A Series of Cyclopentadienyl Lanthanum Complexes with Metalloid Germanium Clusters

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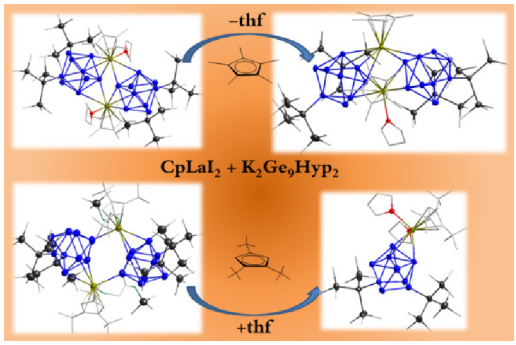
ABSTRACT: A series of cyclopentadienyllanthanum complexes with the disilylated metalloid germanium cluster $[Ge_9(Hyp)_2]^{2-}$ [Hyp = $Si(SiMe_3)_3$] has been prepared and fully characterized. The synthetic procedure is based on the salt metathesis reaction of two different cyclopentadienyllanthanum diiodides $CpLaI_2$ (Cp: Cp*, pentamethylcyclopentadienyl; Cp^{ttt}, 1,2,4-tri-*tert*-butylcyclopentadienyl) with $K_2[Ge_9(Hyp)_2]$ in tetrahydrofuran (THF) with a subsequent extraction with *n*-hexane. The composition of the obtained compounds and the mode of coordination of the germanium cluster to the rare-earth metal are strongly influenced by the steric demand of the cyclopentadienyl ligands and the crystallization conditions. The centrosymmetric dimeric compounds with the common formula $[CpLa(solv)(\eta^{2,3}\text{-}Ge_9(Hyp)_2)]_2$ [**1**, Cp = Cp*, solv—THF; **2**, Cp = Cp^{ttt}, solv—$NCCH_2C(Me)NSiMe_3$] have been isolated by the slow evaporation of a *n*-hexane solution, while a mononuclear complex $[Cp^{ttt}La(THF)_2(\eta^3\text{-}Ge_9(Hyp)_2)]$ (**4**) was found by crystallization from THF. The repeated recrystallization of **1** from *n*-hexane afforded the asymmetric dimer $[Cp^*La(THF)(\eta^{2,3}\text{-}Ge_9(Hyp)_2)][Cp^*La(\eta^{2,3}\text{-}Ge_9(Hyp)_2)]$ (**3**) with only one coordinated THF molecule.



INTRODUCTION

Zintl chemistry is a long-lasting and fascinating research topic in inorganic chemistry, gaining the attention of synthetic and theoretical chemists as well as materials scientists from the 1890s to the present. Over the past 2 decades, Zintl chemistry has undergone unprecedented development with many important breakthroughs in synthetic methods, characterization techniques, and quantum-chemical calculations, establishing its vitality and relevance.[1] Among Group 14 Zintl ions, not only classical Zintl phases, bare clusters representing molecular building blocks of main-group elements mostly soluble in liquid ammonia or polar organic solvents, but also substituent-decorated clusters, endohedral clusters, and clusters coordinated to transition metals as well as different combinations of these types of such derivatives have been of great interest in recent years.[2] The Zintl phases M_4E_9 (M = alkali metal; E = tetrel element) are readily functionalized with various organic and organoelement groups. This leads to a significant reduction in the negative charge of tetrel clusters, increasing the solubility of the substituted compounds in common organic solvents such as tetrahydrofuran (THF) or toluene. The most convenient functionalization pathway of Ge_9, based on the heterogeneous reaction of K_4Ge_9 with a halogenated substituent source in acetonitrile (MeCN) or THF, gives numerous silylated, stannylated, and phosphinated clusters with the common formulas $Ge_9R_3^-$ and $Ge_9R_2^{2-}$ [R = Hyp, $SiPh_3$, $Si(^iBu)_3$, SiH^tBu_2, $SnPh_3$, Sn^nBu_3, and $P(N^iPr_2)_2$], which have been carefully summarized previously.[2b] In this regard, a few more recent examples not included in this review could be mentioned. Among others, a "germyl"-modified cluster $[Ge_9(Hyp)_2\{Ge(SiMe_3)_3\}]^-$ [Hyp = $Si(SiMe_3)_3$ or tris(trimethylsilyl)silyl] with the first Ge_{core}—$Ge_{substituent}$ bond has been prepared by the reaction of $K_2[Ge_9(Hyp)_2]$ with $ClGe(SiMe_3)_3$,[3] which is a common and reliable synthetic route for the synthesis of unsymmetrical mixed-ligand clusters. Recently, three different methods for the synthesis of trissilylated clusters have been established. Along with the classical silylation method of K_4Ge_9 with $ClHyp^{tBuPh_2}$ [Hyp^{tBuPh_2} = $Si(SiMe_3)_2(Si^tBuPh_2)$], which is successfully used for the synthesis of $K[Ge_9(Hyp)_3]$[4] and $K_2[Ge_9(Hyp)_2]$,[5] the disproportionation of a metastable Ge(I)Cl solution in the presence of $KHyp^{tBuPh_2}$, similar to the first discovery of the metalloid germanium cluster $[Ge_9(Hyp)_3]^-$,[6] gives K-$[Ge_9(Hyp^{tBuPh_2})_3]$. Also, the reaction of the germanium

subhalide cluster $Ge_{14}Br_8(PEt_3)_4$[7] with $KHyp^{tBuPh_2}$ affords the corresponding metalloid cluster.[8] Recently, a series of new boranyl-[9] and phosphine-functionalized[10] Ge_9 clusters also deserve attention.

