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Synthesis and Structural Characterization of Monomeric Heterobimetallic Oxides with a Ge(II)–O–M Skeleton (M = Yb, Y)

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The germanium hydroxide complexes LGe(μ-O)M(THF)Cp$_2$ (M = Yb, **1**; Y, **2**; L = HC[C(Me)N(Ar)]$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) were prepared by the reaction of LGeOH with Cp$_3$M (M = Yb, Y) in THF at ambient temperature with the elimination of HCp. **1** and **2** are pale-yellow solids. Both compounds crystallize isotypically as monomers in a triclinic space group $P\bar{1}$ (pseudo-merohedrally twinned, two independent molecules) and were found to be stable in the solid state and in solution at room temperature. The six-membered C$_3$N$_2$Ge rings in **1** and **2** display a boat conformation with the germanium and the γ-C out-of-plane. The Ge–O–M skeleton exhibits a bent arrangement (angles 151–154°). The ^{1}H NMR investigation of **2** confirmed that the solid-state structure is also found in solution.

Introduction

Well-defined heterobimetallic oxides not only involve synthetic challenges in chemistry but also potentially provide prolific precursors for practical application.[1] In recent years, several organometallic hydroxides have been developed with the purpose of preparing structurally characterized oxides containing the M−O−M′ moiety.[2] Starting from the monomeric aluminum hydroxide LAl(Me)OH (L = HC[C(Me)N(Ar)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$), compound LAl(Me)(μ-O)Zr(Me)Cp$_2$ was first obtained (with high activity for ethylene polymerization[3]), followed by a series of new compounds containing Al−O−M (M = Ln,[4] Mg,[5] Ti, Hf[6]) units. Organometallic hydroxides of group 14 were also employed, among which the silanols as alcohol analogues were used to prepare metallasiloxanes.[7] Subsequently, the use of the germanium hydroxide LGeOH,[8] which is considered as a congener of a low-valent carbon analogue, gave oxo-bridged complexes LGe(μ-O)M(Me)Cp$_2$ (M = Zr, Hf).[9] However, until now there is still no reported Ge−O−lanthanide linkage of a monomeric germanium(II) compound. In view of the extensive interest in the chemistry of lanthanide compounds containing heterometallic atoms,[10] we describe herein the preparation and characterization of LGe(μ-O)M(THF)Cp$_2$- (M = Yb, **1**; Y, **2**).

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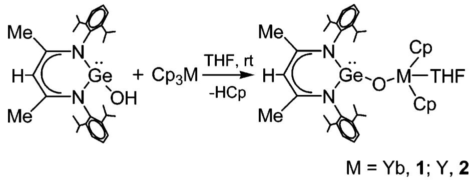
Scheme 1



Results and Discussion

Organometallic hydroxides have proven to be facile precursors of M−O−M′ moieties by the intermolecular elimination of CH_4,[3,6,9] $HN(SiMe_3)_2$,[5,7] and HCp,[4] respectively. In a previous report, LGeOH exhibited its affinity to the methyl group,[9] although Cp groups coexist at the same metal center. Accordingly, further experimental evidence is required to explore its activity with respect to homoleptic complexes where only Cp is available as leaving group.

The reaction of LGeOH with 1 equiv of Cp_3Yb was carried out smoothly in THF at room temperature (Scheme 1). The color of the solution changed from dark green to yellow, providing an indication of the reaction progress. After the removal of all of the volatiles under vacuum, the absence of the OH stretching frequency of LGe(μ-O)Yb(THF)Cp_2 (**1**) was confirmed by IR. In the mass spectrum of **1**, the most intense peak (*m*/*z* 491) is assigned to the fragment [M^+−OYb(THF)Cp_2] with an isotopic pattern that is consistent with the presence of low-valent germanium coordinated by the ligand. The ^1H NMR spectrum of **1** comprises a series of broad resonances due to the paramagnetism of ytterbium. These resonances still can be tentatively attributed to the backbone of the ligand but without precise assignments.

