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New Sterically Hindered Manganese Selenolato Complexes. Isolation and Structural Characterization of a Reaction Intermediate, $[Mn\{N(SiMe_3)_2\}(\mu\text{-}SeC_6H_2\text{-}i\text{-}Pr_3\text{-}2,4,6)(THF)]_2$

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Introduction

The protolysis of metal amido complexes with chalcogenols has proved to be one of the most versatile routes to metal chalcogenolato complexes and is particularly suitable for the synthesis of complexes with sterically highly hindered ligands. For example, the reaction of $M[N(SiMe_3)_2]_2$ with Ar″EH (M = Zn, Cd; E = S, Se; Ar″ = 2,4,6-*t*-$Bu_3C_6H_2$) gives the dimeric compounds $[M(EAr'')_2]_2$;[1-3] these compounds are volatile and can be used as single-source precursors for group II–VI materials.[4] Power et al. have applied this method to the synthesis of analogous transition metal thiolates (M = Mn, Fe, Co),[5] and we have recently prepared a series of manganese(II) selenolato and tellurolato compounds.[6,7] We report here on the course of the reaction between $Mn[N(SiMe_3)_2]_2(THF)$ and Ar′SeH (Ar′ = 2,4,6-*i*-$Pr_3C_6H_2$).

Experimental Section

General Procedures. All reactions were carried out under inert gas using standard vacuum line techniques. Solvents were distilled under nitrogen from sodium–benzophenone [diethylether, thf, petroleum ether (bp 40–60 °C)], or sodium (toluene, heptane). The NMR solvents were stored over 4A molecular sieves under nitrogen or argon and degassed by several freeze–thaw cycles. The compounds 2,4,6-i-$Pr_3C_6H_2SeH$ (Ar′SeH)[2a] and $Mn[N(SiMe_3)_2]_2(THF)$[8] were prepared as described. Melting points are uncorrected. NMR spectra were recorded on a JEOL EX90Q instrument.

Synthesis of $[Mn\{N(SiMe_3)_2\}(SeAr')(THF)]_2$ (1). To a solution of 0.50 g (1.77 mmol) of Ar′SeH in 30 mL of petroleum ether is added 0.79 g (1.77 mmol) of $Mn[N(SiMe_3)_2]_2(THF)$ at −78 °C. A white precipitate forms during the following 20 min, which dissolves on warming the mixture to room temperature. The mixture is stirred for another 30 min, concentrated, and cooled to −78 °C to give a pale pink solid, which is filtered off and recrystallized from heptane at −16 °C to give **1** (0.32 g, 0.28 mmol, 32%). Anal. Calcd for $C_{50}H_{98}Mn_2N_2O_2Se_2Si_4$: C, 52.7; H, 8.6; N, 2.5. Found: C, 52.4; H, 8.7; N, 2.4.

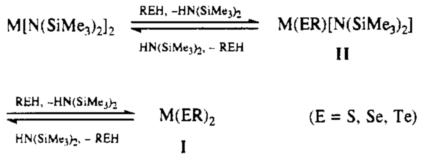
Synthesis of $[Mn(SeAr')_2]_2(THF)$ (2). To a solution of 1.16 g (4.10 mmol) of Ar′SeH in 80 mL of petroleum ether is added 0.92 g (2.05 mmol) of $Mn[N(SiMe_3)_2]_2(THF)$ at −78 °C. The mixture is warmed slowly to room temperature, stirred for 1 h, and concentrated. A pale pink crystalline solid (**2**) is obtained on cooling to −16 °C, which is washed with cold (−40 °C) petroleum ether and dried in vacuo. More product is obtained from the concentrated filtrate: combined yield 0.64 g (0.49 mmol, 48%). The compound gradually decomposes on heating above 165 °C. Anal. Calcd for $C_{64}H_{100}Mn_2OSe_4$: C, 58.6; H, 7.6; N, 0.0. Found: C, 58.6; H, 7.8; N, <0.3.