The trisubstituted monoanion $[Ge_9(Hyp)_3]^-$ and disubstituted dianion $[Ge_9(Hyp)_2]^{2-}$ soluble in common organic solvents (MeCN, THF, and in part in toluene) due to their large silyl group and availability in high yields prove to be versatile reagents in coordination chemistry.[2] Without pretending to cite completely, bis-ligand (Hyp_3Ge_9-M-Ge_9Hyp_3)[11] and mixed-ligand (LM-Ge_9Hyp_3, where L = trialkylphosphine or N-heterocyclic carbene) complexes[12] with η^3- and η^4-coordinated Ge_9 clusters to coinage and some platinum metals could be realized.[13] The latter ones have recently shown a new facet of metalloid germanium clusters, namely, activity in homogeneous catalysis.[13b−d] In addition to η-coordination, some metal compounds lead to cluster expansion and the formation of *closo* clusters.[14] Very recently, in our research group, a successful formation of complexes with f elements has been demonstrated.[15]

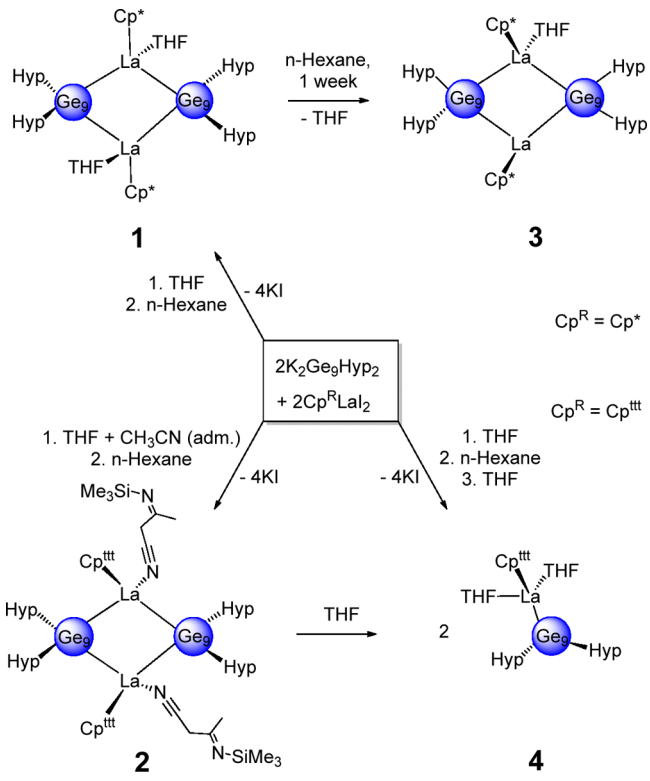
So far, the complexes of divalent lanthanides $[(THF)_2Ln\{\eta^2\text{-}Ge_9(Hyp)_3\}_2]$ (Ln = Eu, Sm),[15a] $[(THF)_5Yb\{\eta^1\text{-}Ge_9(Hyp)_2\}]$, and $[(THF)_5Ln(\eta^{2,3}\text{-}Ge_9(Hyp)_2\}]$ (Ln = Eu, Sm)[15b] with germanium clusters as ligands have been obtained by the salt metathesis of lanthanide diiodides with the corresponding potassium salts. In contrast, lanthanide triiodides LnI_3 (Ln = Eu, Sm, Yb) reacted with both anionic metalloid germanium clusters $[Ge_9(Hyp)_3]^-$ and $[Ge_9(Hyp)_2]^{2-}$ via a one-electron oxidation, resulting in a subsequent enlargement of the cluster core to Ge_{18} ones.[16] Based on our experience with divalent lanthanides, we have also become convinced of the decisive role of the size of rare-earth ions in the formation of clusters with Ge_9-ligands and tested LaI_3 in the same reactions because La^{3+} is the largest ion among Ln^{3+}. The reactions took place at elevated temperatures, and all signs indicated the oxidation of Ge_9 clusters. Unfortunately, we were not able to isolate and identify any product because of the instability at higher temperatures. The next logical step was using cyclopentadienyl complexes because of their lower oxidation ability and higher stability due to the better saturated coordination environment at lanthanum. Indeed, we succeeded in the isolation of four lanthanum complexes with the coordinated disilylated metalloid germanium cluster $[Ge_9(Hyp)_2]^{2-}$: $[Cp^*La(THF)(\eta^{2,3}\text{-}Ge_9(Hyp)_2)]_2$ (**1**), $[Cp^{ttt}La(NCCH_2C(Me)NSiMe_3)(\eta^{1,3}\text{-}Ge_9(Hyp)_2)]_2$ (**2**), $[Cp^*La(THF)(\eta^{2,3}\text{-}Ge_9(Hyp)_2)][Cp^*La(\eta^{2,3}\text{-}Ge_9(Hyp)_2)]$ (**3**), and $[Cp^{ttt}La(THF)_2(\eta^3\text{-}Ge_9(Hyp)_2)]$ (**4**) (Cp: Cp*, pentamethylcyclopentadienyl; Cp^{ttt}, 1,2,4-tri-*tert*-butylcyclopentadienyl). These compounds significantly expand the range of trivalent rare-earth complexes with very rare Ln(III)−Ge bonds.[17]

RESULTS AND DISCUSSION

The lanthanum complexes with two different cyclopentadienyl (Cp) ligands, Cp* and Cp^{ttt}, have been studied to reveal the influence of the steric demand on the molecular structure of cluster compounds.