To elucidate the structure of **1** in solution, diamagnetic LGe(μ-O)Y(THF)Cp_2 (**2**) was prepared by the same procedure (Scheme 1). Although there is no noticeable change in the solution color, the elimination of HCp occurs readily in this reaction. The IR spectrum of **2** provides direct evidence for the absence of the OH group. The mass spectrum of **2** shows the base peak corresponding to the fragment [M^+−OY(THF)Cp_2]. The ^1H NMR spectrum of **2** can be fully interpreted. The characteristic Cp resonance is present as a singlet (5.90 ppm), and two broad peaks (1.41 and 3.31 ppm) are assigned to the proton resonances of the coordinated THF. Other resonances correspond to the backbone of the ligand assuming an unsymmetrical environment. The composition of both compounds was further confirmed by the elemental analysis.

From the concentrated THF extract at 4 °C, pale-yellow crystals of **1** and **2** of X-ray quality are recovered in relatively low yield. They are stable in the solid state under an inert atmosphere at room temperature. The decomposition of **1** and **2** is observed when the solids are heated at moderately high temperature (218 °C for **1**; 210 °C for **2**). Crystallographic data for the structural analyses of **1** and **2** are shown in Table 1. The compounds crystallize isotypically in the triclinic space group $P\bar{1}$. In the asymmetric unit, two crystallographically independent molecules are found with minor differences in their dimensions, as shown in Table 2 for selected bond parameters.

Table 1. Crystal Data and Structure Refinement for **1** and **2**

	1	**2**
formula	$C_{43}H_{59}GeN_2O_2Yb$	$C_{43}H_{59}GeN_2O_2Y$
fw	881.55	797.42
temp (K)	133(2)	100(2)
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
λ (Å)	0.71073	0.71073
a (Å)	8.8701(6)	8.8517(4)
b (Å)	37.489(3)	37.4086(16)
c (Å)	11.9890(8)	12.0005(5)
α (deg)	90.055(3)	90.190(3)
β (deg)	98.337(3)	98.071(3)
γ (deg)	89.994(3)	90.000(3)
V (Å^3)	3944.5(5)	3934.3(3)
Z	4	4
ρ_{calcd} (mg/m^3)	1.484	1.346
μ (mm^{-1})	3.155	2.269
F(000)	1796	1672
cryst size (mm^3)	0.35 × 0.35 × 0.20	0.23 × 0.10 × 0.10
θ range for data collection (deg)	0.54−28.70	1.63−26.37
index ranges	$-11 \le h \le 11$ $-50 \le k \le 50$ $-16 \le l \le 16$	$-11 \le h \le 11$ $-46 \le k \le 46$ $-14 \le l \le 14$
reflns collected	69 676	84 265
independent reflections (R_{int})	19 957 (0.0319)	16 033 (0.0543)
data/restraints/params	19 957/1429/904	16 033/1429/904
GOF on F^2	1.096	1.198
R1, wR2 ($I > 2\sigma(I)$)	0.0385, 0.0682	0.0556, 0.1048
R1, wR2 (all data)	0.0497, 0.0709	0.0716, 0.1095

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) of **1** and **2**[a]

	$\mathbf{1}^{a}$	$\mathbf{1}^{b}$	$\mathbf{2}^{a}$	$\mathbf{2}^{b}$
M-O(1)	2.018(5)	2.048(5)	2.066(5)	2.059(5)
Ge−O(1)	1.769(5)	1.762(5)	1.758(5)	1.763(4)
Ge−N(1)	2.057(5)	2.089(5)	2.056(5)	2.081(5)
Ge−N(2)	2.061(5)	2.063(5)	2.073(5)	2.059(5)
X_{Cp1}−M	2.328	2.337	2.380	2.390
X_{Cp2}−M	2.358	2.365	2.382	2.417
O(1)−Ge−N(1)	102.2(2)	101.3(2)	100.5(2)	100.5(2)
O(1)−Ge−N(2)	101.4(2)	100.0(2)	101.3(2)	101.7(2)
N(1)−Ge−N(2)	87.0(2)	85.9(2)	86.5(2)	86.34(19)
Ge−O(1)−M	153.7(3)	151.3(4)	152.8(3)	152.0(3)
X_{Cp1}−M−X_{Cp2}	127.44	127.08	126.79	127.42

[a] a and b are the two independent molecules.

