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Facile Metalation of Silicon and Germanium Analogues of Thiocarboxylic Acids with Manganese(II) Hydride Precursor

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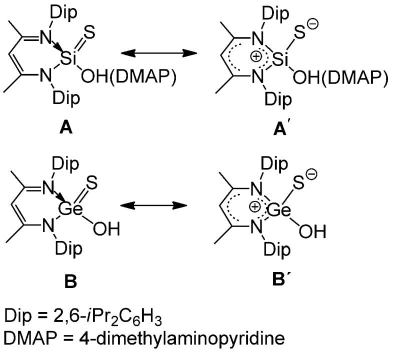
Abstract: Synthesis and characterization of the first manganese(II)-containing heavier thiocarboxylate analogues, [$L^{Dip}Si(=S)OMnL^{Dep}$] (**4**; $L^{Dip}=CH[C(Me)N(2,6\text{-}iPr_2C_6H_3)]_2$, $L^{Dep}=CH[C(Me)N(2,6\text{-}Et_2C_6H_3)]_2$) and [$L^{Dip}Ge(=S)OMnL^{Dep}$] (**5**) are described. They are accessible through reaction of the silicon and germanium analogues of the respective thiocarboxylic acids [$L^{Dip}E(=S)OH$] (E = Si, Ge) with the β-diketiminato (nacnac) manganese(II) hydride precursor [$(L^{Dep}Mn)_2(\mu\text{-}H)_2$] (**3**) in high yield. The first Mn nacnac hydride **3** has been prepared by the reaction of manganese bromide [$(L^{Dep}Mn)_2(\mu\text{-}Br)_2$] (**2**) with $KBEt_3H$. Compounds **4** and **5** represent the first transition-metal heavier thiocarboxylates with the Si=S and Ge=S functionalities. All new compounds are paramagnetic and were characterized by elemental analysis, IR spectroscopy, MS (EI), and single-crystal X-ray diffraction analyses. Due to the N→E (E = Si, Ge) and E = S→Mn donor–acceptor interaction as well as the carboxylate-like π-electron delocalization within the E(S)O moieties, the E=S double bonds in these compounds are resonance stabilized.

Keywords: dioxygen activation · germanium · manganese · silicon · transition metals

Introduction

Due to the central importance of the carbonyl group in chemistry, E=X double-bonds-containing species involving heavier Group XIV elements E and Group XVI elements X as heavier congeners of ubiquitous ketones, carboxylic acids, and related species have attracted considerable interest.[1] As a result, a vast number of striking examples containing an E=X moiety (E = Si, Ge, Sn; X = O, S, Se, Te) has been realized by taking advantage of thermodynamic stabilization through donor–acceptor interaction and/or kinetic stabilization by using sterically demanding substituents.[1] In this context, starting from zwitterionic N-heterocyclic silylene[2] and germylene,[3] we succeeded in synthesizing a series of compounds containing doubly bonded silicon and germanium with Group XVI elements including the isolation of the first Si=O and Ge=O double-bond-containing complexes.[4] Through the reaction of a 4-dimethylaminopyridine (DMAP)-stabilized Si=O compound with hydrogen sulfide, the isolable silathiocarboxylic acid **A** (Scheme 1) with a β-diketiminato ligand L^{Dip} ($L^{Dip}=CH[C(Me)N(2,6\text{-}iPr_2C_6H_3)]_2$) was synthesized as DMAP adduct.[4i] The germanium analogue **B**,[5a] which crystallized as a dimer through two S···H hydrogen bonds has also been described by Roesky and co-workers through the reaction of $L^{Dip}GeOH$ with elemental sulfur.[5b] Both carboxylic acid congeners **A** and **B** contain a thermodynamically well-stabilized E=S unit as illustrated by the respective resonance structure **A′** and **B′** (Scheme 1). They are promising starting material for the synthesis of new types of metal complexes, that is, metal silathiocarboxylates. Their coordination ability toward metal ions is expected to be different from those reported for respective thiocarboxylates due to the presence of the E=S subunits (E = Si, Ge). Metal complexes of **A** and **B** are rare,[4i] and no transition-metal derivative has been reported so far.



Scheme 1. Silathiocarboxylic acid–DMAP adduct **A** and germathiocarboxylic acid **B** with a β-diketiminato ligand.