The reactions of cyclopentadienyllanthanum diiodides $CpLaI_2$ (Cp: Cp*, pentamethylcyclopentadienyl; Cp^{ttt}, 1,2,4-tri-*tert*-butylcyclopentadienyl) with $K_2[Ge_9(Hyp)_2]$ with a molar ratio of 1:1 in THF at room temperature give after workup the novel lanthanum complexes **1** (16%) and **2** (7%) as dark-red single crystals, being the first coordination compounds of a trivalent rare-earth element and a metalloid germanium cluster. It is noteworthy that an extraction with *n*-hexane is absolutely necessary to shift the reactions to the product side (Scheme 1) because precipitation of potassium

Scheme 1



iodide is only moderately observed in the reaction mixture and NMR spectra of the residue after the evaporation of THF show the strong signals of educts (see the Supporting Information).

Compound **2** is a very minor product and the low crystalline yield might be caused by the somewhat strange coordinated neutral ligand $NCCH_2C(Me)NSiMe_3$, which seems to be perfectly suitable for the coordination niche at the lanthanum ion. Once obtained by accident, a few crystals of complex **2** with the presence of some MeCN in the educt $K_2[Ge_9(Hyp)_2]$ encouraged us to reproduce the synthesis by adding a few drops of MeCN to the mixture of reagents before condensation of THF, leading to the proven formation of $NCCH_2C(Me)NSiMe_3$ and reproducible yield of **2**. We thereby suppose the dimerization of MeCN by nucleophilic addition of the anion $NCCH_2^-$, arising by activation with lanthanum, to the C atom of MeCN with the following abstraction of one Me_3Si group from the Hyp ligand.

The compositions and molecular structures of all the presented compounds were determined by means of single-crystal X-ray diffraction analysis and confirmed by NMR spectroscopy and elemental analysis.

The molecular structure of the starting lanthanum compound $[Cp^{ttt}LaI_2(THF)]_2$, as depicted in Figure 1, reveals geometry and metrical parameters very similar to those reported for other lanthanum complexes with a dimeric structure and μ-I bridges.[18−20] The centrosymmetric dimer $[Cp^{ttt}LaI_2(THF)]_2$ contains a planar La_2I_2 core with asymmetrically bridging iodides with La−I bond lengths of 329.45(3) and 323.95(3) pm and a La1−$Cp_{centroid}$ distance of 251.62(2) pm, well comparable with bis(cyclopentadienyl)

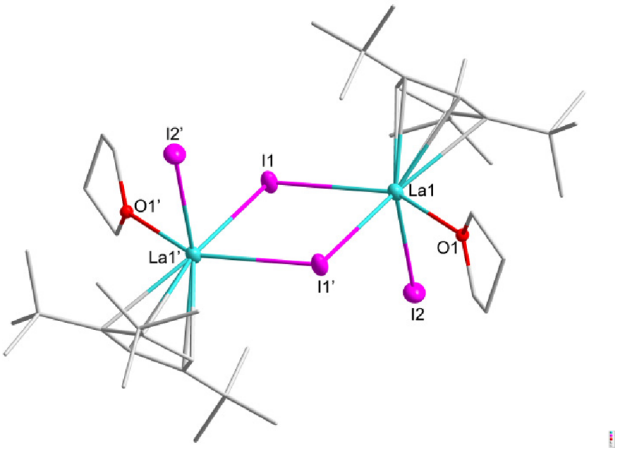


Figure 1. Molecular structure of $[Cp^{ttt}LaI_2(THF)]_2$. Ellipsoids are given with 50% probability. Selected distances (pm) and angles [deg]: La1–I1 329.45(3), La1–I1′ 323.95(3), La1–I2 309.01(3), La1–O1 251.0(2); I1–La–I1′ 77.815(8), I2–La–I1′ 94.996(9), I1–La–I1 87.076(8), La1–I1–La1′ 102.185(8).

lanthanum complexes $[Cp^R{}_2LaI]_2$.[18] The bridging La–I bond distances are slightly longer than the terminal La–I bond length [309.01(3) pm] and La–I bond lengths in $LaI_3(THF)_4$[21] [average 315.4(4) pm], which is consistent with the bridging vs terminal nature of the iodide ligands.[20] Typically, the angle at the La atom is noticeably smaller than that at the I atom (I1–La1–I′ 77.82°; La1–I–La1′ 102.19°). Such bridging La–(μ-I)–La fragments are very common for rare-earth iodide clusters.[22] The La1–O1 distance [251.0(2) pm] to the coordinated THF molecule in $[Cp^{ttt}LaI_2(THF)]_2$ is slightly shorter than those in $LaI_3(THF)_4$ [251.5(8)–257.5(8) pm].[21]

Noteworthy, the coordination mode of the germanium cluster to the lanthanum ion in compounds **1**–**4** is strongly influenced by the steric demand of the cyclopentadienyl and the crystallization conditions. The isolation of the lanthanum compounds **1** and **2** succeeds via extraction with *n*-hexane and subsequent slow evaporation of the *n*-hexane solution. Single-crystal X-ray diffraction analysis shows a centrosymmetric dimeric structure of compounds **1** and **2** (Figure 2). The dimerization is obviously caused by the removal of THF from the coordination sphere of the rare-earth metal.

