Chapter One

DIVALENT MANGANESE, IRON, AND COBALT BIS(TRIMETHYLSILYL)AMIDO DERIVATIVES AND THEIR TETRAHYDROFURAN COMPLEXES

1. INTRODUCTION

The intention of this chapter is to describe in detail reliable synthetic procedures for the uncomplexed metal bissilylamides $M\{N(SiMe_3)_2\}_2$ (M = Mn, Fe, or Co) as well as those of their mono-tetrahydrofuran complexes $M\{N(SiMe_3)_2\}_2$ (THF). In addition, a synthesis for the bis(THF) complex $Mn\{N(SiMe_3)_2\}_2$ (THF)₂ is given.

The bis(trimethylsilyl)amido group $\{N(SiMe_3)_2\}^{-1, 2}$ is one of the simplest, most versatile, and inexpensive bulky monodentate ligands. Its steric properties were first demonstrated by Bürger and Wannagat via the synthesis of several low- (i.e. two- or three-) coordinate transition metal derivatives in the early 1960s. They were prepared by the simple reaction of an alkali metal salt of the amide $\{N(SiMe_3)_2\}^-$ with chromium, manganese, iron, cobalt, nickel, or copper halides.¹⁻⁴ The list of new compounds^{3, 4} included the trivalent complexes $M{N(SiMe_3)_2}_3$ (M = Cr and Fe), the divalent species $M{N(SiMe_3)_2}_2$ $(M = Mn, {}^{4}Co, {}^{3}and Ni^{4} (unstable))$, and the monovalent $Cu\{N(SiMe_{3})_{2}\}$.⁴ The volatility of M(II) and M(III) derivatives supported the notion that the compounds had unassociated molecular structures and were therefore the first stable examples of open-shell (i.e. d^1-d^9) transition metal complexes with coordination numbers less than four. The closed-shell (d¹⁰) Cu(I) derivative, although volatile, proved to be tetrameric $\{CuN(SiMe_3)_2\}_4$ with four coppers arranged in a planar array and bridged by silvlamido ligands⁵. The trigonal planar coordination of the M(III) species was proven for $Fe\{N(SiMe_3)_2\}_3$ via a determination of its crystal

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structure by Bradley, Hursthouse, and Rodesiler in 1969.⁶ It was shown subsequently that the $-N(SiMe_3)_2$ ligand could stabilize three coordination in most of the first-row transition metals,^{7–9} lanthanide,^{9, 10} and some actinide metals.^{11, 12}

The original divalent transition metal silylamides $M{N(SiMe_3)_2}_2$ (M = Mn, Co, and Ni) were later expanded to include the iron analogue $Fe\{N(SiMe_3)_2\}_2$ by Andersen, Lappert, Haaland, and coworkers in 1988.¹³ With the exception of the Ni species, which is unstable, the $M{N(SiMe_3)_2}_2$ (M = Mn, Fe, or Co) complexes were shown to have a linear N-M-N structure in the vapor phase by gas electron diffraction in 1988,¹³ in agreement with the original formulation of Bürger and Wannagat.^{3, 4} Nonetheless, in 1978 it had been shown by Bradley, Hursthouse, and coworkers that the originally reported synthesis of $Mn\{N(SiMe_3)_2\}_2^4$, which was carried out in tetrahydrofuran, probably described its tetrahydrofuran complex $Mn{N(SiMe_3)_2}_2(THF)$, which could be distilled several times without losing the tetrahydrofuran ligand.¹⁴ This view was supported by an exhaustive study of the manganese(II) silylamides by Horvath in 1979.¹⁵ Despite a 1971 paper¹⁶ that seemed to confirm the monomeric, THF-free character of $Co\{N(SiMe_3)_2\}_2$ (synthesized by the original Bürger and Wannagat route),³ recent work has shown that the synthesis of the silvlamides of both cobalt^{17–19} and nickel²⁰ in tetrahydrofuran also yielded the mono-tetrahydrofuran complexes M{N(SiMe₃)₂}₂(THF) (M = Co or Ni), which could be distilled directly from the reaction mixture. In addition, it had also been shown in 1991 that the synthesis of $Fe\{N(SiMe_3)_2\}_2$ could yield $Fe\{N(SiMe_3)_2\}_2(THF)$ when carried out in tetrahydrofuran.²¹ The mono-tetrahydrofuran complexes of the iron and cobalt silylamides are also obtainable by recrystallization of the uncomplexed $M{N(SiMe_3)_2}_2$ (M = Fe or Co) from tetrahydrofuran. However, for $Mn\{N(SiMe_3)_2\}_2$, the recrystallization from tetrahydrofuran produces the bis tetrahydrofuran complex Mn{N $(SiMe)_{2}_{2}(THF)_{2}^{21}$