Of the vast number of classical metal carboxylates with redox-active transition metals, manganese(II) species play an interesting role as catalysts in chemical synthesis and are of enormous importance in nature (e.g., water oxidation in the photosystem II).[6] The versatile role of manganese complexes in chemical and biological catalysis encouraged us to

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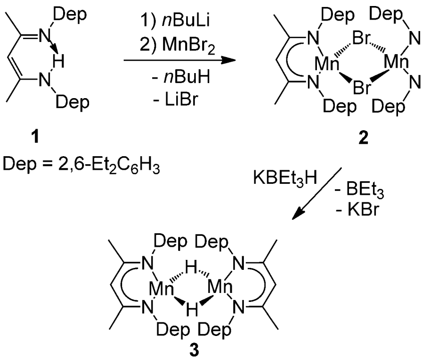
synthesize the first manganese derivatives of **A** and **B**. To enable a straightforward metalation of **A** and **B** by potentially suitable manganese(II) reagents in nonaqueous solutions, various β-diketiminato ("nacnac") Mn precursor complexes have been tested. Recently, LMnX complexes (L = nacnac, X = I,[7a,b] Cl, CH_3COO, Me, Ph, C_5H_5,[7c] $N(SiMe_3)_2$,[7d] $[(\mu\text{-}O)_2MnL]$[8]) have been reported by the research groups of Roesky and Power.[7a–d,8] We anticipated that manganese hydrides would be best suited for clean metalation of **A** and **B**. Herein, we report the synthesis of the first nacnac manganese hydride $[L^{Dep}MnH]$ (**3**; $L^{Dep} = CH[C(Me)N(2,6\text{-}Et_2C_6H_3)]_2$) from the corresponding bromide $[(L^{Dep}Mn)_2(\mu\text{-}Br)_2]$ (**2**). Hydride **3** turned out to be a facile and clean metalation reagent to form the first heavier thiocarboxylate analogues $[L^{Dip}Si(S)OMnL^{Dep}]$ (**4**) and $[L^{Dip}Ge(S)OMnL^{Dep}]$ (**5**).

Results and Discussion

Synthesis of β-diketiminato manganese bromide 2 and hydride 3: The manganese bromide **2** is readily accessible through a one-pot procedure by lithiation of **1** with *n*BuLi followed by transmetalation with manganese dibromide in diethyl ether (Scheme 2). After changing the solvent of the resulting mixture to *n*-hexane, complex **2** can be easily isolated as yellow crystals in 86 % yield. It is worth to note that the similar complex $[(L^{Dip}Mn)_2(\mu\text{-}I)_2]$[7b] was prepared from the reaction of $L^{Dip}K$ and MnI_2, because the reaction of $[L^{Dip}Li(OEt_2)]$ with MnI_2 resulted only in $[L^{Dip}Mn(\mu\text{-}I)_2Li(OEt_2)]$ and the removal of the coordinated lithium salt was unsuccessful.[7a] This is also the case for the preparation of the chloride $[(L^{Dip}Mn)_2(\mu\text{-}Cl)_2]$,[7c] which was synthesized with the β-diketiminato potassium precursor.



Scheme 2. Synthesis of β-diketiminato manganese bromide **2** and hydride **3**.

Complex **2** showed a paramagnetic ^1H NMR spectrum with very broad signals. The solution magnetic susceptibility was found to be 3.6 μ_B per manganese center (Evans method by using C_6D_6 as solvent).[9] The latter value is lower than the theoretical value of 5.5 μ_B for a high-spin Mn^{II} ($S = 5/2$), implying the presence of an interaction between the two Mn centers in the dimeric molecule of **2**. Most likely, the dimers exist with the monomer $[L^{Dip}MnBr]$ in equilibrium in the benzene solution, as was supported by cryoscopic measurement. In the MS (EI) spectrum, $[L^{Dep}MnBr]^+$ was observed at $m/z = 497$ (86 %), followed by $[L^{Dep}Mn]^+$ (at $m/z = 416$, 100 %). The elemental analyses are also consistent with the calculated values. The molecular structure of **2** has been established by single-crystal X-ray diffraction analysis. Complex **2** crystallized in the monoclinic space group $P2_1/n$ and showed a dimeric structure of $[L^{Dep}MnBr]$ with two bromide bridges (Figure 1). Both manganese centers adopt tetrahedral coordination geometry with the slightly puckered six-membered C_3N_2Mn rings perpendicular to the four-membered Mn_2Br_2 ring. The Mn⋯Mn distance is 3.478 Å and is very close to that observed in bis(tetraphenylphosphonium) bis(μ_2-bromo)dibromo manganese(II) (ca. 3.542 Å).[10] The Mn–Br bond lengths of 2.5462(4) and 2.5543(4) Å in **2** are close to the corresponding values observed in the latter complex (ca. 2.58 Å). The Mn–N bond lengths (2.047(2) and 2.0552(2) Å) are also consistent with those found in $[(L^{Dip}Mn)_2(\mu\text{-}Cl)_2]$ (2.0830(9) and 2.0819(10) Å)[7c] and $[(L^{Dip}Mn)_2(\mu\text{-}I)_2]$ (2.067(2) Å).[7b]