The molecular structure of **1** is depicted in Figure 1. The germanium atom is located in a distorted pyramidal geometry involving the chelating β-diketiminato ligand and one bridging oxygen atom (and a stereochemically active lone pair of electrons). Two Cp groups and two oxygen atoms comprise the pseudotetrahedral coordination environment of the ytterbium atom. The deviation of germanium and γ-C from the NCCN ligand plane gives a boat conformation with germanium and γ-C out-of-plane (Figure 3). This is consistent with previous observations.[9] **1** also features a bent Ge−O−Yb (153.7(3), 151.3(4)°) arrangement. The Ge−O bond length (1.769(5), 1.762(5) Å) is even shorter than those in Ge−O−Zr (1.797(2) Å) and Ge−O−Hf (1.799(3) Å) species,[9] whereas the Yb−O (2.018(5), 2.048(5) Å) separation is comparable to that of LAlMe(μ-O)Yb(THF)Cp_2 (2.020(1) Å).[4] The Ge−N bond lengths (2.057(5)−2.089(5) Å) and the N−Ge−N bond angle (87.0(2), 85.9(2)°) are close to those reported in literature.[11] The Yb−X_{Cp} distances (2.328−2.365 Å) are comparable with those of Al−O−Yb compounds, with or without coordinated THF (2.37 and 2.34 Å, respectively), whereas the X_{Cp1}−Yb−X_{Cp2} angle (127.44,

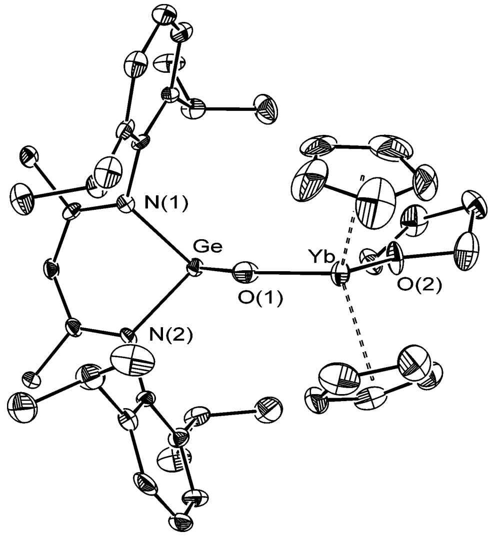


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% level, and the hydrogen atoms are omitted for clarity.

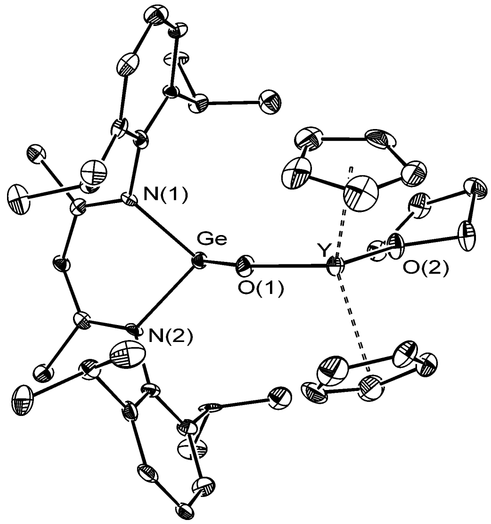


Figure 2. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% level, and the hydrogen atoms are omitted for clarity.