In both compounds, two La atoms are connected by two germanium clusters $[Ge_9(Hyp)_2]^{2-}$ coordinated in different manners. Each La atom in **1** carries one THF molecule and a Cp* ligand and is coordinated by two $[Ge_9(Hyp)_2]^{2-}$ units at their ligand-free Ge vertex (Figure 2, top). Thereby, one Ge_9 cluster is η^3-coorditated and the other one η^2-coorditated to the La atom. The coordination to the triangular face resembles the η^3-coordination mode of $[Ge_9(Hyp)_2]^{2-}$ to europium and samarium within $[(THF)_5Ln(\eta^{2,3}\text{-}Ge_9(Hyp)_2\}]$, with the only difference being that those compounds were mononuclear.[15a] η^3 coordination leads to three La–Ge bonds: La1–Ge7′ 327.06(5) pm, La1–Ge8′ 317.14(5) pm, and La1–Ge9′ 336.18(5) pm. The edge coordination in dimer **1** occurs at a completely different edge than that in the known samarium and europium complexes.[15a] This time it is an η^2 coordination to the edge of the ligand-free Ge vertices in contrast to η^2 coordination to the edge of the base of the Ge_8 antiprism as reported previously.[15a] The corresponding La–Ge bond lengths amount to 346.12(5) and 313.53(5) pm, respectively.

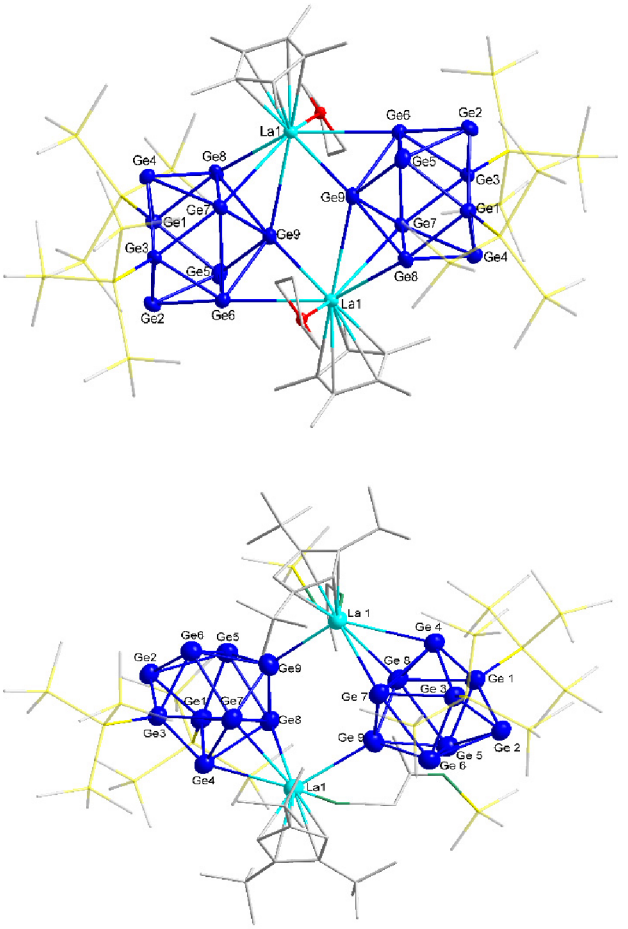


Figure 2. Molecular structure of **1** (top) and **2** (bottom). Ellipsoids are given in 50% probability. Selected distances (pm) for **1**: La1–Ge6 346.12(5), La1–Ge9 313.53(5), La1–Ge7′ 327.06(5), La1–Ge8′ 317.14(5), La1–Ge9′ 336.18(5). Selected distances (pm) for **2**: La1–Ge4 327.64(7), La1–Ge7 327.05(8), La1–Ge8 323.73(8), La1–Ge9′ 312.14(8).

In contrast to the coordination in **1**, in compound **2**, both La atoms are η^1- and η^3-coordinated by two Ge_9 clusters, respectively (Figure 2, bottom). Additionally, the Cp^{ttt} ligand and silylated MeCN dimer are coordinated to the La atom. As usual for the disilylated metalloid germanium cluster $[Ge_9(Hyp)_2]^{2-}$,[23] η^1 coordination is realized via the ligand-free Ge vertex with a La1–Ge9′ bond length of 312.14(8) pm. Thus, $Cp^{ttt}La$ occupies the place of the third Hyp substituent in $Ge_9(Hyp)_3$. The other found η^3-coordination mode is much more typical for transition-metal complexes with $Ge_9(Hyp)_3$ ligands.[11,12] Commonly, η^3 bonding of a $Ge_9(Hyp)_3$ unit to a central metal atom leads to the elongation of bond lengths within the Ge_3 ring bound to the transition metal by 25–30 pm. However, in compound **2**, only a slight elongation of the Ge bonds (between lanthanum-bound Ge atoms, Ge4, Ge7, and Ge8, av. 275 pm, and naked Ge atoms, Ge2, Ge5, and Ge6, av. 269 pm) is observed. The La–Ge bond lengths of 327.64(7), 327.05(8), and 323.73(8) pm thereby show a more symmetric η^3-coordination mode in **2** with respect to **1**. Recently, a very similar dimeric structure with the same η^1- and η^3-coordination patterns of $Ge_9(Hyp)_2$ clusters was found in the copper complexes by Fässler et al.[24a] and in the gold complexes by our group.[24b]

The differences of the lanthanum coordination environment in the dimeric compounds **1** and **2** are obviously caused by the different steric demands of the Cp ligands. The ligand cone angles[25] are 117.0° and 161.6° in the complexes **1** and **2**, respectively; thus, the Cp^{ttt} ligand has more pronounced steric hindrance compared to Cp*. Therefore, for the formation of a dimeric complex in the case of Cp^{ttt}, a donor ligand less than THF is required. By accident, it was found to be a dimerized fragment $NCCH_2C(Me)NSiMe_3$. When $Cp^{ttt}LaI_2$ reacts with $K_2[Ge_9(Hyp)_2]$ without adding CH_3CN, no crystals can be obtained by extraction with *n*-hexane and subsequent slow evaporation.

