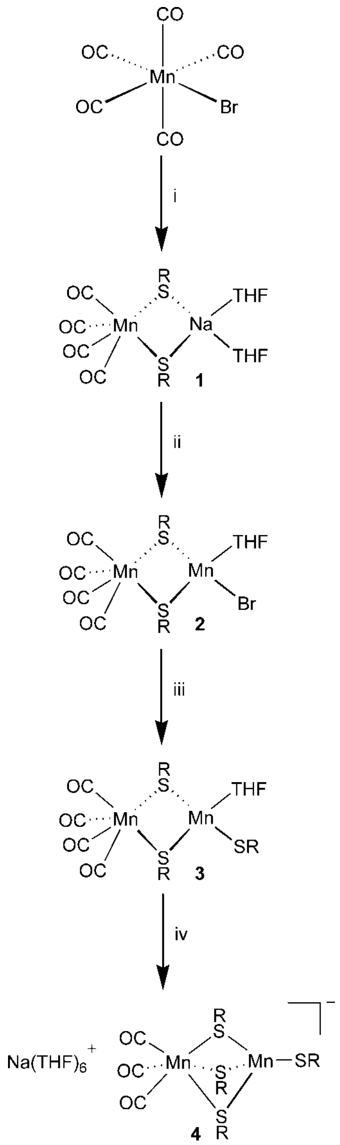
**Scheme 3. Reaction of [Mn(CO)$_5$Br] with Na(THF)$_2$SSi$t$Bu$_3$[a]**



[a] Legend: R = Si$t$Bu$_3$; (i) +2NaR, −NaBr, THF; (ii) +2[Mn(CO)$_5$Br], −NaBr, −5CO, −0.5[Mn$_2$(CO)$_{10}$]; (iii) +NaSR, −NaBr; (iv) +NaSR, −CO.

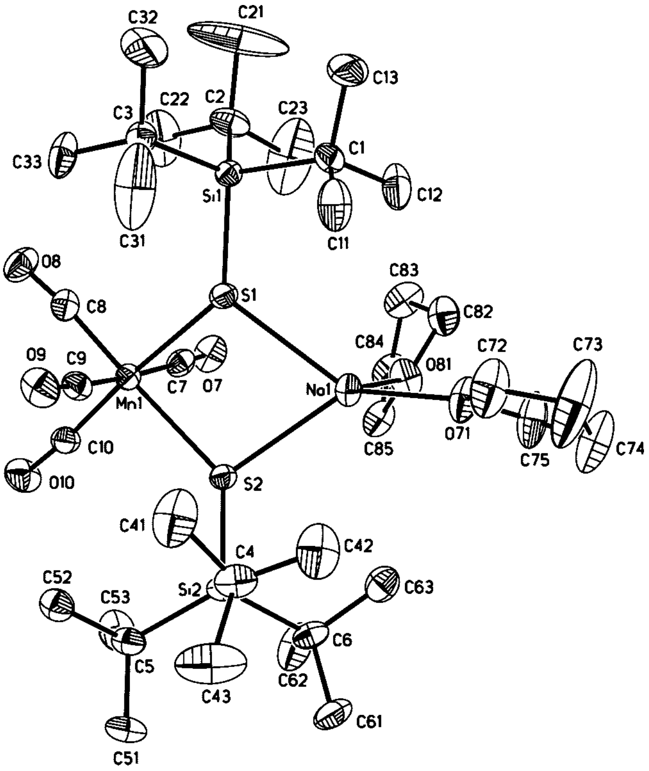


**Figure 1.** Thermal ellipsoid plot of **1** showing the atomic numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mn(1)−C(7) = 1.868(6), Mn(1)−C(8) = 1.785(6), Mn(1)−S(1) = 2.480(1), Na(1)−S(1) = 2.744(3), S(1)−Si(1) = 2.144(2), S(1)−Mn(1)−S(2) = 83.67(5), Mn(1)−S(1)−Na(1) = 99.69(6), Mn(1)−C(9) = 1.874(6), Mn(1)−C(10) = 1.802(6), Mn(1)−S(2) = 2.475(2), Na(1)−S(2) = 2.757(2), S(2)−Si(2) = 2.151(2), S(1)−Na(1)−S(2) = 73.86(6), Mn(1)−S(2)−Na(1) = 99.47(6).

Na(THF)$_2$SSi$t$Bu$_3$ has been completely consumed (as determined by NMR spectroscopy). Changing the solvent to pentane, filtering, and slowly concentrating the filtrate leads to deposition of X-ray-quality crystals of **1** (Scheme 3).

