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# Silole and germole complexes of lanthanum and cerium†

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Using dianionic metallole ligands (silole or germole) and the cyclooctatetraendiide dianion, heteroleptic lanthanide multidecker complexes have been prepared. Due to the heteroatom of the metallole ligands intermolecular bridging between the sandwich complexes takes place. Our work highlights that different combinations of the lanthanide and heterocycle lead to different intermolecular interactions including a dimeric La-silole sandwich complex, a La-germole ladder-type polymeric species and a Ce-germole coordination polymer.

In organometallic chemistry, sandwich complexes and multi-decker species continue to be a highly attractive compound class not only due to their intriguing structure motifs but also their potential application in catalysis and materials science.[1] Specifically, carbocyclic planar π-conjugated ligands with different ring sizes (three to nine) have been utilized and incorporated into such sandwich-type structure motifs.[2] Among those, the 6π-aromatic cyclopentadienyl ($Cp^- = C_5H_5^-$) ligand and its derivatives are the most studied ones.[3] Numerous sandwich and multi-decker compounds have been synthesized using monoanionic Cp systems, whereas depending on the central atoms and substitution patterns of Cp, distinct types of coordination modes can be achieved. Starting from the s-block of the periodic table, $[Li(Cp)]_n$ and $[Na(Cp)]_n$ both have nearly linear polymer chains whereas the heavier $[K(Cp)]_n$ adopts a zigzag chain.[4] The d-block contains countless possible sandwich motifs for example classical metallocenes like ferrocene ($[Fe(\eta^5-Cp)_2]$)[2a,c] or triple-decker species like $[Ni(\eta^5-Cp)_3]^+$.[5] Very similarly, the p-block features a variety of sandwich compounds such as the bent plumbocene ($[Pb(Cp)_2]$)[6] and the dicationic tetra-decker complex ($[[(\eta^5-Cp)Sn(\mu-\eta^5:\eta^5-Cp)Sn(\mu-\eta^5:\eta^5-Cp)Sn(\eta^5Cp)]^{2+}$.[7] Also in lanthanide chemistry, a great variety of sandwich complexes arise from substituted and unsubstituted cyclopentadienyl ligands.[8] In addition, the utilization of the cyclooctatetraendiide dianion ($COT = C_8H_8^{2-}$) and sterically encumbered silyl-substituted COT derivatives has enlarged the family of lanthanide multi-decker complexes. Divalent triple-decker Ln complexes $[(\eta^5-Cp^*)Ln(\mu-\eta^8:\eta^8-COT)Ln(\eta^5-Cp^*)]$[9] (Ln = Sm, Eu, Yb) and the trivalent tetra-decker Yb complex $[[(\eta^5-Cp^*)Yb(\mu-\eta^8:\eta^8-COT^{TMS})Yb(\mu-\eta^8:\eta^8-COT^{TMS})Yb(\eta^5-Cp^*)]$[10] ($Cp^* = C_5Me_5^-$, $COT^{TMS} = 1,3,6-SiMe_3-C_8H_5^{2-}$) were synthesized by combining monoanionic and dianionic Cp and COT derivatives. Recently, our group disclosed the missing structure of the homoleptic mixed-valence tetra-decker species $[(\eta^8-COT^{TIPS})Sm(\mu-\eta^8:\eta^8-COT^{TIPS})Sm(\mu-\eta^8:\eta^8-COT^{TIPS})Sm(\eta^8-COT^{TIPS})]$ ($COT^{TIPS} = 1,4-Si^iPr_3C_8H_6^{2-}$).[11]

The chemistry of aromatic group 14 dianionic metalloles has reemerged as a topic of interest in the recent years.[12] In particular, silole and germole dianions have gained attentions not only due to the potentially aromatic character but also the electronic features acting as ligand. In 2018, the group of Müller reported the synthesis of silyl-substituted silole and germole dianions, which could be applied in gram-scale.[12g] It has been shown that they are useful building blocks and distinct reactivities have been have been reported through salt metathesis reactions.[12j] For instance, reactions with organic halides,[12l] chlorosilanes[13] or metallocene dichlorides are known.[12f,k,14]

Only very lately, such ligands has been successfully introduced into the coordination sphere of rare-earth elements.[15] In a recent report, the group of Tan and co-workers synthesized the homoleptic bis-germole and the heteroleptic Cp*-germole complexes of yttrium.[15] Around the same time, our group prepared the first examples of heteroleptic lanthanide sandwich-type complexes comprising a plumbole and a bulky COT ligand as decks.[16] Such dianionic heterocycles might be ideal starting materials to construct multi-decker lanthanide complexes. Combining the dianionic COT moiety with one heavy group 14 metallole (silole or germole) within the coordination sphere of the larger lanthanide element, resulted in unprecedented coordination modes and coordination polymers.