127.08°) is narrower when compared with those in Al−O−Yb compounds (129.1(3) and 129.6(3)°).[4]

The isotypic structure of **2** is shown in Figure 2; it involves an obtuse Ge−O−Y (152.8(3), 152.0(3)°) angle and a shorter Ge−O (1.758(5), 1.763(4) Å) and a longer Y−O (2.066(5), 2.059(5) Å) bond distance. Simplified side views of the molecular structure of **1** and **2** are shown in Figure 3. The boat conformation of the C_3N_2Ge six-membered ring and the bent Ge−O−M skeleton can be clearly recognized.

It is worth mentioning that the Ge−O bond lengths in **1** and **2** (1.758−1.769 Å) are shorter than those reported in germanium(II) aryloxides (1.8−1.9 Å).[12] This structural feature is attributable to the formation of strong bonds between the high Lewis acidic ytterbium and yttrium elements and the hard donor oxygen, which in turn strengthens the interaction between the germanium atom and the oxygen donor.[8] The same trend is also observed in the aluminum derivatives containing the Al−O−Ln skeleton (Ln = lanthanide).[3,4,6]

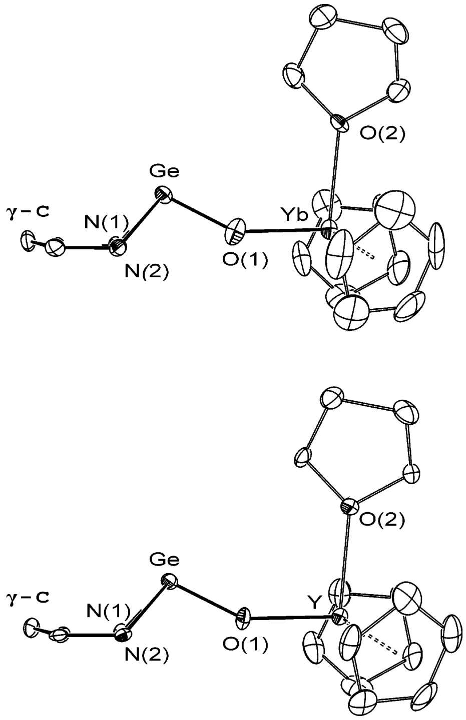


Figure 3. Side view of the molecular structure of **1** and **2**. The Ar and methyl groups of the ligand and all of the hydrogen atoms are omitted for clarity.

Conclusion

For the first time, the synthesis and structural characterization of two monomeric heterobimetallic oxides are reported containing the Ge(II)−O−M (M = Yb, **1**; Y, **2**) skeleton. During the reaction of LGeOH with homoleptic Cp_3M in THF, elimination of HCp was found to occur readily to form the expected oxo-bridged compound. Presently, we are interested in investigating the possible application of these compounds as catalysts.

Experimental Section

General Procedures. All the manipulations were performed under a dry and oxygen-free atmosphere (N_2) using Schlenk-line techniques or inside a Mbraun MB 150-GI glovebox. All the solvents were distilled from Na/benzophenone prior to use. Commercially available chemicals were purchased from Aldrich or Fluka and used as received. An ^1H NMR spectrum was recorded on a Bruker AM 200 spectrometer. EI/MS were measured on a Finnigan MAT 8230 or a Varian MAT CH5 instrument. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points

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were measured in sealed glass tubes and were not corrected. LGe(OH)[8] and Cp_3M (M =Yb, Y)[13] were prepared as described in literature.