In essence, the improved synthetic characterization methods and readily available crystal handling techniques for X-ray crystallographic studies available to modern workers have permitted all of Bürger and Wannagat's originally reported metal bis silylamido compounds to be unambiguously characterized. This work^{7, 14, 15, 17–20} has shown conclusively that these original divalent compounds are not two-coordinate species, but are in fact the tetrahydrofuran complexes $M{N(SiMe_3)_2}_2(THF)$ (M = Mn, Co, and Ni). For these mono-tetrahydrofuran species and their later synthesized iron analogue $Fe{N(SiMe_3)_2}_2(THF)$, the complexed tetrahydrofuran can only be removed with difficulty. For example, the desolvation of $Mn{N(SiMe_3)_2}_2(THF)$ requires heating at 120 °C under argon for 1 h.

The pure tetrahydrofuran-free amides "M{ $N(SiMe_3)_2$ }" (M = Mn, Fe, Co) can be synthesized by performing the synthesis in diethyl ether, which does not bind to the metal as strongly as tetrahydrofuran and is easily removed. They are monomers in the vapor phase,¹³ but they are crystalline solids at room temperature with amido-bridged dimeric structures and three-coordinate metals as shown by X-ray crystallography.^{17, 21–24} Variable temperature ¹H NMR studies of their solutions^{17, 21} have shown that the monomeric and dimeric structures exist in equilibrium with relatively low association energies, so that the major portion of the species present in their solutions consists of the monomers.

An interesting aspect of more than a half-century of work on the compounds is the length of time that was required for the distinction between the bright green $Co{N(SiMe_3)_2}_2$ (THF) and $[Co{N(SiMe_3)_2}_2]_2$ (red/olive) to be delineated. A clear distinction between the two compounds was, in fact, specifically described only in 2013.^{17, 18} This lengthy period is particularly noteworthy in view of the very sharp contrast between the colors of the two compounds that makes them easily distinguishable. In contrast, the colors of the THF-free and THF-complexed amide for each of the metals Mn, Fe, and Ni are similar, which does not allow for easy visual distinction. This author and his group had used $[Co{N(SiMe_3)_2}_2]_2$ (synthesized in diethyl ether solvent) numerous times as a synthon^{9, 23} over a 30-year period, and had in fact characterized it structurally using X-ray crystallography in 1984,²⁴ but he saw the bright green crystals of $Co{N(SiMe_3)_2}_2$ (THF) for the first time (synthesized by graduate student A. M. Bryan) in the fall of 2012.²⁵ One reason for this strange circumstance is that the original Bürger and Wannagat synthetic procedures were all carried out in tetrahydrofuran. This solvent is less commonly used in this author's lab, owing to the general avoidance of the use of tetrahydrofuran as a solvent if diethyl ether suffices. The Co{N (SiMe₃)₂}₂(THF) complex was "rediscovered" recently because the magnetic properties^{17, 19, 26-28} of two- and three-coordinate cobalt complexes, which generally have high orbital magnetism, were being investigated and because of a need for well-defined cobalt precursor complexes in materials chemistry.¹⁸

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2. BIS{BIS(TRIMETHYLSILYL)AMIDO}IRON(II) DIMER: [Fe{N(SiMe₃)₂}₂]₂

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$\text{FeBr}_2(\text{THF})_2 + 2\text{LiN}(\text{SiMe}_3)_2 \rightarrow \text{Fe}\{N(\text{SiMe}_3)_2\}_2 + 2\text{LiBr}$

The hydrocarbon-soluble ironsilylamide, $Fe\{N(SiMe_3)_2\}_{2,1}^{-1}$ is a useful starting material for the synthesis of inorganic, coordination, and organometallic compounds utilizing proton-transfer reactions, since the pK_a of $HN(SiMe_3)_2$ is approximately 26 in THF.² A comprehensive description of the compounds that may be prepared using this methodology is available in an exhaustive review of

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two-coordinate compounds.³ The silylamide is a useful precursor for solid-state materials⁴ and catalysts.⁵ The synthesis of $Fe\{N(SiMe_3)_2\}_2$ has been described in an earlier volume⁶ of this series. Here we provide related syntheses by two routes and provide details of its electronic, mass, IR, and electronic spectra.