When a 1:2 reaction mixture of [Mn(CO)$_5$Br] and Na(THF)$_2$SSi$t$Bu$_3$ is left to stand for a period of several weeks, a few crystals with unit cell parameters different from those of crystals of **1** can be isolated. These contain the mixed-valence manganese complex anion Na(THF)$_6$[(OC)$_3$Mn($\mu$-SSi$t$Bu$_3$)$_3$-Mn(THF)SSi$t$Bu$_3$] (**4**) and the trisulfane $t$Bu$_3$Si−SSS−Si$t$Bu$_3$. The formation of **4** can be explained by the reaction of the mixed-valence dinuclear manganese thiolate complex **3** with NaSSi$t$Bu$_3$ (Scheme 3). It is interesting to note that the trisulfane $t$Bu$_3$Si−SSS−Si$t$Bu$_3$ represents a typical oxidation product of the sodium thiolate NaSSi$t$Bu$_3$.[20,21]

Generally, the NMR spectra of manganese carbonyl thiolate **1** resemble those of the thiolate ligand Na(THF)$_2$SSi$t$Bu$_3$.[2] The $^{29}$Si NMR signal for **1** (C$_6$D$_6$: 29.5 ppm) is shifted downfield compared to that of the sodium thiolate Na(THF)$_2$SSi$t$Bu$_3$ (25.6 ppm).

The IR stretching frequencies of **1** (CH$_2$Cl$_2$ solution) are shifted to lower frequencies by 30−40 cm$^{-1}$ compared to reported complexes of the type [(OC)$_4$Mn($\mu$-SR)$_2$Mn(CO)$_4$] and [Mn($\mu_3$-SR)(CO)$_3$]$_4$.[6,7,12,22] This result can be rationalized by assuming that the thiolate ligands will act as stronger $\sigma$ donors toward a Mn center in the case of **1** rather than toward two Mn centers as in [(OC)$_4$Mn($\mu$-SR)$_2$Mn(CO)$_4$] and three Mn centers as in [Mn($\mu_3$-SR)(CO)$_3$]$_4$, leading to stronger Mn−CO back-bonding and consequently lower CO stretching frequencies in the complex **1** than in [(OC)$_4$Mn($\mu$-SR)$_2$Mn(CO)$_4$] and [Mn($\mu_3$-SR)(CO)$_3$]$_4$, respectively. In the carbonyl stretching region of the IR spectrum, the thiolates **2** and **3** show bands of intensity similar to those in the spectrum of **1**.

The dinuclear manganese complexes **2** and **3** are paramagnetic, since charge balance dictates that they contain one Mn(I) (d$^6$) and one Mn(II) (d$^5$) center. In order to quantify this effect, the Evans method was applied for **3**, and $\mu_{\text{eff}}$ was determined to be 4.9 $\mu_B$, corresponding to four unpaired electrons.[23] This outcome confirms the strong paramagnetism of the dinuclear

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**Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Manganese Carbonyl Thiolates 1−4**

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Mn−C | 1.832(6) (av) | 1.839(4) (av) | 1.822(10) (av) | 1.769(9) |
| Mn−S(bridging) | 2.478(2) (av) | 2.459(1) (av) | 2.506(2) (av) | 2.484(2) |
| Mn−S(terminal) | | | 2.349(2) | 2.269(5) |
| Si−S(terminal) | | | 2.094(3) | 2.064(6) |
| Si−S(bridging) | 2.148(2) (av) | 2.187(2) (av) | 2.210(3) (av) | 2.152(3) |
| Mn−M (M = Mn, Na) | 3.997 | 3.546 | 3.738 | 3.063(3) |
| Mn−S(terminal)−Si | | | 130.9(2) | 180.0(1) |

Mn(I)Mn(II) complex **3**, but it is inconsistent with the expected result of $\mu_{\text{eff}} = 5.9\ \mu_B$ for a high-spin Mn(II) center (five unpaired electrons). Since the Evans method is sensitive to the concentration of analyte in the solution, it is possible that, despite careful washing, the sample of **3** was contaminated with diamagnetic species which would decrease the overall paramagnetism of the sample, leading to a smaller experimental value for $\mu_{\text{eff}}$.

The crystal structure of the manganese carbonyl thiolate **1** is shown in Figure 1; selected bond lengths and angles can be found in the corresponding caption and in Table 1. X-ray-quality crystals of **1** were grown from pentane. This complex crystallizes in the monoclinic space group $P2_1/c$ with two crystallographically independent molecules in the asymmetric unit. These two molecules, however, display very similar structural parameters, and only one is shown in Figure 1. The core of **1** is formed by a four-membered $MnS_2Na$ ring in which two bridging thiolate ligands bind to both the manganese and the sodium atom. Although a number of structurally characterized dimanganese complexes with $(OC)_4Mn$ moieties and bridging thiolate ligands are known in the literature,[6,22,24] heterodinuclear complexes are less common,[25] and none with alkali metals have been reported.[25] In contrast to the $Na_2E_2$ four-membered rings formed by the sodium chalcogenolates $Na(THF)_2SSi\mathit{t}Bu_3$, the M−S−M angles in **1** are significantly larger than 90°, while the S−M−S angles are smaller than 90°. Furthermore, the core four-membered rings of the sodium supersilyl chalcogenolates are planar, but the $M_2S_2$ unit in **1** is bent. The two planes defined by sodium, manganese, and one sulfur atom meet at an angle of 21.3° (29.1° for the second molecule), while the $S_2Mn$ plane meets the $S_2Na$ plane at an angle of 17.8° (24.8° for the second molecule).