Synthesis of LGe(μ-O)Yb(THF)Cp_2 (1). THF (60 mL) was added to a mixture of LGeOH (0.86 g, 1.69 mmol) and Cp_3Yb (0.62 g, 1.69 mmol) at room temperature. The mixture was stirred overnight, and the color of the solution turned yellow from dark green. After the removal of all of the volatiles in vacuo, the residue was extracted with THF (40 mL). Partial removal of the solvent and keeping the flask at 4 °C afforded pale-yellow crystals of X-ray quality. Yield: 0.34 g (25%); mp, 218 °C (decomp). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ =1697 (w), 1624 (w), 1553 (w), 1533 (w), 1261 (w), 1172 (w), 1101 (w), 1058 (w), 1017 (w), 936 (w), 890 (w), 834 (w), 796 (w), 771 (m), 755 (w), 723 (w). EI-MS: *m*/*z* (%) 491.25 (100) [$M^+ - OYb(THF)Cp_2$]. Anal. Calcd for $C_{43}H_{59}GeN_2O_2Yb$ (881.6): C, 58.58; H, 6.75; N, 3.18. Found C, 58.41; H, 6.78; N, 3.11.

Synthesis of LGe(μ-O)Y(THF)Cp_2 (2). Preparation of **2** was accomplished like that of **1** from LGeOH (0.51 g, 1.00 mmol) and Cp_3Y (0.28 g, 1.00 mmol). Yield: 0.18 g (22%); mp, 210 °C (decomp). ^1H NMR (200.13 MHz, C_6D_6): δ 1.20 (d, J = 6.8 Hz, 6 H, $CH(CH_3)_2$), 1.26 (d, J = 6.8 Hz, 6 H, $CH(CH_3)_2$), 1.47 (d, J = 6.8 Hz, 6 H, $CH(CH_3)_2$), 1.41 (b, 4H, $O-(CH_2CH_2)_2$), 1.53 (s, 6 H, C*Me*), 1.58 (d, J = 6.8 Hz, 6 H, $CH(CH_3)_2$), 3.31 (b, 4H, $O-(CH_2CH_2)_2$), 3.54 (sept, J = 6.8 Hz, 2 H, $CH(CH_3)_2$), 3.80 (sept, J = 6.8 Hz, 2 H, $CH(CH_3)_2$), 4.76 (s, 1 H, γ-C*H*), 5.90 (s, 10 H, $(C_5H_5)_2$), 7.10−7.20(m, Ar). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ = 2416 (m), 1759 (w), 1624 (m), 1553 (s), 1514 (m), 1319 (s), 1260 (s), 1172 (m), 1100 (m), 1059 (m), 1012 (s), 932 (w), 888 (w), 861 (m), 838 (m), 795 (s), 772 (s), 756 (s), 724 (s), 664 (m). EI-MS: *m*/*z* (%) 491.25 (100) [$M^+ - OY(THF)Cp_2$]. Anal. Calcd for $C_{43}H_{59}GeN_2O_2Y$ (797.5): C, 64.76; H, 7.46; N, 3.51. Found C, 64.53; H, 7.52; N, 3.43.

X-ray Structure Determination and Refinement. Data were recorded on Bruker SMART (**1**) and APEX-2 (**2**) diffractometers using Mo-Kα radiation. Absorption corrections were based on multiple scans. The structures were refined using *SHELXL-97*.[14] Hydrogen atoms were included using a riding model or rigid methyl groups.

Special Features. The structure of **1** was originally solved and refined with one independent molecule in the monoclinic space group $P2_1/n$, but the refinement displayed some unusual and unsatisfactory features; the R1 value was high (7%) and many systematically absent reflections had significant intensity. Assuming the structure to be pseudosymmetric, the symmetry was lowered to $P2_1$, whereupon the R1 value was lowered to 4%. However, an analysis of the geometry showed no significant deviations from $P2_1/n$, and the Flack twinning parameter refined to 0.5. Following a suggestion from Dr. Regine Herbst-Irmer (University of Göttingen), an alternative model was tested that involved a triclinic space group with α and γ angles close to 90°, plus pseudo-merohedral twinning by 180° rotation about the *y* axis. This model refined satisfactorily. The structure of **2** showed an α angle differing significantly from 90°. This necessarily led to lower data quality because the twinning components were not completely overlapped but did at least provide further evidence for the triclinic symmetry.[15]

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Supporting Information Available: Crystallographic data for **1** and **2** as CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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