General Procedures

All reactions are performed under an atmosphere of nitrogen. Ether solvents are distilled from sodium-benzophenone and hydrocarbons are distilled from sodium under an atmosphere of nitrogen. It is important that the distillation of Fe{N(SiMe₃)₂}₂ is carried out in an all-glass distillation apparatus directly connected to a diffusion-pump vacuum system with greased, ground-glass joints. The FeBr₂(THF)₂ is obtained by Soxhlet extraction of anhydrous FeBr₂ with THF as described in the literature.⁷ The ratio of THF to FeBr₂ is determined by combustion analysis or hydrolysis of a known mass suspended in C₆D₆ containing a reference, such as ferrocene, with D₂O in a NMR tube and integrating the resulting ¹H NMR spectrum. Crystalline LiN(SiMe₃)₂(0.80 Et₂O) is prepared by dropwise addition of HN(SiMe₃)₂ in diethyl ether to *n*-butyllithium in hexane in a 1 : 1 molar ratio at 0 °C followed by crystallization by cooling a concentrated solution to -20 °C. The ratio of HN(SiMe₃)₂ to Et₂O is obtained by hydrolysis of a crystal dissolved in C₆D₆ with D₂O in a NMR tube and integrating ¹H NMR spectrum.

Caution. *n*-Butyllithium is pyrophoric in air and reacts rapidly and exothermically with water.

A. BIS{BIS(TRIMETHYLSILYL)AMIDO}IRON(II) DIMER: [Fe{N(SiMe₃)₂}₂]₂

The lithium silylamide, LiN(SiMe₃)₂ (0.80 Et₂O) (10.4 g, 0.046 mol), dissolved in diethyl ether (100 mL) is added by cannula to a suspension of FeBr₂(THF)₂ (8.3 g, 0.023 mol) in diethyl ether at *ca*. 0 °C, and the suspension is stirred at 0 °C for 12 h.^a The diethyl ether is removed under reduced pressure. The green-yellow residue is extracted with pentane (2 × 50 mL), and the combined red filtrates are taken to dryness under reduced pressure, resulting in a dark red viscous oil. The oil is dissolved in a small amount of pentane (*ca*. 7–8 mL) and transferred to a distillation apparatus, and the volatile material (including residual THF) is removed at

^a The checkers report that the synthesis may also be performed on the same scale, without the use of THF or FeBr₂(THF)₂, by reacting two equivalents of in situ generated LiN(SiMe₃)₂ in diethyl ether with anhydrous FeCl₂, freshly generated by dehydrating FeCl₂·4H₂O by the method of Horvath⁸ (cf. also the preparation of THF-free manganese(II) and cobalt(II) silylamides in this volume). There are three other syntheses of [Fe{N(SiMe₃)₂]₂]₂ from LiN(SiMe₃)₂ and FeCl₂^{6, 9} or FeBr₂¹⁰ in diethyl ether.

20 °C under dynamic diffusion-pump vacuum. After all of the volatile material is removed, the red oil is distilled at *ca.* 0.01 mmHg over the temperature range of 80–90 °C (bath temperature 115–125 °C) into a receiver flask cooled in an ice bath. The distillate is a green-yellow mobile liquid that slowly solidifies to a soft green-yellow solid. The yield is 6.0 g (70%).^b