The Mn atom is coordinated in a distorted-octahedral fashion. Those C−Mn−C and C−Mn−S angles which are closest to 90° range between 82.2(2)° (C(7)−Mn(1)−S(2)) and 97.9(2)° (C(8)−Mn(1)−S(1)) for the first molecule and 80.2(2)° (C(7A)−Mn(1A)−S(2A)) and 99.1(2)° (C(9A)−Mn(1A)−S(2A)) for the second molecule, while those that are close to linearity are between 172.2(2)° (C(8)−Mn(1)−S(2)) and 175.0(2)° (C(7)−Mn(1)−C(9)) for the first molecule and 169.2(2)° and 175.7(2)° for the second molecule. The sodium atom has a distorted coordination sphere, with L−Na−L angles ranging from 73.86(6)° (S(1)−Na(1)−S(2) = 73.75(6)° for the second molecule) to 138.1(2)° (O(71)−Na(1)−S(2) = 134.51° for the second molecule). Furthermore, the Mn−S bond lengths are the longest found for a structurally characterized $(CO)_4Mn{-}SR$ compound (Table 1).[26]

The mixed-valence manganese silyl thiolate **2**, shown in Figure 2, crystallizes in the monoclinic space group $P2_1/n$ (selected bond lengths and angles in Table 1 and the figure caption). The two Mn atoms and two sulfur atoms of thiolate ligands form a nearly planar square. The S−Mn−S angles, at 83.18(3)° (average), and the Mn−S−Mn angle, at 92.29(3)° (average), deviate slightly from 90°, while the Mn−S bond lengths, which average 2.45562(9) Å, are somewhat shorter than those found in **1**, **3**, and **4**. The MnMn distance is quite long (3.546 Å), suggesting only a weak interaction between the metal centers. Similar structural motifs have been observed for dinuclear Mn(I)Mn(I) thiolate complexes. The related complexes $[(OC)_4Mn(\mu\text{-}SC_6H_4Me\text{-}p)_2Mn(CO)_4]$[6] and $[(OC)_4Mn(\mu\text{-}SPh)_2$-

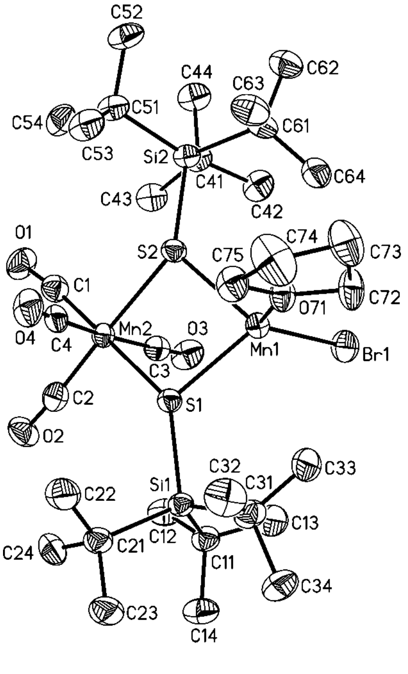

**Figure 2.** Thermal ellipsoid plot of **2** showing the atomic numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mn(1)−O(71) = 2.132(2), Mn(1)−S(1) = 2.4368(9), Mn(1)−Br(1) = 2.4380(6), Mn(1)−S(2) = 2.4478(9), Mn(2)−C(2) = 1.794(4), Mn(2)−C(1) = 1.797(4), Mn(2)−C(3) = 1.877(4), Mn(2)−C(4) = 1.889(4), Mn(2)−S(2) = 2.4710(9), Mn(2)−S(1) = 2.4800(9), S(1)−Si(1) = 2.1887(12), S(2)−Si(2) = 2.1846(11), C(1)−O(1) = 1.155(4), C(2)−O(2) = 1.159(4), C(3)−O(3) = 1.133(4), C(4)−O(4) = 1.128(4), O(71)−Mn(1)−S(1) = 104.97(6), O(71)−Mn(1)−Br(1) = 115.07(6), S(1)−Mn(1)−Br(1) = 122.38(3), O(71)−Mn(1)−S(2) = 100.70(7), S(1)−Mn(1)−S(2) = 83.86(3), Br(1)−Mn(1)−S(2) = 124.22(3), S(2)−Mn(2)−S(1) = 82.49(3), Si(1)−S(1)−Mn(1) = 124.34(4), Si(1)−S(1)−Mn(2) = 134.63(4), Mn(1)−S(1)−Mn(2) = 92.31(3), Si(2)−S(2)−Mn(1) = 126.50(4), Si(2)−S(2)−Mn(2) = 133.65(4), Mn(1)−S(2)−Mn(2) = 92.26(3).