Further removal of THF by the recrystallization of **1** from *n*-hexane affords another dimer with only one coordinated THF molecule (Scheme 1). Thereby, the asymmetric dimer **3** is formed (Figure 3). Thus, extraction with nonpolar solvents is

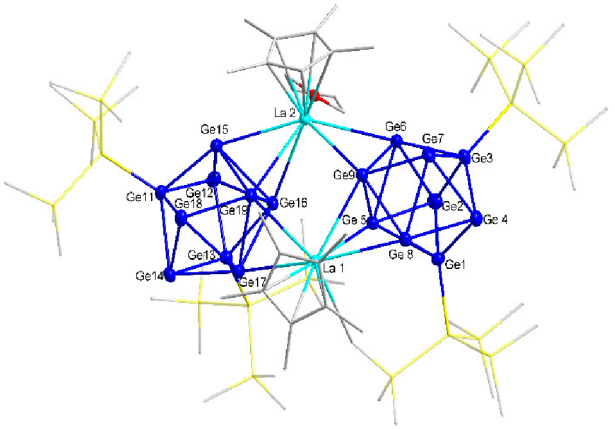


Figure 3. Molecular structure of **3**. Ellipsoids are given in 50% probability. Selected distances [pm]: La1–Ge5 321.72(4), La1–Ge8 326.49(4), La1–Ge9 314.83(4), La1–Ge17 324.61(3), La1–Ge19 315.08(3), La2–Ge6 326.64(4), La2–Ge9 318.97(4), La2–Ge15 327.90(4), La2–Ge16 322.33(3), La2–Ge19 320.05(4).

crucial for the coordination of metalloid germanium clusters to rare earths, which was also shown for divalent lanthanides.[15a] This time, the coordination changes significantly. The coordination sphere of one lanthanum atom (La1) is saturated only by η^2- and η^3-coordinated germanium clusters, while the second sphere (La2) is coordinated with THF. Both η^2- and η^3-coordination modes are still very similar to those found in compound **1**. Coordination also occurs via triangular faces around the ligand-free Ge vertex, but the clusters seem to be turned toward each other in comparison to those of dimer **1**. The La–Ge distances for η^3 bonding [La1–Ge 321.0(4) pm on av. and La2–Ge 323.4(4) pm on av.] and especially for η^2 bonding [La1–Ge17 324.61(3), La1–Ge19 315.08(3) pm and La2–Ge6 326.64(4), La2–Ge9 318.97(4) pm] are closer to each other than those in the centrosymmetric compound **1**, which indicates a more centered position of lanthanum relative to the faces and edges of the Ge_9 cluster in **2** in comparison with **1**.

Also the addition of THF leads to a different coordination compound. Adding a small amount of THF to a dried *n*-hexane extract results in the instantaneous formation of the mononuclear compound **4** (Scheme 1 and Figure 4). This time the structure essentially resembles the η^3-coordination mode in the complexes $[(THF)_5Ln(\eta^3\text{-}Ge_9(Hyp)_2\}]$ (Ln = Eu, Sm)[15b] and especially the η^3-coordination mode in the dimeric

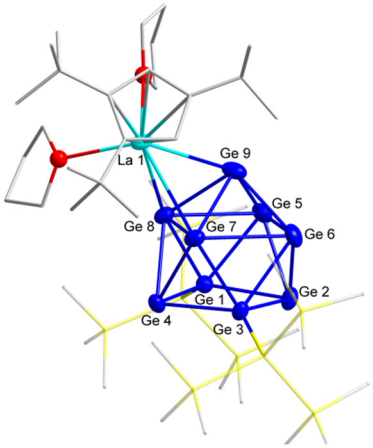


Figure 4. Molecular structure of **4**. Ellipsoids are given in 50% probability. Selected distances [pm]: La1–Ge7 310.89(11), La1–Ge8 334.30(12), La1–Ge9 307.77(13).

compound **1** described above. Fragment $Cp^{ttt}La(THF)_2$ is coordinated to the Ge_3 triangle at the cap of the monocapped square-antiprismatic Ge_9 cluster with the La–Ge bond lengths of 310.89(11), 334.30(12) and 307.77(13) pm. The remaining coordination sites at La are saturated by two THF molecules and the Cp^{ttt} ligand, resulting in pseudotetrahedral coordination geometry.