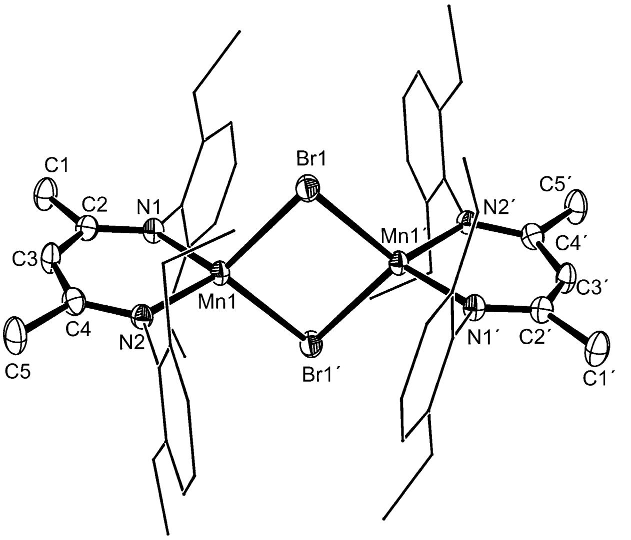


Figure 1. Molecular structure of complex **2**. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn1–Br1 2.5543(4), Mn1′–Br1 2.5462(4), Mn1–N2 2.047(2), Mn1–N1 2.055(2), Mn1–Br1′ 2.5462(4), N1–C2 1.328(3), N2–C4 1.330(3), C2–C3 1.410(3), C3–C4 1.397(3); Mn1′-Br1-Mn1 86.00(1), N2-Mn1-N1 93.96(7), Br1′-Mn1-Br1 94.01(1), C2-N1-Mn1 123.3(1), C4-N2-Mn1 122.5(2), N1-C2-C3 123.6(2), C4-C3-C2 130.7(2), N2-C4-C3 124.9(2). Symmetry transformations were used to generate equivalent atoms with (′): $-x+1$, $-y$, $-z$.

Treatment of **2** with one equivalent of $K[BEt_3H]$ (1 M in THF) in toluene at room temperature for 3 h led to the formation of compound **3**, which can be easily isolated as yellow crystals in 77 % yield. Similar to **2**, compound **3** revealed also a paramagnetic ^{1}H NMR spectrum with very broad resonances. The solution magnetic-susceptibility measurement showed 2.5 μ_B per manganese center, which is much lower than the theoretical value of 5.5 μ_B for a high-spin Mn^{II}. The difference between the observed and theoretical μ_{eff} values of **3** suggests an even stronger interaction between the two manganese centers than in **2**. Similar Mn$\cdots$Mn interaction in a dimeric manganese hydride complex has been suggested by Chomitz and Arnold.[11] The composition of **3** is confirmed by MS (EI) with $[(L^{Dep}MnH)_2]^+$ observed at $m/z = 833$ (40 %) followed by $[L^{Dep}Mn]^+$ (at $m/z = 416$, 100 %). The molecular structure of complex **3** has been established by single-crystal X-ray diffraction analysis (Figure 2). Compound **3** crystallizes in the monoclinic space group $P2_1/n$ and is a dimer formed by two Mn-H-Mn three-center two-electron bonds. The conformation of the ring subunits in **3** is quite similar to that of **2**, except for the short distance between the two Mn centers (2.7464(7) Å). The latter Mn−Mn distance is reminiscent of that observed in $Mn_2(\mu\text{-}H)_2$ core of $[(\{tBuN^{(-)}SiMe_2N(CH_2CH_2PiPr_2)_2\}Mn)_2(\mu\text{-}H)_2]$ (2.7945(7) Å),[11] suggesting electronic unsaturation of the Mn atoms.[12] The Mn−H bond lengths (1.86(2) and 1.87(2) Å) of **3** are in the range of Mn−H distances reported previously.[11,12]

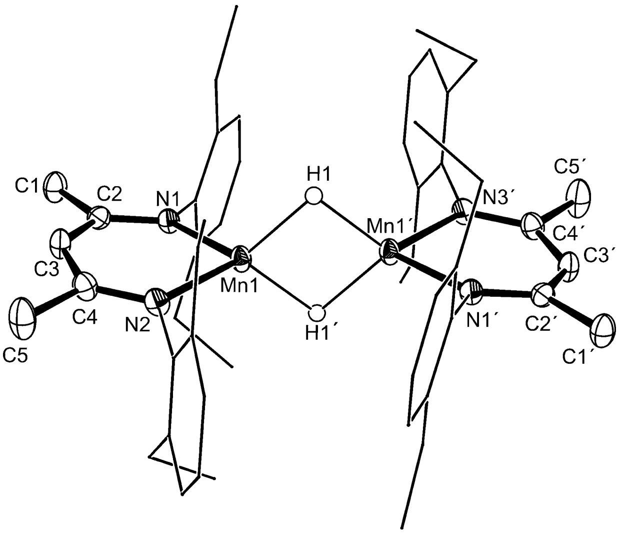
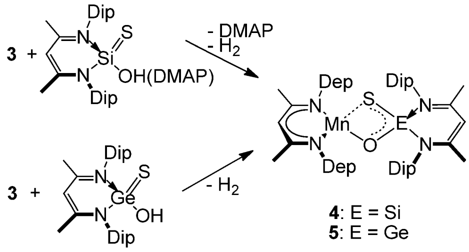


Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms, except for those at Mn atoms, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn1−N1 2.064(2), Mn1−N2 2.068(2), Mn1$\cdots$Mn1′ 2.7464(7), Mn1−H1 1.86(2), Mn1′−H1 1.87(2), N1−C2 1.328(2), C4−N2 1.331(3), C2−C3 1.403(3), C3−C4 1.403(3); N1-Mn1-N2 92.21(6), C2-N1-Mn1 124.2(1), C4-N2-Mn1 123.3(1), N2-C4-C3 124.9(2), N1-C2-C3 124.1(2), C2-C3-C4 129.6(2). Symmetry transformations were used to generate equivalent atoms with (′): $-x+1, -y, -z$.



Scheme 3. Synthesis of manganese silathiocarboxylate **4** and germathiocarboxylate **5**.

Synthesis of manganese silathiocarboxylate 4 and germathiocarboxylate 5: Reaction of silathiocarboxylic acid adduct **A** with **3** in THF at room temperature led to the formation of manganese silathiocarboxylate **4** under release of DMAP and dihydrogen gas (Scheme 3). Concentration of the resulting solution and cooling to −20 °C gave complex **4** as yellow crystals in 91 % yield.

Complex **4** represents the first transition-metal complex of a heavier thiocarboxylate. Its composition has been confirmed by MS and elemental analysis. Its MS (EI) spectrum revealed the molecular ion peak at $m/z = 909$ (100 %). The compound is sparingly soluble in n-hexane, but soluble in diethyl ether, toluene, and THF. As expected, it is paramagnetic in the solution, as was indicated by ^{1}H NMR, which showed very broad signals. Magnetic measurements performed for solution of **4** revealed a μ_{eff} value of 5.3 μ_B at room temperature, corresponding to a spin-only value of five unpaired electrons ($S = 5/2$).

A single-crystal X-ray diffraction analysis revealed a monomeric structure of **4** with three THF molecules in the asymmetric unit in a monoclinic space group $C2/c$ (Figure 3). As a thiocarboxylate analogue, the sulfur and

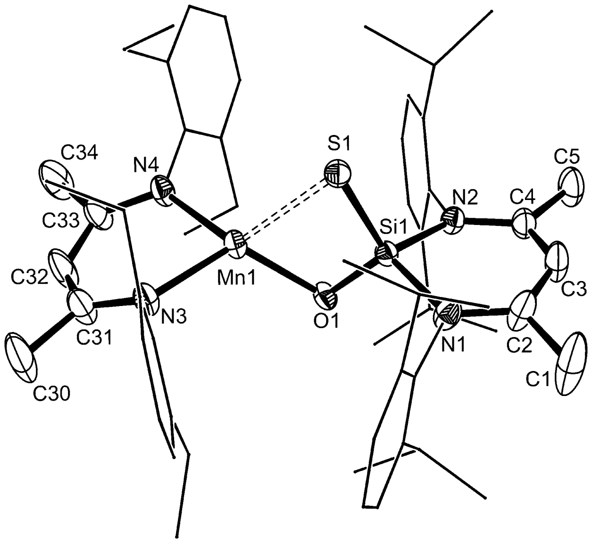


Figure 3. Molecular structure of **4**. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn1−O1 2.070(3), Mn1−N4 2.112(4), Mn1−N3 2.114(4), Mn1−S1 2.536(1), Mn1$\cdots$Si1 2.790(1), S1−Si1 2.058(2), Si1−O1 1.583(3), Si1−N2 1.805(4), Si1−N1 1.809(4); N4-Mn1-N3 89.7(1), O1-Mn1-S1 79.27(8), Si1-S1-Mn1 73.94(5), N2-Si1-N1 96.7(2), O1-Si1-S1 108.0(1), Si1-O1-Mn1 98.7(1).