Properties

The [Fe{N(SiMe₃)₂]₂]₂ complex is air and moisture sensitive, but it can be stored in a stoppered flask inside of a dry box for extended periods of time. The solid is soluble in hydrocarbons and gives a monomeric molecular ion in the mass spectrum, M⁺ m/z (calculated intensity, found relative intensity): 376 (100, 100), 377 (36.8, 33.6), 378 (19.8, 17.3), and 379 (4.93, 3.54). The infrared spectrum recorded as a Nujol mull between CsI windows has absorption at 1250 (sh, s), 1240 (s), 1175 (w), 1020 (sh, m), 990 (s), 970 (s), 845 (s), 825 (s), 783 (s), 745 (m), 700 (w), 657 (m), 628 (w), 605(m), and 355 (s) cm⁻¹. The ¹H NMR spectrum in C₇D₈ (30 °C) is a broad resonance at δ = 63. The structure of Fe{N(SiMe₃)₂} in the gas phase is a linear monomer with two-coordinate iron atoms.¹ The structure in the solid state is dimeric with two silylamide groups bridging the threecoordinate iron atoms. In toluene solution a monomer–dimer equilibrium exists, for which ΔG = +3 kcal/mol at 300 K.¹¹

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^bThe checkers report that the melting point of $[Fe{N(SiMe_3)_2}_2]_2$ (recrystallized from pentane) is 35–37 °C (cf. 36–38 °C in Ref. 6). Its UV–Vis spectrum in hexane features absorptions at 380 nm ($\varepsilon = 810 \text{ M}^{-1} \text{ cm}^{-1}$) and 626 nm ($\varepsilon = 5 \text{ M}^{-1} \text{ cm}^{-1}$). Its Mössbauer spectrum at 80 K features a $\delta = 0.59 \text{ mm/s}$ and $|\Delta E_Q|$ of 1.02 mm/s.⁹ Furthermore, it forms the complex Fe{N(SiMe_3)_2}_2(THF) (m. p. 42–45 °C) when recrystallized from THF¹¹ (the binding constant in hexanes was determined to be 7.8 × 10³ ± 1.4% at 25 °C¹²).

3. BIS{BIS(TRIMETHYLSILYL)AMIDO}COBALT(II) DIMER, [Co{N(SiMe₃)₂}₂]₂, AND BIS{BIS (TRIMETHYLSILYL)AMIDO}(TETRAHYDROFURAN) COBALT(II), Co{N(SiMe₃)₂}₂(THF)

Submitted by AIMEE M. BRYAN* and PHILIP P. POWER* Checked by RICHARD A. ANDERSEN[†]

$CoCl_2 + 2LiN(SiMe_3)_2 \rightarrow Co\{N(SiMe_3)_2\}_2 + 2LiCl$

In the early 1960s, Bürger and Wannagat reported a series of low-coordinate first-row transition metal complexes using the silylamido ligand -N(SiMe₃)₂. The complexes were synthesized via the reaction of NaN(SiMe₃)₂ with the respective halides in THF solution.^{1, 2} The resulting hydrocarbon-soluble amido complexes proved to be useful sources of M^{2+} and M^{3+} ions for various inorganic and organometallic reactions.^{3, 4} However, subsequent work⁵⁻⁷ showed that the original route of Bürger and Wannagat, involving the use of CoI2 and $NaN(SiMe_3)_2$ in THF solvent, yielded the complex $Co{N(SiMe_3)_2}_2(THF)$, and not Co{N(SiMe₃)₂}₂ as originally reported. The divalent Co(II) silylamide, Co $\{N(SiMe_3)_2\}_2$, which can be most conveniently obtained by carrying out the synthesis in diethyl ether, has been shown to be monomeric in the gas phase,⁸ to be dimeric in the solid state,⁹ and to exist in a monomer-dimer equilibrium in hydrocarbon solution.⁵ Although its crystal structure was reported in 1984,⁹ the physical, magnetic, and spectroscopic properties of THF-free $[Co{N(SiMe_3)_2}_2]_2$ were not described in detail until 2013.⁵ The spectroscopic,^{5, 6} magnetic,^{5–7} and structural⁵⁻⁷ characterization of $Co{N(SiMe_3)_2}_2(THF)$ were described in three different publications in 2013-2014.

General Procedures

All reactions are performed with the use of modified Schlenk techniques or in a Vacuum Atmospheres dry box under nitrogen or argon atmosphere. Solvents are dried and collected using a Grubbs-type solvent purification system (Glass Contour)¹⁰ and degassed by using the freeze–pump–thaw method.

■ **Caution.** *n*-Butyllithium is pyrophoric in air and should be handled under a nitrogen or argon atmosphere. In addition, *n*-butyllithium reacts rapidly and exothermically with water. *n*-BuH is released during the addition of *n*-BuLi to protic reagents. Such reactions should be vented through an oil bubbler.