All of the La–Ge distances found are well comparable with the only known La-ate complex $[(DME)_3Li][Cp_3LaGePh_3]$ [316.46(4) pm][17c] and La-germole complex [330.48(5) pm].[17d] The distances between La and the geometry centers of the cyclopentadienyl ligands are in all compounds [250.16(4) pm (**1**), 250.66(8) pm (**2**), 250.16(4) and 249.59(4) pm (**3**), and 251.87(6) pm (**4**)] among the common values for cyclopentadienyllanthanum complexes[18] and similar to the values for the starting material $[Cp^{ttt}LaI_2(THF)]_2$ and $Cp^*LaI_2(THF)_3$ [254.4(6) pm].[22a]

Apart from some minor features mentioned above, the structures of the $[Ge_9(Hyp)_2]^{2-}$ unit in the neutral complexes **1**–**4** are close to a monocapped square antiprism of nine Ge atoms where two Ge atoms bear a Hyp ligand.[5,23] The Ge–Ge distances between the vertex Ge atoms and their four neighboring Ge atoms are about 10–12 pm on average shorter than the Ge–Ge distances within the triangular faces formed by naked Ge atoms. The cluster ligand $[Ge_9(Hyp)_2]^{2-}$ in all complexes **1**–**4** can be assigned 22 electrons, assuming that the ligand-bound Ge atoms provide three electrons for the cluster core, which fit $2n + 4$ bonding electrons of the *nido*-cluster Ge_9.

Complexes **1**–**4** are stable for a long time in the solid state under an inert atmosphere but extremely sensitive to oxygen and moisture. In solutions of donor solvents such as THF, the dimeric structure appears unstable, and the formation of monomeric complexes like **4** is expected. Stronger donors (MeCN or 1,2-dimethoxyethane) destroy complexes **1**–**4**.

All new lanthanum complexes have been characterized by means of NMR spectroscopy in THF-d_8 (for details, see the Supporting Information). NMR spectra of compounds **1** and **3** did not show any differences. Thus, we assume a monomeric form for lanthanum complexes with Cp* ligand in a THF solution, which could be different from both dimers **1** and **3**. NMR spectra show one set of signals of Hyp groups for complexes **1** and **3** (^{1}H, 0.22 ppm; ^{13}C, 3.26 ppm; ^{29}Si, −9.1

and −109.0 ppm), for dimer **2** (^{1}H, 0.23 ppm; ^{13}C, 3.34 ppm; ^{29}Si, −9.1 and −102.9 ppm), and for monomer **4** (^{1}H, 0.23 ppm; ^{13}C, 3.32 ppm; ^{29}Si, −9.6 and −104.1 ppm), indicating their equivalence in solution and a slight difference between the found chemical shifts and those observed for educt $K_2[Ge_9(Hyp)_2]$ (^{1}H, 0.16 ppm; ^{13}C, 3.3 ppm; ^{29}Si, −10.3 and −113.0 ppm).[5] Thus, NMR data display a negligible effect of the lanthanum ion on $[Ge_9(Hyp)_2]^{2-}$, which is also evidenced by the slight distortion of the monocapped square antiprism Ge_9 in all lanthanum complexes. The ratio of the signals belonging to the Cp ligands and Hyp groups in all compounds corresponds to 1:2, confirming the composition of compounds **1**−**4** described above.

CONCLUSIONS

In conclusion, it can be unambiguously stated that metalloid germanium clusters form an exo bond to trivalent lanthanum when the coordination sphere is supplemented with a cyclopentadienyl ligand. We have established the synthesis of a series of mixed-ligand lanthanum complexes with rare La(III)−Ge bonds $[Cp^*La(THF)(\eta^{2,3}\text{-}Ge_9(Hyp)_2)]_2$ (**1**), $[Cp^{ttt}La(NCCH_2C(Me)NSiMe_3)(\eta^{1,3}\text{-}Ge_9(Hyp)_2)]_2$ (**2**), $[Cp^*La(THF)(\eta^{2,3}\text{-}Ge_9(Hyp)_2)][Cp^*La(\eta^{2,3}\text{-}Ge_9(Hyp)_2)]$ (**3**), and $[Cp^{ttt}La(THF)_2(\eta^3\text{-}Ge_9(Hyp)_2)]$ (**4**). They are the first compounds of trivalent rare-earth metal bearing metalloid germanium clusters as ligands. Single-crystal X-ray diffraction revealed three different coordination types (η^1, η^2, and η^3) of the metalloid germanium cluster to lanthanum, depending on the steric demand of the Cp ligands and crystallization conditions. The removal of THF from the coordination sphere of lanthanum leads to the dimeric structure of complexes **1**−**3**, while crystallization in THF affords a mononuclear complex **4**. The new lanthanum complexes with metalloid germanium clusters as ligands have also been characterized by multinuclear NMR spectra in a THF solution.

EXPERIMENTAL SECTION

Materials and Methods. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual-manifold Schlenk line, interfaced to a high-vacuum (10^{-3} Torr) line, or in an argon-filled glovebox. Elemental analyses were carried out with an Elementar vario MICRO Cube. Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone ketyl and degassed before storage over a Na/K alloy. $K_2[Ge_9(Hyp)_2]$,[5] $Cp^*LnI_2(THF)_2$,[26] $LaI_3(THF)_4$,[27] and KCp^{ttt}[28] were prepared according to literature procedures.

NMR Spectroscopic Measurements. NMR spectroscopic measurements were performed using a Bruker AVIIIHD-300 spectrometer. The chemical shifts are given in parts per million against the residual solvent peak. THF-d_8 was dried with the Na/K alloy and stored in a glovebox under an argon atmosphere. The INEPT pulse program was used for the ^{29}Si NMR spectroscopic experiments.