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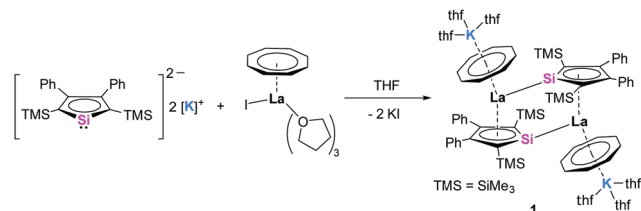
**Scheme 1** Synthesis of [K(thf)$_3$($\mu$-$\eta^8$:$\eta^8$-COT)La($\eta^5$-L$^{Si}$)]$_2$ (**1**).



**Fig. 1** Molecular structure of the complex **1** (left) and cut-out of the polymeric structure of compound **2** (right) in the solid state with thermal ellipsoids at 25% level. H atoms and non-coordinating solvent molecules are omitted for clarity. The Me groups of the SiMe$_3$ substituents are omitted for clarity. Selected bond distances [Å] and angles [°] in **1**: La–Si1' 3.2908(6), La–Si1 3.0888(5), Si1–C9 1.867(2), Si–C12 1.856(2), C9–C10 1.443(3), C10–C11 1.420(3), C11–C12 1.435(3); C9–Si1–C12 90.20(9), Si1–C9–C10 109.21(13), C9–C10–C11 115.3(2), C10–C11–C12 114.8(2), C11–C12–Si1 110.12(14). in **2**: La–Ge' 3.3048(5), La–Ge 3.1461(4), Ge–C9 1.958(4), Ge–C12 1.945(4), C9–C10 1.426(6), C10–C11 1.426(6), C11–C12 1.435(6); C9–Ge–C12 86.2(2), Ge–C9–C10 110.8(3), C9–C10–C11 116.2(4), C10–C11–C12 115.2(4), C11–C12–Ge 111.4(3).

The dipotassium salts of the 1,4-bis-(trimethylsilyl)-2,3-diphenylsilole dianion [K$_2$][L$^{Si}$] and 1,4-bis-(trimethylsilyl)-2,3-dimethylgermole dianion [K$_2$][L$^{Ge}$] were synthesized *in situ* according to a synthetic protocol of the group of Müller.[12g] The necessary lanthanide starting materials [Ln($\eta^8$-COT)I(thf)$_3$] (Ln = La, Ce) were prepared according to a recently established procedure from our group,[2j] that is based on a protocol from Mashima *et al.*[17] As a first attempt, a THF solution of [K$_2$][L$^{Si}$] was added to a THF solution of [La($\eta^8$-COT)I(thf)$_3$] dropwise at −88 °C and stirred for 1 h at −88 °C before it was allowed to warm up to room temperature (Scheme 1). Small amounts of an off-white precipitate were formed during the reaction time. A clear solution was collected by filtration and slow evaporation of the THF solution at room temperature afforded the dimeric sandwich complex **1** as dark red crystals in 25% yield. The molecular structure of **1** was determined by X-ray diffraction analysis. Complex **1** crystallizes in the monoclinic space group $P2_1/n$ with one half of the dimeric complex in the asymmetric unit. As expected, the central La atom is coordinated to the COT ligand in an $\eta^8$-fashion and to the planar silole ring in a $\eta^5$-fashion (Fig. 1). The distances to the ring centroids are 2.126 Å (Ct$_{COT}$) and 2.137 Å (Ct$_{LSi}$), respectively (Ct = ring centroid). The thf-solvated K atom is additionally $\eta^8$-coordinated to the COT ring with a K–Ct$_{COT}$ distance of 2.528 Å. Due to the presence of a lone pair at the Si atom (orthogonal to the cyclic $\pi$-system), an additional La–Si bond (La–Si' = 3.2908(6) Å) is formed to the neighboring double-decker sandwich species. Thus, resulting in the dimeric structure of **1**. The La–Si bond length is about 0.1 Å longer than in another reported La silylene complex (3.1868(8) Å),[18] even though a direct comparison of the bond lengths is hampered due to the distinct characteristics of dianionic silole compared to neutral silylene ligands and the different coordination numbers of both species. NMR spectra of **1** were recorded in THF-d$_8$. In the $^1$H NMR spectrum, the signal of the COT protons is found at $\delta$ = 6.22 ppm, and the singlet signals of the SiMe$_3$ protons at $\delta$ = −0.02 ppm. In the $^{29}$Si{$^1$H} NMR spectrum, two signals were found at $\delta$ = 187.9 and −13.9 ppm, the former one could be assigned to the silole silicon nucleus and is significantly downfield shifted compared to the dipotassium silole [K$_2$][L$^{Si}$] ($\delta$ = 148.5).[12g]