Table 1. Crystallographic Data for $[Mn\{N(SiMe_3)_2\}(\mu\text{-}SeC_6H_2\text{-}i\text{-}Pr_3\text{-}2,4,6)(THF)]_2$ (**1**)

formula	$C_{50}H_{98}Mn_2N_2O_2Se_2Si_4$	T, K	295
fw	1139.5	λ, Å	0.71073
a, Å	11.427(4)	space group	$P\bar{1}$
b, Å	11.791(4)	Z	1
c, Å	13.393(7)	D(calcd), g cm^{-3}	1.189
α, deg	78.00(3)	μ, cm^{-1}	15.16
β, deg	63.74(3)	θ range, deg	1–25
γ, deg	72.23(3)	R^a	0.0445
V, Å^3	1591.8(11)	$R_w{}^b$	0.0677

[a] $R = \sum|\Delta F|/\sum|F_o|$. [b] $R_w = [\sum w|\Delta F|^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(F) + 0.00550F^2$.

Scheme 1



$$M[N(SiMe_3)_2]_2 \underset{HN(SiMe_3)_2,\ -REH}{\overset{REH,\ -HN(SiMe_3)_2}{\rightleftharpoons}} \underset{\mathbf{II}}{M(ER)[N(SiMe_3)_2]} \underset{HN(SiMe_3)_2,\ -REH}{\overset{REH,\ -HN(SiMe_3)_2}{\rightleftharpoons}} \underset{\mathbf{I}}{M(ER)_2} \qquad (E = S, Se, Te)$$

Synthesis of 1 from 2 and $Mn[N(SiMe_3)_2]_2(THF)$. To a solution of 0.28 g of **2** (0.21 mmol) in 15 mL of THF is added at room temperature 0.19 g (0.42 mmol) of $Mn[N(SiMe_3)_2]_2(THF)$. The solution is stirred for 1 h before the solvent is removed in vacuo. The residue is dissolved in 25 mL of *n*-heptane, filtered, and concentrated. **1** is obtained as pale pink crystals on cooling to −78 °C (0.40 g, 0.35 mmol, 83%).

Crystallographic Determination for 1

Crystallographic data are given in Table 1. X-ray data were collected using a Siemens R3m/V diffractometer [Mo Kα radiation (λ = 0.710 73 Å); 2θ range 2–50°, ω scans, 5895 reflections collected; 5631 unique; h = −12 to +13, k = −13 to 14, l = 0 to +15] at 295 K for a pale pink needle (0.20 × 0.24 × 0.50 mm). The data were corrected for absorption effects using a semiempirical treatment based on azimuthal ψ-scan data (minimum/maximum transmission = 0.2804/0.3186). The structure was solved using a Patterson synthesis to locate the Mn and Se atoms. All other non-hydrogen atoms were located after successive cycles of full-matrix least-squares methods and refined anisotropically. Hydrogen atoms were constrained to their idealized positions using a riding model. The halves of the molecule are related by a crystallographic inversion center located at the centroid of the molecule. No unusual features in the final difference map outside the range ± 0.31 e Å^{-3}. Refinement on 280 parameters converged with R = 0.045 and R_w = 0.0677 for 3166 observed reflections ($F_o > 6\sigma|F|$).

Results and Discussion

Although the reaction of metal amido complexes $M[N(SiMe_3)_2]_2$ with chalcogenols proceeds stepwise, the product obtained is usually that with the least solubility in the reaction medium, i.e., the reaction equilibrium is rapidly displaced to the right to give metal chalcogenolates **I** (Scheme 1). Intermediates of type **II** are rarely observed.[7]

Treatment of $Mn[N(SiMe_3)_2]_2(THF)$[7a,8] with 1 equiv of Ar′SeH[2a] in light petroleum at −78 °C gives a colorless precipitate which dissolves on warming to room temperature. Recrystallization at −16 °C gave air-sensitive pale pink crystals of $[Mn\{N(SiMe_3)_2\}(\mu\text{-}SeC_6H_2\text{-}i\text{-}Pr_3\text{-}2,4,6)(THF)]_2$ (**1**) (Scheme 2). The structure was elucidated by X-ray diffraction. Crystal data are given in Table 1, and fractional positional parameters, in Table 2. The structure of the complex is shown in Figure 1. Selected bond lengths and angles are given in Table 3.