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A. BIS{BIS(TRIMETHYLSILYL)AMIDO}COBALT(II) DIMER: [Co{N(SiMe₃)₂}₂]₂

A diethyl ether suspension of $\text{LiN}(\text{SiMe}_3)_2^{11, 12}$ is synthesized *in situ* by adding n-BuLi (16 mL, 2.5 M solution in hexanes, 0.040 mol) dropwise to HN(SiMe₃)₂ (8.4 mL, 6.47 g, 0.040 mol) in diethyl ether (40 mL), cooled in an ice bath.^a The solution is allowed to come to room temperature and stirring is continued for 12 h. The resulting colorless suspension is added dropwise via cannula over 30 min to a diethyl ether (40 mL) slurry of CoCl₂ (2.86 g, 0.022 mol) chilled in an ice bath. An immediate color change of the slurry from blue to dark green is observed. When the addition is complete, the suspension is warmed to *ca.* $35 \,^{\circ}\text{C}$ and stirred for 12 h. The ether is removed under reduced pressure, and the resulting dark green solids are extracted with hexanes (ca. 40 mL), which results in a dark green solution with a gray precipitate. The solution is then filtered through a Celitepadded filter stick to afford a clear dark green solution. The hexanes are removed under reduced pressure to give a dark green oil. The oil is distilled as a dark green vapor at *ca*. 100 °C (0.05 Torr) using a short-path distillation apparatus. Upon cooling, the vapor solidifies to a red/olive mass. The solid is redissolved in hexanes (ca. 30 mL) at ca. 65 $^{\circ}$ C which affords an olive-green solution. Cooling slowly to 0 °C gives a precipitate of $[Co{N(SiMe_3)_2}_2]_2$ in the form of red/olive dichroic crystals with a yield of 5.7 g (7.5 mmol, ca. 68%).

Properties

The cobalt(II) bis(silylamide) is both air and moisture sensitive but can be stored inside a nitrogen or argon dry box for several months without noticeable decomposition. If decomposition does occur, redistillation and then recrystallization in hexanes can be used to purify the compound. The compound is soluble in hydrocarbon solvents but exists in a monomer–dimer equilibrium with an association energy (ΔG_{reacn}) of -0.30(20) kcal mol⁻¹ at 300 K in benzene solution.⁵ As a solid, the red/olive dichroic compound is dimeric with bridging silylamide ligands between two three-coordinate cobalt(II) ions.^{5, 9} In the gas phase, Co{N(SiMe₃)₂}₂ is monomeric with strictly linear coordination at the cobalt(II) ion.⁸ M.p. 89–90 °C. UV–Vis/NIR (hexane, 298 K, nm [ε , M⁻¹ cm⁻¹]): 209 [3000], 223 [11 000], 281 [3400], 324 [6500], 604 [140], 668 [200]. IR (Nujol, CsI, cm⁻¹): 3140, 2890, 2710, 2650, 1450, 1368, 1357, 1340, 1290, 1250, 1239, 1150, 1070, 1010, 955, 918, 880, 840, 828, 810, 794, 726, 710, 657, 600, 348, 265. μ_{eff} = 4.7(2) μ_{B} (C₆D₆, 298 K, Evans' method). ¹H NMR (295 K, 400 MHz, C₆D₆): 8.97 (br s,

^a The checker reports that he used a diethyl ether solution of $\text{LiN}(\text{SiMe}_3)_2(\text{OEt}_2)_x$ (x = 0.80) crystallized from diethyl ether at -20 °C.

 $-SiMe_3$, $[Co{N(SiMe_3)_2}_2]_2$, 0.51 (s, $-SiMe_3$ (terminal), $[Co{N(SiMe_3)_2}_2]_2$), -4.22 (br s, $-SiMe_3$ (bridging), $[Co{N(SiMe_3)_2}_2]_2$) ppm.