oxygen atoms of the Si(=S)O moiety coordinate to the manganese center. Both manganese and silicon centers achieve a distorted tetrahedral coordination sphere and feature puckered six-membered C_3N_2M rings (M = Mn, Si). The Mn−N distances of 2.112(2) and 2.114(2) Å are slightly elongated compared with those observed in **2** and **3** (2.047(2)–2.068(2) Å). The Mn−O bond length (2.070(3) Å) is slightly longer than respective values observed in $[(L^{Dip}Mn)_2(\mu\text{-}OOCCH_3)_2]$ (1.991(7)–2.031(7) Å).[7c] The Mn−S distance [2.536(1) Å] is longer than the average value of Mn-$[(OPPh_2)(SPPh_2)N]_2$ with a MnO_2S_2 core (2.447(1) Å).[13] The Si−N distances of 1.805(4) and 1.809(4) Å are similar with those observed for precursor **A** (1.809(2) and 1.827(2) Å),[4i] whereas the Si−O bond length in **4** is shorter than that in precursor **A** (1.620(2) Å). In contrast, the Si−S distance of 2.058(2) Å in **4** is longer than the value in **A** (1.993(1) Å) due to larger π-electron resonance within the Si-S-O carboxylic-like moiety. However, this value is still significantly shorter than a normal Si−S single bond (≈2.14 Å).[14]

Similarly, metalation of germathiocarboxylic acid **B**[5a] with **3** in THF at ambient temperature afforded the expected manganese(II) germathiocarboxylate **5** (Scheme 3). Due to the dimer nature of **B**, the reaction is solvent dependent. For example, in toluene solution, the reaction occurs very slowly even after 12 h at room temperature. However, in THF, the reaction proceeds quite fast and is completed after 12 h. After work-up, complex **5** was isolated as yellow crystals in 90 % yield. The solubility and magnetic property of **5** is similar to that of the silicon analogue **4**. The solution magnetic susceptibility of **5** was found to be 5.6 μ_B, again suggesting a high-spin manganese(II) species. Its MS (EI) spectrum revealed the molecular peak at $m/z = 955$ (100 %). Complex **5** crystallizes readily from diethyl ether solutions without co-crystallized solvent molecules, as was indicated by X-ray diffraction analysis. However, the structure is disordered. Suitable single crystals without disordering of **5** could be obtained in toluene solution after two weeks at −20 °C. Their X-ray analysis revealed that the compound crystallizes in the monoclinic space group *Pn* (Figure 4). The refined structure of **5** is akin to that of **4** with almost the same features for the geometric parameter around the manganese center. The Ge−N bond lengths (1.923(3) and 1.925(3) Å) are comparable to those observed in the precursor **B** (1.911(2) and 1.916(2) Å).[5a] The shortening of the Ge−O distance (1.722(2) Å in **5** vs. 1.751(2) Å in **B**) and elongation of the Ge−S distance (2.1401(9) Å in **5** versus 2.077(1) Å in **B**) is reminiscent of those of **4** compared with its precursor **A**. The Mn−S distance of 2.545(1) Å in **5** is also similar to that found in **4** (2.536(1) Å). The latter observation suggests the presence of π-electron delocalization within the Ge-S-O moiety in **5**.

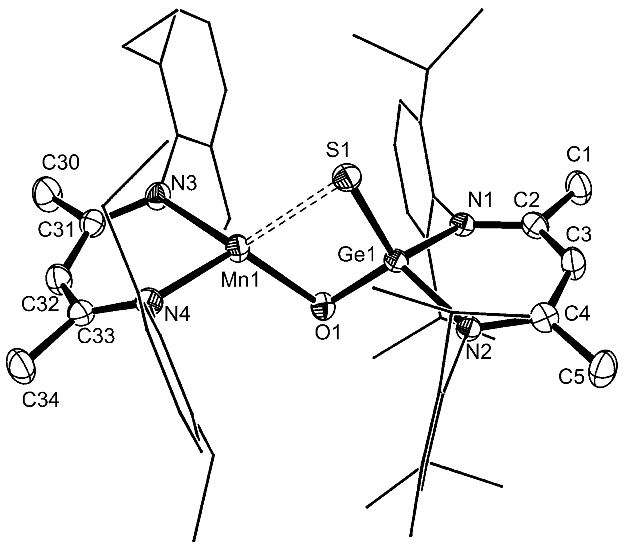


Figure 4. Molecular structure of complex **5**. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1−O1 1.722(2), Ge1−N2 1.922(3), Ge1−N1 1.925(3), Ge1−S1 2.1401(9), Mn1−O1 2.074(2), Mn1−N4 2.113(3), Mn1−N3 2.128(3), Mn1−S1 2.545(1), Mn⋯Ge 2.847 (2); N2-Ge1-N1 94.8(1), O1-Ge1-S1 105.71(8), N4-Mn1-N3 90.1(1), O1-Mn1-S1 83.28(7), Ge1-S1-Mn1 74.28(3), Ge1-O1-Mn1 96.7(1).