In a similar manner, the *in situ*-generated dipotassium germole [K$_2$][L$^{Ge}$] was reacted with an equimolar amount of [La($\eta^8$-COT)I(thf)$_3$] and by slow evaporation of the solvents, orange-red crystals of the product **2** were obtained in 34% yield (Scheme 2). X-ray diffraction analysis confirmed that **2** has a
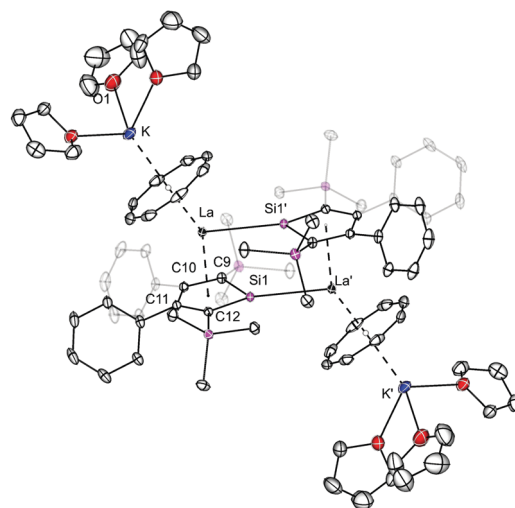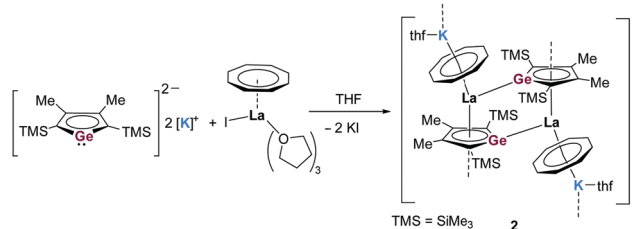