B. BIS{BIS(TRIMETHYLSILYL)AMIDO}(TETRAHYDROFURAN) COBALT(II): Co{N(SiMe₃)₂}₂(THF)

Using a preparation similar to that described originally by Bürger and Wannagat, solid LiN(SiMe₃)₂¹¹ (6.68 g, 40 mmol) is added to a rapidly stirred suspension of CoCl₂ (2.6 g, 20 mmol) in THF (*ca.* 40 mL) with cooling in an ice bath. After 1 h, the ice bath is removed and stirring is continued for 12 h to afford a green solution. The THF is pumped off under reduced pressure, and the residue is extracted with pentane (50 mL) and filtered using a Celite-padded medium frit. The pentane is removed under reduced pressure, and the residual oily green solid is sublimed at *ca.* 70 °C under reduced pressure (*ca.* 0.02 Torr) to afford the product Co{N(SiMe₃)₂}₂(THF) as bright green crystals with a yield of 6.23 g, 69%.^b Co {N(SiMe₃)₂}₂(THF) can also be obtained by dissolving [Co{N(SiMe₃)₂}₂]₂ (2.5 g, 3.29 mmol, see Section 3.A) in THF (*ca.* 30 mL), which affords a bright green solution. The solution is concentrated under reduced pressure until a green precipitate is formed. Gentle warming to redissolve the solids and cooling for 12 h in a *ca.* 4 °C refrigerator affords the product [Co{N(SiMe₃)₂}₂(THF)] (2.72 g, *ca.* 91%).^c

Properties

The cobalt(II) bis(silylamide)tetrahydrofuran complex has a bright green color apparently corresponding to the color (giftgrün¹) of the product originally described by Bürger and Wannagat as Co{N(SiMe₃)₂}. The THF complex is soluble in hydrocarbon solvents. Mp. 71–73 °C. UV–Vis/NIR (hexane, nm [ϵ , M⁻¹ cm⁻¹]): 680 [90], 1565.¹⁰ IR (Nujol, CsI, cm⁻¹): 2980, 2950, 2840, 2720, 1445, 1368, 1252, 1070, 1010, 658, 620, 600, 408, 375, 348, 315, 270. ¹H NMR (400 MHz, C₆D₆, 298 K): 166.9 (br, CH₂O), 99.5 (br, CH₂O), –17.3 (br s, SiMe₃) ppm.

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^b The checker reports that he repeated the Bürger and Wannagat preparation (Ref. 1) using CoCl₂ and NaN(SiMe₃)₂ in tetrahydrofuran and upon workup obtained green crystals, Co{N(SiMe₃)₂}₂(THF). A sample of these crystals sublimed at 35–40 °C under a dynamic vacuum (0.01 Torr) and left a dark red-brown residue that was identified as Co{N(SiMe₃)₂}₂ by ¹H NMR spectroscopy.

^c A recent publication¹³ has described studies of the binding of THF to $Co\{N(SiMe_3)_2\}_2$ in hexane. The binding constant was determined to be $1.3 \times 10^5 \pm 1.4\%$, which is *ca*. 17 times stronger than that of the corresponding iron species (cf. Section 2 above).

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4. BIS{BIS(TRIMETHYLSILYL)AMIDO}MANGANESE(II) DIMER, [Mn{N(SiMe₃)₂}₂]₂, AND ITS THF COMPLEXES Mn {N(SiMe₃)₂}₂(THF) AND Mn{N(SiMe₃)₂}₂(THF)₂

Submitted by MICHELLE FAUST* and PHILIP P. POWER* Checked by RICHARD A. ANDERSEN^{\dagger}

 $MnCl_2 + 2NaN(SiMe_3)_2 \rightarrow Mn\{N(SiMe_3)_2\}_2 + 2NaCl$

In the early 1960s, Bürger and Wannagat reported a series of low-coordinate firstrow transition metal complexes of the silylamido ligand $-N(SiMe_3)_2$.^{1, 2} These hydrocarbon-soluble compounds proved to be useful sources of M²⁺ ions for various inorganic and organometallic syntheses.^{3, 4} The divalent Mn(II) silylamide, Mn{N(SiMe_3)_2}, was later shown to be monomeric in the gas phase⁵ and dimeric in the solid state.^{6, 7} Investigations of the originally reported synthetic route² revealed that the mono-THF complex, Mn{N(SiMe_3)_2}_2(THF), is formed first, rather than the THF-free Mn(II) silylamide,^{5, 6, 8, 9} and the THF can be removed by heating under argon to form Mn{N(SiMe_3)_2}_2,⁵ which has a dimeric structure in the crystalline state.^{7, 10} A subsequent report showed that the bis-THF complex,

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 $Mn\{N(SiMe_3)_2\}_2(THF)_2$, can also be formed, and it has been shown to have a four-coordinate distorted tetrahedral structure in the solid state.^{10, 11}

General Procedures

All reactions are performed with the use of modified Schlenk techniques or in a Vacuum Atmospheres dry box under nitrogen or argon atmosphere. Solvents are dried and collected using a Grubbs-type solvent purification system¹² (Glass Contour) and degassed by using the freeze–pump–thaw method.