Both manganese silathiocarboxylate **4** and germathiocarboxylate **5** are very sensitive towards air and moisture. Preliminary experiments showed that **4** and **5** are capable to activate dioxygen under mild condition. Thus, reactions of **4** and **5** with dry dioxygen in toluene led to an immediate color change from yellow to dark brown and formation of a mixture of unidentified products. Interestingly, **4** and **5** mediate clean and mild stoichiometric oxygenation of Ph_3P to $Ph_3P{=}O$ in the presence of dioxygen. Further investigations are needed to elucidate the nature of the respective $Mn{-}O_2$ complexes formed initially and the mechanism of oxygenation of Ph_3P.

Conclusion

The coordination chemistry of divalent manganese complexes supported by silathiocarboxylate **4** and germathiocarboxylate **5** ligands is presented. Both complexes were readily obtained in high yield from reaction of silathiocarboxylic adduct **A** and germathiocarboxylic acid **B** with nacnac manganese hydride **3**. The latter could be easily prepared from the corresponding manganese bromide **2**. Complexes **4** and **5** represent the first transition-metal sila- and germathiocarboxylates, respectively. The E=S (E = Si, Ge) bonds in **4** and **5** are stabilized by S→Mn and N→E dative interaction as well as π-electron delocalization of the E(S)O moieties. Our results showed that sila- and germathiocarboxylato ligands can serve as competent supporting ligands for transition metals. Preliminary experiments revealed that both complexes are capable to activate dioxygen and oxygenate triphenylphosphine into its oxide under mild conditions. The synthesis of other redox-active transition-metal complexes by using the Si(=S)O and Ge(=S)O carboxylate-like ligands and their use for activation of small molecules is currently in progress.

Experimental Section

General: All experiments and manipulations were carried out under dry oxygen-free nitrogen by using standard Schlenk techniques or in an MBraun inert atmosphere dry box with an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior use. The starting material **1**,[15] silathiocarboxylic acid DMAP adduct **A**,[4i] and germathiocarboxylic acid **B**[5a] were prepared according to literature procedures. $KBEt_3H$ (1 M in THF) was purchased from Aldrich. MS (EI) spectra were recorded on a Finnigan MAT 955 instrument. The solution magnetic susceptibility values were determined by using the solution Evans method[9] in C_6D_6 at RT. The IR spectra were recorded on a Nicolet Magna 750 spectrometer with nitrogen gas purge. Elemental analyses were performed on a FlashEA 1112 CHNS analyzer.

Single-crystal X-ray structure determination: Each crystal was mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data of **2**, **3**, **4**, and **5** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97[16] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC-876620 (**2**), CCDC-876621 (**3**), CCDC-876622 (**4**), and CCDC-876623 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 2: Monoclinic; space group $P2_1/n$; $a = 13.2014(3)$, $b = 10.6285(2)$, $c = 17.6446(3)$ Å; $\beta = 101.430(2)°$; $V = 2426.63(8)$ Å^3; $Z = 4$; $\rho_{calc} = 1.359$ mg m^{-3}; $\mu(Mo_{K\alpha}) = 2.203$ mm^{-1}; 17819 collected reflections; 4265 crystallographically independent reflections [$R_{int} = 0.0338$]; 3326 reflections with [$I > 2\sigma(I)$]; $\theta_{max} = 25.00°$; $R(F_o) = 0.0271$ [$I > 2\sigma(I)$]; $wR(F_o^2) = 0.0575$ (all data); 268 refined parameters.

Compound 3: Monoclinic; space group $P2_1/n$; $a = 13.366(1)$, $b = 12.1017(9)$, $c = 15.334(1)$ Å; $\beta = 110.69(1)$; $V = 2320.4(3)$ Å^3; $Z = 2$; $\rho_{calc} = 1.195$ mg m^{-3}; $\mu(Mo_{K\alpha}) = 0.581$ mm^{-1}; 18030 collected reflections; 4079 crystallographically independent reflections [$R_{int} = 0.0461$]; 3588 reflections with [$I > 2\sigma(I)$]; $\theta_{max} = 25°$; $R(F_o) = 0.0360$ [$I > 2\sigma(I)$]; $wR(F_o^2) = 0.0830$ (all data); 262 refined parameters.

Compound 4: Monoclinic; space group $C2/c$; $a = 22.5724(9)$, $b = 13.5902(7)$, $c = 40.703(2)$ Å; $\beta = 93.6009(4)$; $V = 12461.3(9)$ Å^3; $Z = 4$; $\rho_{calc} = 1.047$ mg m^{-3}; $\mu(Mo_{K\alpha}) = 0.303$ mm^{-1}; 30355 collected reflections; 10561 crystallographically independent reflections [$R_{int} = 0.0687$]; 7338 reflections with [$I > 2\sigma(I)$]; $\theta_{max} = 25°$; $R(F_o) = 0.0845$ [$I > 2\sigma(I)$]; $wR(F_o^2) = 0.2129$ (all data); 641 refined parameters.