X-ray Diffraction Analysis. Crystals from the mother liquor were placed in a mineral oil in the glovebox, then selected under a microscope, and mounted on the diffractometer at 150 K. The data were collected on a Rigaku XtaLAB Synergy-S X-ray diffractometer for single-crystal X-ray diffraction equipped with a PhotonJet-S microfocus sealed tube for monochromated Mo Kα radiation (λ = 0.71073 Å; **1**, **3**, **4**, and $[Cp^{ttt}LaI_2(THF)]_2$) or Cu Kα radiation (λ = 1.54184 Å; **2**) and equipped with an Oxford Cryosystems cryostat. A numerical absorption correction based on Gaussian integration over a multifaceted crystal model was applied by using the program *CrysAlisPro*. The structure was solved by direct methods and refined against F^2 for all observed reflections. Programs used: *SHELXL* and *SHELX*[29] within the *Olex2* program package.[30] The H-atom positions in all compounds were refined by using a riding model. *SQUEEZE* was used to model disordered solvent molecules (compound **2**, 20 THF; compound **3**, 10 hexane per unit cell). Compound **4** was refined as a two domain twin with HKLF5 refinement and a batch scaling factor of 0.49.

Synthesis of $[Cp^{ttt}LaI_2(THF)]_2$. A total of 30 mL of THF was condensed onto a liquid-nitrogen-precooled mixture of $LaI_3(THF)_4$ (808 mg, 1 mmol) and KCp^{ttt} (273 mg, 1 mmol) in an ampule equipped with a Young high-pressure stopper (Rettberg). The reaction mixture was allowed to warm to room temperature with stirring and then refluxed in an oil bath at 80 °C for 20 h to give a white slurry. After precipitation of a colorless solid (KI), the solution was filtered, and THF was completely removed in vacuum. The remaining solid was washed with 30 mL of *n*-hexane and dried in vacuum. The colorless solid was dissolved in THF (5 mL) and layered with toluene (15 mL) to give within a week colorless crystals of $[Cp^{ttt}LaI_2(THF)]_2$ suitable for single-ray X-ray diffraction analysis. The solvents were decanted off, and the crystals were dried in vacuum and collected in a glovebox (414 mg, yield 59%).

Anal. Calcd for $C_{42}H_{74}I_4La_2O_2$ (1396.46): C, 36.12; H, 5.34. Found: C, 36.03; H, 5.29. ^{1}H NMR (THF-d_8, 300 MHz): δ 1.40 (s, 9 H, ^{t}Bu), 1.53 (s, 18 H, ^{t}Bu), 1.78 (m, 4 H, THF), 3.62 (m, 4 H, THF), 6.34 (s, 2 H, arom. C_5H_2). ^{13}C{^{1}H} NMR (THF-d_8, 75 MHz): δ 26.52 (THF), 32.46 (CH_3, ^{t}Bu), 33.62 (C, ^{t}Bu), 34.86 (CH_3, ^{t}Bu), 34.89 (C, ^{t}Bu), 68.38 (THF), 115.63 (CH, arom. C_5H_2), 141.28 (C, arom. C_5H_2), 142.66 (C, arom. C_5H_2).

*Synthesis of $[Cp^*La(THF)(\eta^{2,3}\text{-}Ge_9(Hyp)_2)]_2$ (**1**) and $[Cp^*La(THF)(\eta^{2,3}\text{-}Ge_9(Hyp)_2)][Cp^*La(\eta^{2,3}\text{-}Ge_9(Hyp)_2)]$ (**3**).* A 20 mL portion of THF was condensed onto a liquid-nitrogen-cooled mixture of $Cp^*LnI_2(THF)_2$ (101 mg, 0.15 mmol) and $K_2[Ge_9(Hyp)_2]$ (184 mg, 0.15 mmol). The reaction mixture was allowed to warm to room temperature with stirring and was stirred for 24 h at room temperature. Then THF was removed by evaporation in vacuum, and the residue was extracted with *n*-hexane (50 mL) by stirring for 24 h. The *n*-hexane extract was filtered into a two-section ampule, concentrated to 15 mL under vacuum, and flame-sealed to grow crystals by slow evaporation. The red rhomboid-shaped crystals of **1** suitable for single-crystal X-ray diffraction analysis were washed carefully with *n*-hexane, dried in vacuum, and collected in a glovebox in the amount of 37 mg (yield 16%). The obtained crystals of **1** lose their crystallinity when dried, and in order to recrystallize them, they were dissolved in *n*-hexane (10 mL) again to give a red solution over some amount of undissolved solid within 2 days. The solution was slowly concentrated, and from the very concentrated solution, dark-red crystals of **3** (12 mg) suitable for single-crystal X-ray diffraction analysis formed within a week. NMR spectra were recorded in THF-d_8 and did not show any differences between compounds **1** and **3**. We assume a monomeric form of lanthanum complex in a THF solution different from that of both dimers **1** and **3**.

1. Anal. Calcd for $C_{64}H_{154}Ge_{18}La_2O_2Si_{16}$ (2990.60): C, 25.70; H, 5.19. Found: C, 25.63; H, 5.15. ^{1}H NMR (THF-d_8, 300 MHz): δ 0.22 (s, 54 H, $Si(SiMe_3)_3$), 1.77 (m, 4 H, THF), 2.25 (s, 15 H, Cp*), 3.62 (m, 4 H, THF). ^{13}C{^{1}H} NMR (THF-d_8, 75 MHz): δ 3.26 ($SiMe_3$ of Hyp), 13.70 (CH_3 of Cp*), 26.55 (THF), 68.39 (THF), 124.81 (C, arom. Cp*). ^{29}Si-inept-NMR (THF-d_8, 119.2 MHz): δ −9.4 ($-Si(\underline{Si}Me_3)_3$), −109.0 ($-\underline{Si}(SiMe_3)_3$).