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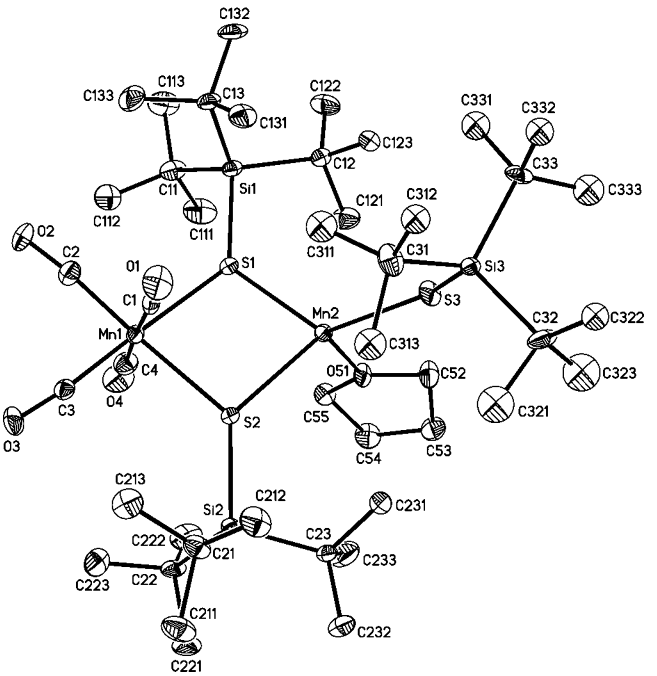

**Figure 3.** Thermal ellipsoid plot of **3** showing the atomic numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mn(1)−C(1) = 1.832(9), Mn(1)−C(2) = 1.788(10), Mn(1)−C(3) = 1.844(9), Mn(1)−C(4) = 1.822(9), Mn(1)−S(1) = 2.543(2), Mn(1)−S(2) = 2.484(2), Mn(2)−S(1) = 2.478(2), Mn(2)−S(2) = 2.517(2), Mn(2)−S(3) = 2.349(2), Mn(2)−O(51) = 2.145(6), S(1)−Mn(1)−S(2) = 81.41(7), S(1)−Mn(2)−S(2) = 82.04(7), Mn(1)−S(1)−Mn(2) = 96.20(8), Mn(1)−S(2)−Mn(2) = 96.73(8), O(51)−Mn(2)−S(3) = 94.2(2), O(51)−Mn(2)−S(1) = 104.6(2), S(1)−Mn(2)−S(3) = 127.45(9), O(51)−Mn(2)−S(2) = 101.1(2), S(2)−Mn(2)−S(3) = 141.94(9), Si(3)−S(3)−Mn(2) = 130.9(2).

Mn(CO)$_4$][7,12] both display a central Mn$_2$S$_2$ four-membered ring, feature Mn−Mn distances of 3.606 and 3.594 Å and average Mn−S bond lengths of 2.394(1) and 2.395(2) Å, respectively. The distances between 1.128(4) and 1.159(4) Å in **2** have a characteristic length for MnC−O bonds.

Complex **3** crystallizes in the monoclinic space group *C*2/*c* with one complete molecule in the asymmetric unit (Figure 3, selected bond lengths and angles in Table 1 and the corresponding figure caption). The core of the complex is formed by a Mn$_2$S$_2$ four-membered ring. As in **2**, the S−Mn−S angles are considerably smaller than 90°, while the Mn−S−Mn angles are considerably larger. Mn(1) is coordinated by four terminal carbonyl ligands and two bridging thiolates in a distorted-octahedral fashion, while Mn(2) is bound to two bridging thiolates and one terminal thiolate ligand. Its distorted coordination sphere is completed by one molecule of THF. The L−Mn−L angles around Mn(2) range from 82.04(7)° (S(1)−Mn(2)−S(2)) to 141.94(9)° (S(2)−Mn(2)−S(3)), and the Mn−S distances to the bridging thiolates are longer than those found in **1**, **2**, and **4**.

The Mn(2)−S(3)−Si(3) unit in **3** is not linear, but the terminally bound thiolate ligand features a quite large angle (130.9(2)°). The Mn(2)−S(3) bond length is 2.349(2) Å; it is nearly 0.1 Å longer than the terminal Mn−S bond for the linearly bound thiolate in **4**, supporting the conclusion that a bent coordination angle leads to less electron donation from the thiolate ligand.