Compound 5: Monoclinic; space group Pn; $a = 13.5314(3)$, $b = 12.4916(3)$, $c = 19.7563(5)$ Å; $\beta = 107.446(3)°$; $V = 3185.8(1)$ Å^3; $Z = 2$; $\rho_{calc} = 0.995$ mg m^{-3}; $\mu(Mo_{K\alpha}) = 0.735$ mm^{-1}; 26521 collected reflections; 8345 crystallographically independent reflections [$R_{int} = 0.0291$]; 8036 reflections with [$I > 2\sigma(I)$], $\theta_{max} = 25°$; $R(F_o) = 0.0368$ [$I > 2\sigma(I)$]; $wR(F_o^2) = 0.0987$ (all data); 575 refined parameters.

Syntheses of 2: To a solution of **1** (18.8 g, 51.9 mmol) in diethyl ether (180 mL) was added a solution of *n*BuLi (32.4 mL, 1.6 M in *n*-hexane, 51.9 mmol) by syringe with stirring at −30 °C. The reaction solution was allowed to warm to RT and stirred for 3 h. To the resulting solution, a solid of $MnBr_2$ (11.13 g, 51.9 mmol) was added, and the reaction mixture was stirred further for 12 h at RT. Volatiles were removed in vacuo, the residue extracted with *n*-hexane (3×80 mL). Subsequently, the concentrated reaction solution (ca. 100 mL) was chilled to −20 °C for 48 h, affording yellow crystals of **2** suitable for X-ray diffraction analysis (yield: 22.1 g, 22.3 mmol, 86 %). M.p. 243 °C (decomp); IR (KBr): 521 (w), 630 (w), 757 (m), 804 (m), 852 (w), 934 (w), 1024 (w), 1108(w), 1178 (m), 1266 (m), 1324 (m), 1390 (s), 1442 (s), 1521 (s), 1541 (s), 2877 (m), 2934 (m), 2967 (m), 3061 cm^{-1} (w); μ_{eff} (Evans, C_6D_6): 7.2 μ_B; cryoscopic measurement (C_6H_6): $M = 732$ g mol^{-1} (dimer: $M = 993$ and monomer 497 g mol^{-1}; both might exist in the solution); MS (EI): *m*/*z* (%): 497 (90) [$L^{Dep}MnBr$]$^+$, 416 (100) [$L^{Dep}Mn$]$^+$; elemental analysis calcd (%) for $C_{50}H_{66}N_4Mn_2Br_2$ (992.78): C 60.49, H 6.70, N 5.64; found: C 59.92, H 6.52, N 4.53.

Syntheses of 3: To a solution of **2** (3.61 g, 3.64 mmol) in toluene (50 mL) was added a solution of $KBEt_3H$ (7.3 mL, 1 M in THF, 7.28 mmol) by syringe at RT. After stirring for 3 h, volatiles were removed in vacuo. The residue was extracted with toluene (80 mL). The concentrated reaction solution (ca. 20 mL) was chilled to −20 °C for 24 h, affording yellow crystals of **3** suitable for X-ray diffraction analysis (yield: 2.22 g, 2.66 mmol, 73 %). M.p. 232 °C (decomp); IR (KBr): 674 (w), 761 (m), 801 (w), 851 (w), 1022 (w), 1106 (w), 1181 (w), 1267(w), 1329 (w), 1397 (s), 1445 (s), 1524 (s), 2873 (m), 2931 (m), 2961 (m), 3062 cm^{-1} (w); μ_{eff} (Evans, C_6D_6): 5.0 μ_B; cryoscopic measurement (C_6H_6): $M = 604$ g mol^{-1} (dimer: $M = 835$ and monomer 417 g mol^{-1}; both might exist in the solution); MS (EI): *m*/*z* (%): 833 (40) [*M*]$^+$, 416 (100) [$L^{Dep}Mn$]$^+$; elemental analysis calcd (%) for $C_{50}H_{68}N_4Mn_2$ (834.99): C 71.92, H 8.21, N 6.71; found: C 71.30, H 8.41, N 7.07.