**Scheme 2** Synthesis of [{K(thf) ($\mu$-$\eta^8$:$\eta^8$-COT)La($\eta^5$-L$^{Ge}$)}$_2$]$_n$ (**2**).

novel one-dimensional coordination polymeric structure with repeating dimeric [K(thf)($\eta^8$-COT)La($\eta^5$-L$^{Ge}$)]$_2$ units, in which the La center is coordinated by the germole dianion and the COT dianion in $\eta^5$ and $\eta^8$ coordination motifs, respectively (Fig. 2, left). Each La atom in **2** is additionally coordinated by another germole moiety in a $\eta^1$ fashion. Due to the bridged double chain, the structure consists of an infinite ladder structure (Fig. 2, right). The dimeric triple-decker chain links are similar to **1**. However, in the polymeric chains of **2** the COT and germole moieties are acting as bridging ligands. In contrast to the $\sigma$,$\pi$-bridging silole ligand, the germole can act as a $\sigma$,$\pi$,$\pi$-triply bridging entity. Compared to **1**, in which three THF molecules are coordinated towards the potassium atom, in **2**, only one THF molecule is bonded to the K atom. Due to the larger size of Ge, the respective La–Ge' (3.3048(5) Å) and La–Ct$_{LGe}$ (2.567 Å) distances are longer than in the silole analogue **1**. In addition, the central sandwich structure of **2** is more bent
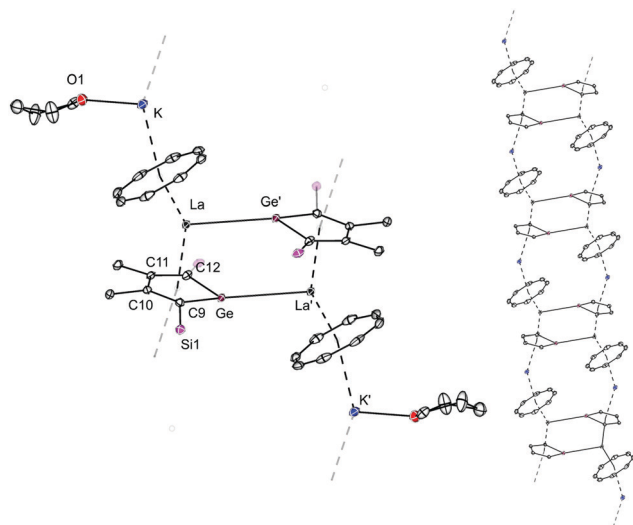
**Fig. 2** Dimeric repeating unit of compound **2** (left) and part of the 1D chain of **2** (right) in the solid state with thermal ellipsoids at 25% level. H atoms and non-coordinating solvent molecules are omitted for clarity. The Me groups of the SiMe₃ substituents are omitted for clarity. For the 1D chain, all substituents of the germole and the coordinated THF molecules are omitted for clarity. Selected bond distances [Å] and angles [°] in **2**: La–Ge′ 3.3048(5), La–Ge 3.1461(4), Ge–C9 1.958(4), Ge–C12 1.945(4), C9–C10 1.426(6), C10–C11 1.426(6), C11–C12 1.435(6); C9–Ge–C12 86.2(2), Ge–C9–C10 110.8(3), C9–C10–C11 116.2(4), C10–C11–C12 115.2(4), C11–C12–Ge 111.4(3).

compared to that in **1** (Ct$_{COT}$–La–Ct$_{LGe}$ = 144.2° and Ct$_{COT}$–La–Ct$_{LSi}$ = 147.7°). It is noteworthy to mention that molecular compounds comprising Ln(III)–Ge bonds are very scarce,[15,19] therefore, complex **2** is the rare example of a structurally characterized molecule with La–Ge bonds. In the ¹H NMR spectrum, aside from the signals of the coordinated THF molecules, three singlet signals are visible at δ = 6.17, 2.45 and 0.14 ppm, which can be assigned to the protons of COT, Me and SiMe₃, respectively.

The successful incorporation of germole and silole ligands into lanthanum sandwich complexes has prompted us to further study the coordination properties of those dianionic ligands. Formation of **2** has shown that the five-membered germole ring can act as a bridging ligand in construction of linear 1D polymeric assemblies, keeping this in mind, it is particularly interesting to see whether a triple-decker complex with germole as middle deck and COT as outer decks can be formed. Therefore, the reaction between [K₂][L$^{Ge}$] and [La(η⁸-COT)I(thf)₃] in 1:2 molar ratio was carried out, however, only single crystals of complex **2** were obtained.

In a next attempt, the reaction between one equivalent of [K₂][L$^{Ge}$] and two equivalents of [Ce(η⁸-COT)I(thf)₃)] was tested in THF (Scheme 3). From the resulting purple reaction mixture, small amounts of dark red crystals of **3** were isolated and their identity was confirmed by X-ray diffraction analysis. Interestingly, instead of the expected triple-decker compound, a 2D coordination polymer **3** was obtained in 20% yield. Fig. 3 depicts the repeating unit of the coordination polymer. The asymmetric unit of **3** contains two distinct Ce atoms (Ce1 and
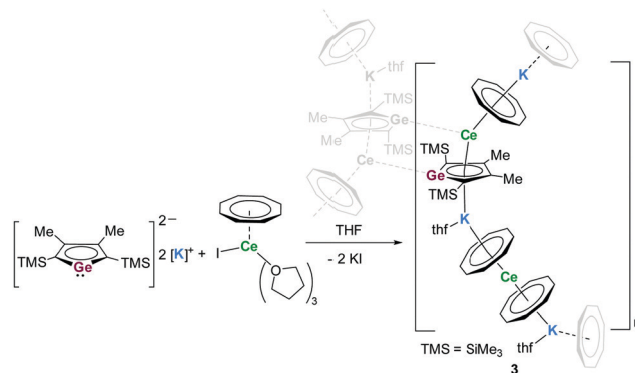


**Scheme 3** Synthesis of [{K₀.₅(μ-η⁸:η⁸-COT)Ce(μ-η⁵:η⁵-L$^{Ge}$)K(thf)(μ-η⁸:η⁸-COT)Ce(μ-η⁸:η⁸-COT)K₀.₅(thf)₀.₅}₂]$_n$ (**3**).