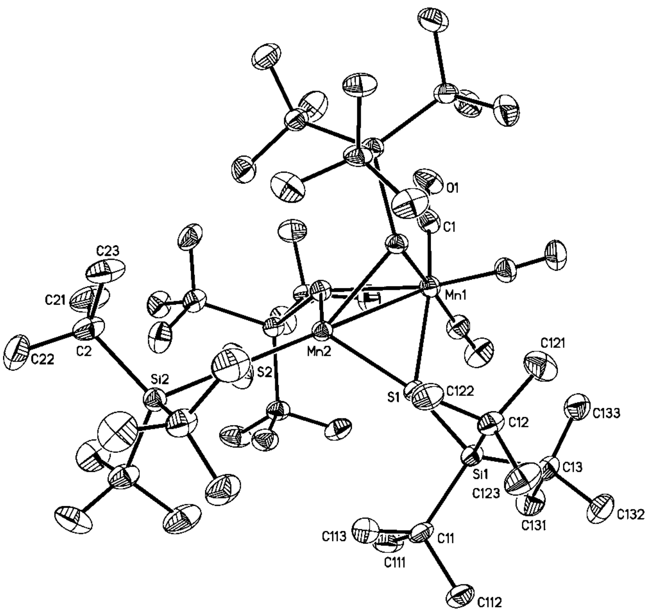

**Figure 4.** Thermal ellipsoid plot of the anion of **4** showing the atomic numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mn(1)−C(1) = 1.769(9), Mn(1)−S(1) = 2.496(2), Mn(1)−Mn(2) = 3.063(3), Mn(2)−S(2) = 2.269(5), S(1)−Si(1) = 2.152(3), S(2)−Si(2) = 2.064(6), S(1)−Mn(2) = 2.471(2), C(1)#1−Mn(1)−C(1) = 91.0(4), C(1)#1−Mn(1)−S(1) = 84.4(3), C(1)#2−Mn(1)−S(1) = 100.2(3), C(1)−Mn(1)−S(1) = 167.9(3), S(1)−Mn(1)−S(1)#1 = 85.43(8), S(1)#1−Mn(2)−S(1)#2 = 86.50(8), S(2)−Mn(2)−S(1) = 127.71(6), Si(2)−S(2)−Mn(2) = 180.000(1), Si(1)−S(1)−Mn(2) = 126.16(10), Si(1)−S(1)−Mn(1) = 134.32(10), Mn(2)−S(1)−Mn(1) = 76.14(7). Symmetry transformations used to generate equivalent atoms: (#1) $-y + 1, x - y, z$; (#2) $-x + y + 1, -x + 1, z$.

The mixed-valence manganese carbonyl thiolate complex **4** (anion of **4** shown in Figure 4; selected bond lengths and angles in Table 1 and the corresponding figure caption), cocrystallizes with one molecule of the trisulfane $t$Bu$_3$Si−SSS−Si$t$Bu$_3$ (Figure 5; selected bond lengths and angles in the corresponding figure caption), in the trigonal space group $R\bar{3}$. The complex anion is situated on a 3-fold rotational axis in the crystal, with the result that one-third of the molecule is contained in the asymmetric unit. The core of the structure consists of two manganese atoms bridged by three thiolate ligands. The Mn−S distances for the bridging thiolates are in the same range as those observed for **1**. The Mn−S bond to the terminal thiolate, however, is quite short (2.269(5) Å). Moreover, the Mn−S−Si angle is strictly linear, since the Mn−S and S−Si bonds lie on the 3-fold rotational axis. The thermal ellipsoid of S2 (from the terminally bound thiolate) is fairly small, indicating that the Si−S−Mn unit does not deviate from linearity. This is significant, because there are a very limited number of transition-metal complexes of silyl or alkyl chalcogenolates with linear coordination.[27] It has been postulated in the literature that chalcogenolate ligands can act as six-electron donors (analogous to Cp) by donating

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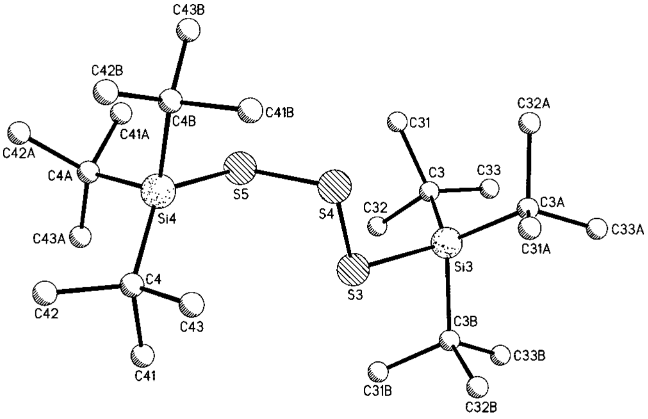

**Figure 5.** Plot of $t\mathrm{Bu}_3\mathrm{Si}-\mathrm{SSS}-\mathrm{Si}t\mathrm{Bu}_3$ showing the atomic numbering scheme. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(3)−C(3A) = 1.928(10), Si(3)−C(3B) = 1.928(11), Si(3)−C(3) = 1.928(10), Si(3)−S(3) = 2.225(17), Si(4)-C(4A) = 1.894(16), Si(4)−C(4B) = 1.894(17), Si(4)−C(4) = 1.895(16), Si(4)−S(5) = 2.208(16), S(3)−S(4) = 1.932(16), S(4)−S(5) = 1.904(19), S(4)−S(3)−Si(3) = 107.1(7), S(5)−S(4)−S(3) = 95.1(11), S(4)−S(5)−Si(4) = 102.7(8).

two $\sigma$ and four $\pi$ electrons.[17,28] The prerequisite for this type of donation, however, is linear coordination, which is rarely observed. In the case of **4**, the significant steric hindrance of the supersilyl groups enforces such linear coordination, thus allowing for six-electron donation.