Syntheses of 4: To a solution of **A** (0.31 g, 0.50 mmol) in THF (10 mL) was added a solution of **3** (0.21 g, 0.25 mmol) in THF (8 mL) at RT. After stirring for 10 min, the volume of the resulting solution was concentrated to about 5 mL under reduced pressure. The concentrated reaction solution was chilled to −20 °C for 24 h, affording yellow crystals of **4** (yield: 0.41 g, 0.46 mmol, 91 %). M.p. 236 °C (decomp); IR (KBr): 434 (w), 463 (w), 548 (w), 590 (w), 615 (m), 659 (m), 762 (m), 778 (w), 802 (m), 848 (w), 895 (w), 934 (w), 1001 (m), 1025 (m), 1058 (w), 1105 (w), 1179 (m), 1267 (m), 1321 (m), 1393 (s), 1442 (s), 1523 (s), 1552 (s), 2868 (m), 2929 (m), 2963 (m), 3060 cm^{-1} (w); μ_{eff} (Evans, C_6D_6): 5.3 μ_B; MS (EI): *m*/*z* (%): 909 (100) [*M*]$^+$; elemental analysis calcd (%) for $C_{54}H_{74}N_4MnSiSO$ (910.29): C 71.25, H 8.19, N 6.15; found: C 70.82, H 8.17, N 6.27.

Syntheses of 5: To a solution of **B** (0.27 g, 0.50 mmol) in THF (10 mL) was added a solution of **3** (0.21 g, 0.25 mmol) in THF (8 mL) at RT. After stirring for 12 h, volatiles were removed in vacuo and the residue was extracted with toluene (10 mL). The concentrated reaction solution was chilled to −20 °C for one week, affording yellow crystals of **5** (yield: 0.43 g, 0.45 mmol, 90 %). M.p. 251 °C (decomp); IR (KBr): 419 (m), 466 (m), 537 (w), 592 (w), 642 (w), 761 (m), 778 (m), 803 (m), 848 (w), 872 (w), 934 (w), 1023 (m), 1058 (w), 1104 (w), 1178 (m), 1262 (m), 1325 (m), 1396 (s), 1452 (s), 1526 (s), 1543 (s), 2867 (m), 2927 (m), 2967 (m), 3060 cm^{-1} (w); μ_{eff} (Evans, C_6D_6): 5.6 μ_B; MS (EI): *m*/*z* (%): 955 (100) [*M*]$^+$; elemental analysis calcd (%) for $C_{54}H_{74}N_4MnGeSO$ (954.79): C 67.93, H 7.81, N 5.87; found: C 67.72, H 7.69, N 6.20.

Reactivity investigation. ***Reaction with dioxygen:*** Compound **4** or **5** (0.03 mmol) was dissolved in toluene at RT. The color of the solution changed immediately from yellow to brown, when dry dioxygen was introduced in the solution. After stirring for 10 min at RT, a brown precipitate was observed. ^1H NMR spectra of the reaction mixture showed a large amount of free ligand, $L^{Dip}H$ and $L^{Dep}H$. Addition of triphenyl phosphine to the resulted mixture did not lead to significant conversion of triphenyl phosphine to triphenylphosphine oxide.

Reaction with dioxygen in the presence of triphenyl phosphine: Compound **4** or **5** (0.03 mmol) was dissolved in toluene under N_2 and triphenyl phosphine (2 equiv) was added. An immediate color change occurred upon exchange of the N_2 to dry dioxygen, and the initial yellow solution turned brown. After stirring for 24 h at RT, ^1H NMR spectra of the reaction mixture showed that a large amount of free ligand $L^{Dip}H$ and $L^{Dep}H$ were formed. Volatiles were removed under reduced pressure. The resulting brown residue was dissolved in CH_2Cl_2 and passed through a thin silica pad (to remove the manganese complex), which was washed with ethyl acetate. The volatiles in the filtrates were removed under vacuum, and the resulting residue was characterized with ^1H and ^{31}P NMR spectroscopy and MS (LC-ESI). In both cases, one equivalent of the triphenyl phosphine was converted to triphenylphosphine oxide. The same experiment with $^{18}O_2$ (97 %) resulted in the formation of ^{18}O-labeled $Ph_3P{=}O$ in 97 % yield.

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Transition-Metal Complexes

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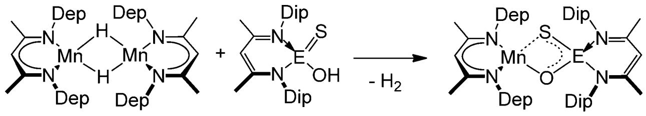
Facile Metalation of Silicon and Germanium Analogues of Thiocarboxylic Acids with Manganese(II) Hydride Precursor



Dip = 2,6-$i$$Pr_2C_6H_3$
Dep = 2,6-$Et_2C_6H_3$

E = Si, Ge

Active guys: The first transition-metal sila- and germathiocarboxylates were obtained by facile metalation of the corresponding heavier thiocarboxylic acids with currently unknown β-diketiminato manganese hydride. Preliminary investigations revealed that these complexes are capable to activate dioxygen and to oxygenate triphenylphosphane at ambient temperature (see scheme).