Complex **1** is dimeric, with bridging selenolato and terminal bis(trimethylsilyl)amido ligands. The distorted tetrahedral coordination geometry of the metal center is completed by a THF ligand retained from the starting amido complex. The Mn_2Se_2

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Scheme 2

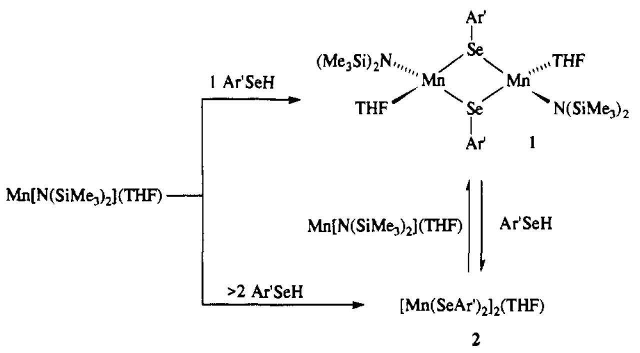

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	U(eq)[a]
Se(1)	1342(1)	4011(1)	4283(1)	46(1)
Mn(1)	586(1)	6314(1)	3940(1)	46(1)
Si(1)	−1265(2)	8563(2)	3040(2)	60(1)
Si(2)	1319(2)	7404(2)	1473(2)	59(1)
N(1)	194(5)	7506(4)	2730(4)	48(2)
O(1)	2077(5)	6842(5)	4241(4)	73(3)
C(1)	2029(6)	3262(5)	2953(5)	52(3)
C(2)	1220(7)	3215(6)	2416(5)	63(3)
C(3)	1792(9)	2872(8)	1369(6)	85(5)
C(4)	3131(10)	2582(7)	876(6)	85(4)
C(5)	3914(9)	2524(7)	1475(7)	86(4)
C(6)	3384(7)	2871(6)	2497(6)	67(3)
C(7)	−254(7)	3514(7)	2896(6)	68(4)
C(8)	−780(11)	2470(10)	2877(8)	115(6)
C(9)	−897(10)	4644(10)	2334(9)	115(6)
C(10)	3675(13)	2344(10)	−299(7)	129(7)
C(11)	3562(11)	3442(10)	−1038(7)	124(7)
C(12)	3623(14)	1312(11)	−541(8)	147(9)
C(13)	4329(7)	2772(8)	3089(7)	88(4)
C(14)	5463(10)	3303(11)	2420(10)	134(7)
C(15)	4824(10)	1494(10)	3487(9)	137(7)
C(16)	−2661(7)	7885(7)	3360(6)	75(4)
C(17)	−1427(9)	9800(7)	1933(7)	94(4)
C(18)	−1502(8)	9277(7)	4238(6)	80(4)
C(19)	714(10)	7201(9)	414(6)	98(5)
C(20)	2721(8)	6091(8)	1505(7)	91(4)
C(21)	2011(8)	8736(8)	941(7)	89(4)
C(22)	3207(8)	6084(9)	4469(9)	102(6)
C(23)	4073(14)	6778(15)	4313(13)	173(11)
C(24)	3581(12)	7955(12)	3836(13)	162(10)
C(25)	2225(10)	8033(9)	3982(8)	101(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

ring forms a planar parallelogram, with Mn–Se distances of 2.582(2) and 2.645(2) Å. These distances are comparable to those found in $[Mn(SeC_6H_2Me_3\text{-}2,4,6)_2]_\infty$[6] [2.593(4) Å] but slightly longer than the terminal Mn–Se bonds in the anion $[Mn(SePh)_4]^{2-}$ (average 2.567 Å).[9] The bridging Mn–Se distances in **1** differ markedly. Similar asymmetric bridging has previously been observed for group 12 chalcogenolato complexes $[M(EAr'')_2]_2$ (M = Zn, Cd) and was explained as the result of changes in the metal–chalcogen orbital overlap resulting from the displacement of the organic substituents of the bridging chalcogenolato ligands away from the symmetrical positions along the S–S vector toward the metal centers.[3] In agreement with this pattern of distortion, the smaller of the Mn–Se–C(1) angles in **1** is associated with the shorter Mn–Se bond.