## Summary and Conclusion

In summary, it has been shown that the manganese carbonyl thiolates **1**−**4** can be prepared from the precursors $\mathrm{Na(THF)_2SSi}t\mathrm{Bu_3}$ and $[\mathrm{Mn(CO)_5Br}]$. When $[\mathrm{Mn(CO)_5Br}]$ is treated with 1 or 2 equiv of $\mathrm{Na(THF)_2SSi}t\mathrm{Bu_3}$, the 1:2 substitution product **1** is formed quickly (Scheme 3). When an additional 1 equiv of $[\mathrm{Mn(CO)_5Br}]$ is present (as in the 1:1 reaction) or is subsequently added to the reaction mixture, the dinuclear Mn(I)Mn(II) complex **2** can be isolated along with $[\mathrm{Mn_2(CO)_{10}}]$ (Scheme 3). Treatment of **2** with 1 equiv of $\mathrm{Na(THF)_2SSi}t\mathrm{Bu_3}$ gives the mixed-valence dinuclear manganese thiolate complex **3**. The formation of **4**, however, can be explained by the reaction of **3** with a further 1 equiv of $\mathrm{NaSSi}t\mathrm{Bu_3}$ (Scheme 3). The complex anion of **4** contains a terminal thiolate ligand with a linear Mn−S−Si unit. The prerequisite for six-electron donation (two $\sigma$ and four $\pi$ electrons) is thus fulfilled, clearing the way for comparisons to the analogous six-electron donor $\mathrm{Cp}^-$. It is interesting to note that the supersilyl thiolates **2**−**4** represent the first structurally characterized mixed-valence Mn(I)Mn(II) carbonyl thiolate complexes.

## Experimental Section

**General Procedures.** All experiments were carried out under dry nitrogen or argon with strict exclusion of air and moisture using standard Schlenk techniques or a glovebox. $\mathrm{Na(THF)_2Si}t\mathrm{Bu_3}$[29] and $\mathrm{Na(THF)_2SSi}t\mathrm{Bu_3}$[2] were prepared according to literature procedures. The solvents (benzene, toluene, tetrahydrofuran) were distilled from sodium/benzophenone prior to use.

The NMR spectra were recorded on a Bruker AM 250, a Bruker DPX 250, a Bruker Avance 300, and a Bruker Avance 400 spectrometer. The $^{29}$Si NMR spectra were recorded using the INEPT pulse sequence with empirically optimized parameters for polarization transfer from the *t*Bu substituents. Mass spectra were recorded with a VG PLATFORM II mass spectrometer.

**Synthesis of 1.** To a solution of $[\mathrm{Mn(CO)_5Br}]$ (128 mg, 0.46 mmol) in 15 mL of THF was added $\mathrm{Na(THF)_2SSi}t\mathrm{Bu_3}$ (378 mg, 0.95 mmol) in one portion. The orange solution quickly became cloudy. After 3 h, volatiles were removed in vacuo and the brown residue was extracted with pentane (10 mL). The extract was filtered over diatomaceous earth on a frit. The filter cake was washed with pentane (2 × 5 mL). Slow concentration of the filtrate led to the deposition of the product as a microcrystalline solid. X-ray-quality crystals were obtained by recrystallization from pentane at −20 °C. Yield: 167 mg (45%). IR ($\mathrm{CH_2Cl_2}$, cm$^{-1}$): $\tilde{\nu}$ (CO absorptions) 2035 (m), 2001 (s), 1972 (m), 1925 (m). $^1$H NMR (250.1 MHz, $\mathrm{C_6D_6}$): $\delta$ 1.38 (s, 54H, *t*Bu), $\delta$ 3.45 (br, 8H, $\mathrm{OCH_2}$), $\delta$ 1.40 (br, 8H, $\mathrm{CH_2}$). $^{13}$C NMR (62.9 MHz, $\mathrm{C_6D_6}$): $\delta$ 25.3 ($C\mathrm{CH_3}$), $\delta$ 31.7 ($\mathrm{C}C\mathrm{H_3}$), $\delta$ 222.5 (CO), THF not observed. $^{29}$Si NMR (79.5 MHz, $\mathrm{C_6D_6}$): $\delta$ 29.5. MS (ESI$^+$): *m/z* (%) 797.4 (100) 798.4 (60) 799.5 (40) $[\mathrm{M+H}]^+$, calcd for $[\mathrm{M+H}]^+$ 797.3 (100) 798.3 (52) 799.3 (30). Anal. Calcd for $\mathrm{C_{36}H_{70}MnNaO_6S_2Si_2}$ (797.17): C, 54.24; H, 8.85. Found: C, 52.77; H, 8.88.