3. Anal. Calcd for $C_{60}H_{146}Ge_{18}La_2OSi_{16}$ (2918.50): C, 24.69; H, 5.04. Found: C, 24.61; H, 5.07. ^{1}H NMR (THF-d_8, 300 MHz): δ 0.22 (s, 54 H, $Si(SiMe_3)_3$), 1.77 (m, 2 H, THF), 2.25 (s, 15 H, Cp*), 3.62 (m, 2 H, THF). ^{29}Si-inept-NMR (THF-d_8, 119.2 MHz): δ −9.4 ($-Si(\underline{Si}Me_3)_3$), −109.1 ($-\underline{Si}(SiMe_3)_3$).

*Synthesis of $[Cp^{ttt}La(NCCH_2C(Me)NSiMe_3)(\eta^{1,3}\text{-}Ge_9(Hyp)_2)]_2$ (**2**) and $[Cp^{ttt}La(THF)_2(\eta^3\text{-}Ge_9(Hyp)_2)]$ (**4**).* Compound **2** was obtained according to the procedure described for **1** from $[Cp^{ttt}LnI_2(THF)_2]_2$ (105 mg, 0.075 mmol) and $K_2[Ge_9(Hyp)_2]$ (184 mg, 0.15 mmol) and isolated in the amount of 18 mg (yield 7%) as red rhomboid-shaped crystals. The only difference in the synthetic procedure included an addition of 5 drops of MeCN to the starting mixture of reagents. After

isolation of **2**, the dark-red washing *n*-hexane solution was dried off, and the remaining solid was dissolved in 1 mL of THF. The slow evaporation of THF afforded red-brown needle-shaped crystals of mononuclear complex **4** that were suitable for single-crystal X-ray diffraction analysis and collected after drying in a glovebox (45 mg, yield 18%).

2. Anal. Calcd for $C_{84}H_{194}Ge_{18}La_2N_4Si_{18}$ (3351.34): C, 30.10; H, 5.83; N, 1.67. Found: C, 29.97; H, 5.75; N, 1.60. ^{1}H NMR (THF-d_8, 300 MHz): δ 0.23 (s, 54 H, Si(SiMe$_3$)$_3$), 0.29 (s, 9H, SiMe$_3$), 1.49 (s, 9 H, ^{t}Bu), 1.53 (s, 18 H, ^{t}Bu), 2.25 (s, 3 H, CH$_3$), 4.24 (s, 2H, CH$_2$), 6.61 (s, 2 H, arom C_5H_2). ^{13}C{^{1}H} NMR (THF-d_8, 75 MHz): δ 2.20 (SiMe$_3$ of NCCH$_2$C(Me)NSiMe$_3$), 3.34 (SiMe$_3$ of Hyp), 33.65 (CH$_3$, ^{t}Bu), 33.71 (CH$_2$ of NCCH$_2$C(Me)NSiMe$_3$), 34.72 (C, ^{t}Bu), 34.93 (CH$_3$, ^{t}Bu), 34.95 (C, ^{t}Bu), 35.63 (CH$_3$ of NCCH$_2$C(Me)-NSiMe$_3$), 115.47 (CH, arom. C_5H_2), 136.55 (C, arom. C_5H_2), 139.08 (C, arom. C_5H_2) [the signals from the C atoms of the C≡N and C═N groups of NCCH$_2$C(Me)NSiMe$_3$ were not accumulated]. ^{29}Si-inept-NMR (THF-d_8, 119.2 MHz): δ −7.0 (SiMe$_3$), −9.6 (−Si-(SiMe$_3$)$_3$), −103.0 (−Si(SiMe$_3$)$_3$).

4. Anal. Calcd for $C_{43}H_{99}Ge_9LaO_2Si_8$ (1665.59): C, 31.01; H, 5.99. Found: C, 30.94; H, 5.91. ^{1}H NMR (THF-d_8, 300 MHz): δ 0.23 (s, 54 H, Si(SiMe$_3$)$_3$), 1.49 (s, 9 H, ^{t}Bu), 1.53 (s, 18 H, ^{t}Bu), 1.77 (m, 8 H, THF), 3.62 (m, 8 H, THF), 6.67 (s, 2 H, arom. C_5H_2). ^{13}C{^{1}H} NMR (THF-d_8, 75 MHz): δ 3.32 (SiMe$_3$ of Hyp), 26.54 (THF), 33.43 (CH$_3$, ^{t}Bu), 33.76 (C, ^{t}Bu), 34.97 (CH$_3$, ^{t}Bu), 35.00 (C, ^{t}Bu), 68.38 (THF), 115.97 (CH, arom. C_5H_2), 147.08 (C, arom. C_5H_2), ^{29}Si-inept-NMR (THF-d_8, 119.2 MHz): δ −9.3 (−Si(SiMe$_3$)$_3$), −103.9 (−Si(SiMe$_3$)$_3$).

In all cases, the crystalline yields are given, which relate only to the crystallization conditions described above and do not reflect the reaction mechanism.

Accession Codes

CCDC 2339916−2339920 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The experimental work was performed by K.W. (compounds **1** and **4**), A.I.P. (starting materials), A.M. (compound **2**), and S.V.K. (compound **3**). C.S. performed single-crystal X-ray diffraction analysis and solved the single-crystal structures. S.V.K. wrote the original draft. A.S. and S.V.K. supervised the project. The manuscript was written through contributions of all authors. All authors have given approval of the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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