A. BIS{BIS(TRIMETHYLSILYL)AMIDO}(TETRAHYDROFURAN) MANGANESE(II), Mn{N(SiMe₃)₂}₂(THF), AND BIS{BIS (TRIMETHYLSILYL)AMIDO}MANGANESE(II) DIMER, [Mn{N(SiMe₃)₂}₂]₂

The sodium amide, NaN(SiMe₃)₂ (5.187 g, 28.3 mmol), synthesized by literature methods,^{13, 14} is dissolved in tetrahydrofuran (ca. 25 mL). The resulting colorless solution is added dropwise via cannula to a tetrahydrofuran (ca. 20 mL) slurry of freshly dehydrated⁹ MnCl₂ (1.77 g, 14.1 mmol) at room temperature. A gradual color change of the slurry from pink to tan is observed. When the addition is complete, the suspension is heated and maintained at a gentle reflux for 2 h. The tetrahydrofuran is then removed under reduced pressure, and the resulting tan residue is distilled at 110° C (0.01 Torr) using a short-path distillation apparatus and a receiving flask cooled with liquid nitrogen. Upon cooling, the vapor solidifies as the salmon-pink-colored crystalline species $Mn\{N(SiMe_3)_2\}_2(THF)^{8, 9}$ (4.31 g, 9.6 mmol, 68% yield). (Note: Under analogous conditions, the THF-free $Mn\{N(SiMe_3)_2\}_2$ can be synthesized directly by exchanging THF for Et₂O as a solvent; however, decomposition during distillation can be extensive and consequently yields are lower.⁹) The THF-free silylamide $Mn{N(SiMe_3)_2}_2$ can be more conveniently obtained by removing the THF from Mn{N(SiMe₃)₂}₂(THF) via heating for 1 h at 120 °C under argon.^{6, 9} Pink crystals of dimeric $[Mn{N(SiMe_3)_2}_2]_2$ are subsequently grown from pentane (ca. 10 mL in a ca. -18 °C freezer) and isolated in 57% yield (3.02 g, 4.02 mmol).

Properties

The manganese(II) bis(silylamide) mono-THF complex is a salmon-pink extremely air- and moisture-sensitive crystalline solid, but it can be stored inside a nitrogen or argon dry box for several months without noticeable decomposition. It is soluble in hydrocarbon solvents and can readily be purified by recrystallization from pentane if contamination does occur.

Mp 35–36 °C. IR (Nujol, CsI, cm⁻¹): 2910, 2730, 2670, 1455, 1375, 1301, 1252, 1242, 1155, 1031, 999, 863, 843, 828, 781, 748, 720, 668, 625, 611,

414, 359, 249. No ¹H NMR signals due to the complex could be observed, probably owing to the high magnetic moment.

The manganese(II) bis(silylamide) dimer $[Mn{N(SiMe_3)_2}_2]_2$ is an extremely air- and moisture-sensitive pink crystalline solid but can be stored inside a nitrogen or argon dry box for several months without noticeable decomposition. It is soluble in hydrocarbon solvents and can readily be purified by recrystallization from pentane if contamination does occur. $[Mn{N(SiMe_3)_2}_2]_2$ dissociates to $Mn{N}(SiMe_3)_2$ monomers in the gas phase with strictly linear coordination at the manganese(II) ion.⁵

In the solid state, $[Mn\{N(SiMe_3)_2\}_2]_2$ is dimerized via bridging silylamide ligands to afford two three-coordinate manganese(II) ions.^{6, 7} Mp 57–58 °C. IR (Nujol, CsI, cm⁻¹): 2990, 2710, 2650, 1445, 1362, 1290, 1245, 1235, 1148, 1062, 988, 919, 850, 835, 818, 775, 740, 710, 655, 621, 600, 348, 268. $\mu_{eff} = 5.7(2) \mu_B (d_8$ -Tol, 298 K, Evans' method). Owing to the high magnetic moment, severe broadening of the ¹H NMR spectrum occurs and no signal due to the complex could be assigned.