**Synthesis of 2.** A mixture of **1** (97 mg, 0.12 mmol), $[\mathrm{Mn(CO)_5Br}]$ (71 mg, 0.25 mmol), and 4 mL of benzene was stirred for 4 days at ambient temperature. After filtration, crystals of **2** were grown from the benzene solution at ambient temperature. The IR spectrum of the mother liquor revealed bands which could be assigned to $[\mathrm{Mn_2(CO)_{10}}]$ (IR (benzene, cm$^{-1}$): $\tilde{\nu}$ (CO absorptions) 2046 (m), 2014 (s), 1982 (w)). Yield: 51 mg (52%). Selected data for **2**: IR (KBr, cm$^{-1}$): $\tilde{\nu}$ (CO absorptions) 2038 (m), 1997 (s), 1964 (m), 1946 (m). Anal. Calcd for $\mathrm{C_{32}H_{62}Mn_2BrO_5S_2Si_2}$ (836.91): C, 45.92; H, 7.47. Found: C, 46.33; H, 6.95.

X-ray-quality crystals of **2** were obtained from **1** (44 mg, 0.06 mmol) and $[\mathrm{Mn(CO)_5Br}]$ (32 mg, 0.12 mmol) in benzene at ambient temperature.

**Synthesis of 3.** To a solution of $[\mathrm{Mn(CO)_5Br}]$ (143 mg, 0.53 mmol) in 15 mL of THF was added $\mathrm{Na(THF)_2SSi}t\mathrm{Bu_3}$ (205 mg, 0.51 mmol) in one portion. The orange solution quickly became cloudy. After 4 h, no unreacted thiolate could be observed in the NMR spectra of the reaction mixture, and signals consistent with a substitution product had grown ($\mathrm{C_6D_6}$, $^1$H NMR $\delta$ 1.32; $^{13}$C NMR $\delta$ 31.5, 26.0; $^{29}$Si NMR $\delta$ 31.4). Volatiles were removed in vacuo, and the brown residue was extracted with pentane (10 mL). The extract was filtered over diatomaceous earth on a frit. The filter cake was washed with pentane (2 × 5 mL). After standing at −20 °C for several weeks, X-ray-quality crystals of **3** could be obtained from a pentane solution. Yield: 50 mg (0.05 mmol, 29%). IR (hexane, cm$^{-1}$): $\tilde{\nu}$ (CO absorptions) 2037 (m), 1992 (s), 1949 (m). $^1$H NMR ($\mathrm{C_6D_6}$, 250.1 MHz): 1.40 (s, *t*Bu). MS (ESI$^-$): *m/z* (%) 987.9 (100), 988.9 (60), 988.9 (66), 990.0 (51), 991.0 (21) $[\mathrm{M}]^-$, calcd for $[\mathrm{M}]^-$ 987.4 (100), 988.4 (66), 989.4 (46), 990.4 (20). Anal. Calcd for $\mathrm{C_{44}H_{89}Mn_2O_5S_3Si_3}$ (988.50): C, 53.46; H, 9.08. Found: C, 51.13; H, 8.80.

**Reaction of 2 with $\mathrm{Na(THF)_2SSi}t\mathrm{Bu_3}$.** To a solution of **2** (98 mg, 0.12 mmol) in 5 mL of benzene was added $\mathrm{Na(THF)_2SSi}t\mathrm{Bu_3}$ (95 mg, 0.24 mmol). After filtration the IR spectrum of reaction solution revealed bands which could be assigned to **3**. Volatiles were removed in vacuo, and the red residue was extracted with THF (5 mL). The THF solution was stirred for 7 days. After the solvent had been removed in vacuo, an IR spectrum was measured from the residue. IR (KBr, cm$^{-1}$): $\tilde{\nu}$ (CO absorptions) 2045 (m), 2010 (m), 1980 (s), 1960 (s). Anal. Calcd for $\mathrm{C_{63}H_{129}Mn_2NaO_9S_3Si_3}$ (1344.01): C, 56.30; H, 9.67. Found: C, 54.76; H, 8.93.