The steric requirements of the bulky amido and selenolato ligands are reflected in the wide N(1)–Mn–Se(1) angle of 136.4(2)°, while the O(1)–Mn–Se(1) and Se(1)–Mn–Se(1A) angles are reduced to 100.7(1) and 82.0(1)°, respectively. The geometries of the THF and the bis(trimethylsilyl)amido ligands are unexceptional; the Mn(1)–N(1) distance in **1** is identical within experimental error to the Mn–N bond lengths to the terminal amido ligands in $[Mn\{N(SiMe_3)_2\}_2]_2$[10] and in $Li[Mn\{N(SiMe_3)_2\}(OC\text{-}t\text{-}Bu_3)_2]$,[7b] while the Mn–O bond [2.168(7) Å] is slightly shorter than that in $Mn[N(SiMe_3)_2]_2(THF)_2$ (average 2.238 Å).[11]

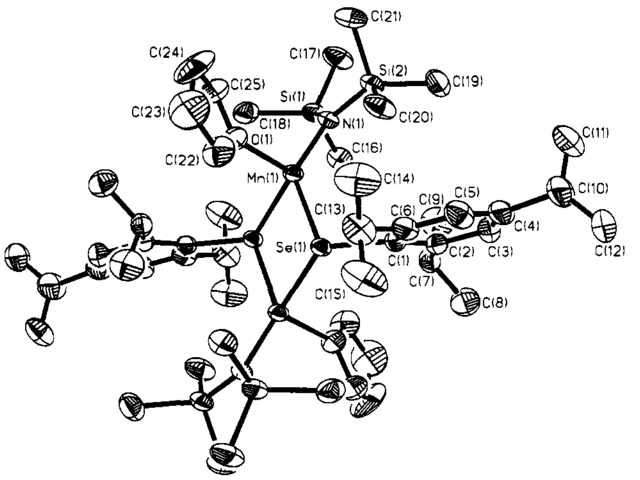

Figure 1. Molecular structure of $[Mn\{N(SiMe_3)_2\}(\mu\text{-}SeC_6H_2\text{-}i\text{-}Pr_3\text{-}2,4,6)(THF)]_2$ (**1**), showing the atomic numbering scheme. Ellipsoids correspond to 30% probability.

Table 3. Selected Bond Distances and Angles for **1**

(a) Bond Distances (Å)			
Se(1)–Mn(1)	2.582(2)	Se(1)–Mn(1A)	2.645(2)
Se(1A)–Mn(1)	2.645(2)	Mn(1)–O(1)	2.168(7)
Mn(1)–N(1)	2.000(5)	Se(1)–C(1)	1.946(7)
Si(1)–N(1)	1.717(5)	Si(2)–N(1)	1.710(5)
O(1)–C(22)	1.424(11)	C(22)–C(23)	1.402(23)
(b) Bond Angles (deg)			
Mn(1)–Se(1)–Mn(1A)	98.0(1)	Se(1)–Mn(1)–Se(1A)	82.0(1)
Se(1)–Mn(1)–N(1)	136.4(2)	N(1)–Mn(1)–O(1)	104.1(2)
Se(1)–Mn(1)–O(1)	100.7(1)	N(1)–Mn(1)–Se(1A)	119.0(1)
O(1)–Mn(1)–Se(1A)	112.8(1)	Mn(1)–Se(1)–C(1)	111.8(2)
C(1)–Se(1)–Mn(1A)	130.2(2)	N(1)–Si(1)–C(16)	111.6(3)
Mn(1)–N(1)–Si(1)	116.9(2)	Mn(1)–N(1)–Si(2)	118.2(2)
Mn(1)–O(1)–C(22)	127.7(6)	Mn(1)–O(1)–C(25)	122.8(6)
C(22)–O(1)–C(25)	107.9(8)	Se(1)–C(1)–C(2)	121.1(4)

The reaction of $Mn[N(SiMe_3)_2]_2(THF)$ with an excess of Ar'SeH in light petroleum gives a clear solution from which $[Mn(SeAr')_2]_2(THF)$ (**2**) is obtained as a pale pink crystalline solid. Attempts to grow X-ray quality crystals were unsuccessful. The composition of the compound was ascertained by elemental analysis and ^1H NMR spectroscopy on the organic products after air-oxidation of a solution of the complex. Once crystallized, **2** is poorly soluble in saturated hydrocarbons. The compound is thought to be dimeric in analogy to **1**; the THF ligand is probably coordinated to one of the manganese atoms. Since ligand exchange is facile, **2** can readily be converted to **1** by comproportionation with $Mn[N(SiMe_3)_2]_2(THF)$ (Scheme 2).

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Supplementary Material Available: Tables of bond distances and angles, thermal parameters, and H atom fractional coordinates (3 pages). Ordering information is given on any current masthead page.

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