B. BIS{BIS(TRIMETHYLSILYL)AMIDO}BIS (TETRAHYDROFURAN)MANGANESE(II)

Recrystallization of the mono-THF complex $Mn\{N(SiMe_3)_2\}_2(THF)$ (*ca.* 10 mmol, 4.5 g) by dissolving in 15 mL of THF and cooling in a *ca.* –18 °C freezer resulted in beige crystals of $Mn\{N(SiMe_3)_2\}_2(THF)_2^{10, 11}$ (4.01 g, 76.8%).

Properties

The bis(silylamido) manganese(II)bis-THF complex is extremely air and moisture sensitive but can be stored inside a nitrogen or argon dry box for several months without noticeable decomposition. The structure of $Mn\{N(SiMe_3)_2\}_2(THF)_2$ features a substantially distorted tetrahedral coordination at manganese.^{10, 11} Mp 47–49 °C. IR (Nujol, CsI, cm⁻¹): 2895, 2715, 1455, 1448, 1368, 1245, 1238, 1065, 1023, 990, 856, 833, 821, 772, 741, 714, 691, 661, 618, 603, 411, 352, 240.

C. AN ALTERNATIVE SYNTHESIS OF Mn{N(SiMe₃)₂}₂(THF) AND [Mn{N(SiMe₃)₂}₂]₂

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General Procedures

The preparation of the starting reagents, $MnBr_2(THF)_2$ by Soxhlet extraction of anhydrous $MnBr_2$ with THF, and of $Li\{N(SiMe_3)_2\}(0.80 \text{ Et}_2O)$, is outlined in the synthesis of $Fe\{N(SiMe_3)_2\}_2$.

Mn{N(SiMe₃)₂}₂(THF)

The lithium silylamide, Li{N(SiMe₃)₂}(0.80 Et₂O) (12.0 g, 0.052 mol) and MnBr₂(THF)₂ (9.3 g, 0.026 mol), are placed in a 500 mL round-bottom flask, and THF (150 mL) is added. The solids dissolve forming an orange-colored solution that is refluxed for 5 h. The solution is allowed to cool to room temperature, the THF is removed under reduced pressure, and the resulting dark colored solid is exposed to a dynamic vacuum for 12 h. Pentane is added (2 × 75 mL), the suspension is allowed to settle, and the filtrates are combined. The volume of the filtrate is concentrated to 20 mL, and the orange-red solution is transferred to a round-bottom flask, attached to an all-glass distillation apparatus that is connected to a diffusion-pump vacuum line with greased, ground-glass joints. The volatile material is removed at 20 °C and the orange-red liquid is distilled from 75 to 80 °C (bath temperature 100–110 °C) into a receiver flask cooled in ice. The yellow-red liquid slowly solidifies as pink-reddish needles appear in the liquid on prolonged standing at 20 °C. The yield is 6.0 g, 62%.¹

$[Mn\{N(SiMe_3)_2\}_2]_2$

The THF complex, $Mn\{N(SiMe_3)_2\}_2(THF)$ (3.0 g, 0.0086 mol), is dissolved in toluene (150 mL) in a 250 mL round-bottom flask with a greaseless O-ring joint and stopcock. The flask is attached to a vacuum line connected to an oil-pump vacuum, and the flask is evacuated. The solution is heated slowly with the stopcock closed; when the toluene vapor reaches the bottom of the greaseless stopcock, the stopcock is opened slowly and toluene is removed over 2 h. The yellowish residue is dissolved in pentane (30 mL) and filtered, and filtrate is concentrated to 15 mL. Cooling to -10 °C affords pink needles from a green mother liquor. The yield is 2.5 g, 77%.

Physical Properties

The melting point for the THF complex was not determined,^a but the IR spectrum agrees with that reported by the submitter. The base-free silylamide melts at 54–55 ° C, in agreement with the value reported by the submitter, and sublimes at 55–65 °C in a diffusion-pump vacuum. Mp = 57–58 °C.

^a Checkers report a Mp = 35-36 °C.

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