**Formation of 4.** When a reaction solution of $[\mathrm{Mn(CO)_5Br}]$ with $\mathrm{Na(THF)_2SSi}t\mathrm{Bu_3}$ in 1:2 stoichiometry was left to stand for several

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**Table 2. Crystal Data and Structure Refinement Details for 1−3 and 4·$t$Bu$_3$Si−SSS−Si$t$Bu$_3$**

| | **1** | **2** | **3** | **4**·$t$Bu$_3$Si−SSS−Si$t$Bu$_3$ |
|---|---|---|---|---|
| empirical formula | $C_{36}H_{70}MnNaO_6S_2Si_2$ | $C_{32}H_{62}BrMn_2O_5S_2Si_2$ | $C_{44}H_{89}Mn_2O_5S_3Si_3$ | $C_{99}H_{210}Mn_2NaO_9S_7Si_6$ |
| color | light brown | orange | dark red | orange |
| shape | needle | plate | block | plate |
| fw | 797.15 | 836.91 | 988.48 | 2070.50 |
| cryst syst | monoclinic | monoclinic | monoclinic | trigonal |
| space group | $P2_1/c$ | $P2_1/n$ | $C2/c$ | $R\bar{3}$ |
| $a$, Å | 23.1442(11) | 8.8106(5) | 24.9621(12) | 14.6380(5) |
| $b$, Å | 17.4691(6) | 17.3613(7) | 13.3952(4) | 14.6380(5) |
| $c$, Å | 23.2056(12) | 27.1951(16) | 34.7460(18) | 101.570(7) |
| $\beta$, deg | 104.506(4) | 92.666(5) | 109.554(4) | 90 |
| $V$, Å$^3$ | 9083.1(7) | 4155.4(4) | 10 948.0(8) | 18 847.7(16) |
| $Z$ | 8 | 4 | 8 | 6 |
| calcd density, Mg/m$^3$ | 1.166 | 1.338 | 1.199 | 1.095 |
| abs coeff $\mu$(Mo K$\alpha$), mm$^{-1}$ | 0.482 | 1.761 | 0.679 | 0.423 |
| $F$(000) | 3440 | 1756 | 4264 | 6798 |
| cryst size, mm$^3$ | 0.31 × 0.12 × 0.12 | 0.23 × 0.22 × 0.11 | 0.33 × 0.30 × 0.27 | 0.27 × 0.25 × 0.14 |
| $\theta$ range, deg | 2.72−25.64 | 2.35−26.00 | 2.31−26.25 | 2.13−25.01 |
| index ranges | $-28 \le h \le 28$,<br>$-20 \le k \le 21$,<br>$-27 \le l \le 28$ | $-10 \le h \le 10$,<br>$-21 \le k \le 21$,<br>$-30 \le l \le 33$ | $-30 \le h \le 30$,<br>$-16 \le k \le 16$,<br>$-42 \le l \le 42$ | $-17 \le h \le 17$,<br>$-17 \le k \le 17$,<br>$-120 \le l \le 120$ |
| no. of rflns collected | 78 803 | 50 736 | 88 081 | 70 191 |
| no. of indep rflns | 17 283 | 8095 | 10 102 | 7364 |
| $R$(int) | 0.1118 | 0.0966 | 0.1224 | 0.1004 |
| $T_{max}$, $T_{min}$ | 0.9444, 0.8649 | 0.8299, 0.6875 | 0.8379, 0.8070 | 0.9431, 0.8942 |
| no. of data/restraints/params | 17 283/0/867 | 8095/0/408 | 10 102/126/508 | 7364/0/392 |
| goodness of fit on $F^2$ | 0.957 | 0.928 | 1.199 | 1.036 |
| final $R$ indices ($I > 2\sigma(I)$): R1, wR2 | 0.0566, 0.1214 | 0.0405, 0.0807 | 0.1296, 0.2596 | 0.1075, 0.2847 |
| $R$ indices (all data): R1, wR2 | 0.0884, 0.1345 | 0.0680, 0.0881 | 0.1388, 0.2642 | 0.1766, 0.3175 |
| peak/hole, e Å$^{-3}$ | 0.579/−0.375 | 0.468/−0.443 | 1.139/−1.065 | 1.077/−0.873 |

weeks, crystals of the composition Na(THF)$_6$[(CO)$_4$Mn($\mu$-SSi$t$Bu$_3$)$_3$Mn(SSi$t$Bu$_3$)] (**4**) and $t$Bu$_3$Si−SSS−Si$t$Bu$_3$ could be isolated. Due to the low yield of these species, no further characterization could be undertaken.

**X-ray Structure Determination.** Data collection: Stoe-IPDS-II diffractometer, graphite-monochromated Mo K$\alpha$ radiation; $T$ = 173 K, empirical absorption correction using MULABS,[30] structure solution by direct methods.[31] Structure refinement: full-matrix least squares on $F^2$ with SHELXL-97.[32] Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. CCDC reference numbers: 678303 (**1**), 678305 (**2**), 678304 (**3**), and 678302 (**4**·$t$Bu$_3$Si−SSS−Si$t$Bu$_3$). Table 2 gives crystal data and structure refinement details for **1**−**4**.

**Acknowledgment.** We are grateful to the University of Frankfurt for financial funding and the Chemetall GmbH for a gift of *tert*-butyllithium.

**Supporting Information Available:** CIF files giving X-ray parameters, atomic coordinates and thermal parameters, and bond distances and angles for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800211K

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