Ce2), three different K atoms (K1, K2 and K3), three COT rings as well as one germole ring. K1 and K3 are located on two crystallographically independent symmetry elements and both have an occupancy of 0.5. Each germole ligand is coordinated *via* its lone pair to the Ce atom of the next polymeric chain, therefore resulting in a 2D polymeric network. Each repeating unit can be considered formally as a heteroleptic anionic sandwich structure [(η⁸-COT)Ce(η⁵-L$^{Ge}$)]⁻ and a homoleptic anionic sandwich structure [(η⁸-COT)Ce(η⁸-COT)]⁻ that are interlinked by different K cations. If sandwich complexes form coordination polymers, they usually have one kind of sandwich complex as repeating unit. In contrast,
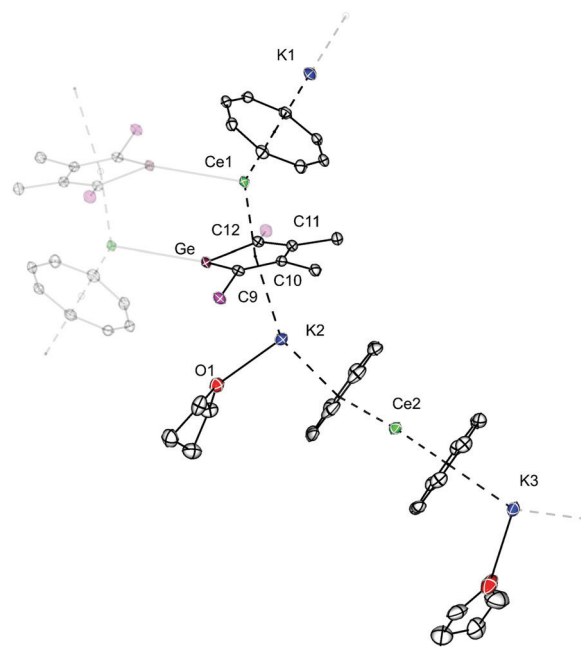


**Fig. 3** Cut-out of the polymeric structure of **3** in the solid state with thermal ellipsoids at 25% level. H atoms and non-coordinating solvent molecules are omitted for clarity. The Me groups of the SiMe₃ groups are omitted for clarity. Selected bond distances [Å] and angles [°]: Ce1–Ge′ 3.2158(4), Ce–Ge 3.1088(4), Ge–C9 1.956(3), Ge–C12 1.952(3), C9–C10 1.436(4), C10–C11 1.416(5), C11–C12 1.434(4); C9–Ge–C12 86.46(13), Ge–C9–C10 110.5(2), C9–C10–C11 116.0(3), C10–C11–C12 116.1(3), C11–C12–Ge 110.7(2).

compound **3** features two different sandwich complexes as chain links. They are arranged in an ABABAB alternating mode. The structural motif of the heteroleptic coordination polymer of **3** is unique. The bent heteroleptic sandwich motif Ct$_{COT}$–Ce–Ct$_{LGe}$ (angle: 142.8°) is comparable to that in the La-germole complex **2**. The homoleptic $[(\eta^8\text{-COT})Ce(\eta^8\text{-COT})]^-$ unit is close to be perfectly linear with a Ct$_{COT}$–Ce–Ct$_{COT}$ angle of 173.6°. The reason of the unexpected formation of **3** remains to be clarified. A possible explanation might be the formation of the polymeric system in order to maximize the number of interlinking Ce–Ge bonds.

Our results highlight that dianionic group 14 metallole ligands are suitable bridging ligands for the synthesis of lanthanide multi-decker species. By using different combinations of the employed elements (La and Si, La and Ge, Ce and Ge), an increase in dimensionality of the respective complexes could be achieved. This allowed us to isolate a dimeric La-silole sandwich complex (**1**), a 1D La-germole coordination polymer (**2**) and a 2D Ce-germole coordination polymer (**3**). Thus, the application of heterocycles as ligands for the construction of sandwich complexes opens the door to new and unprecedented structural motifs.

## Conflicts of interest

There is no conflict of interest to declare.

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