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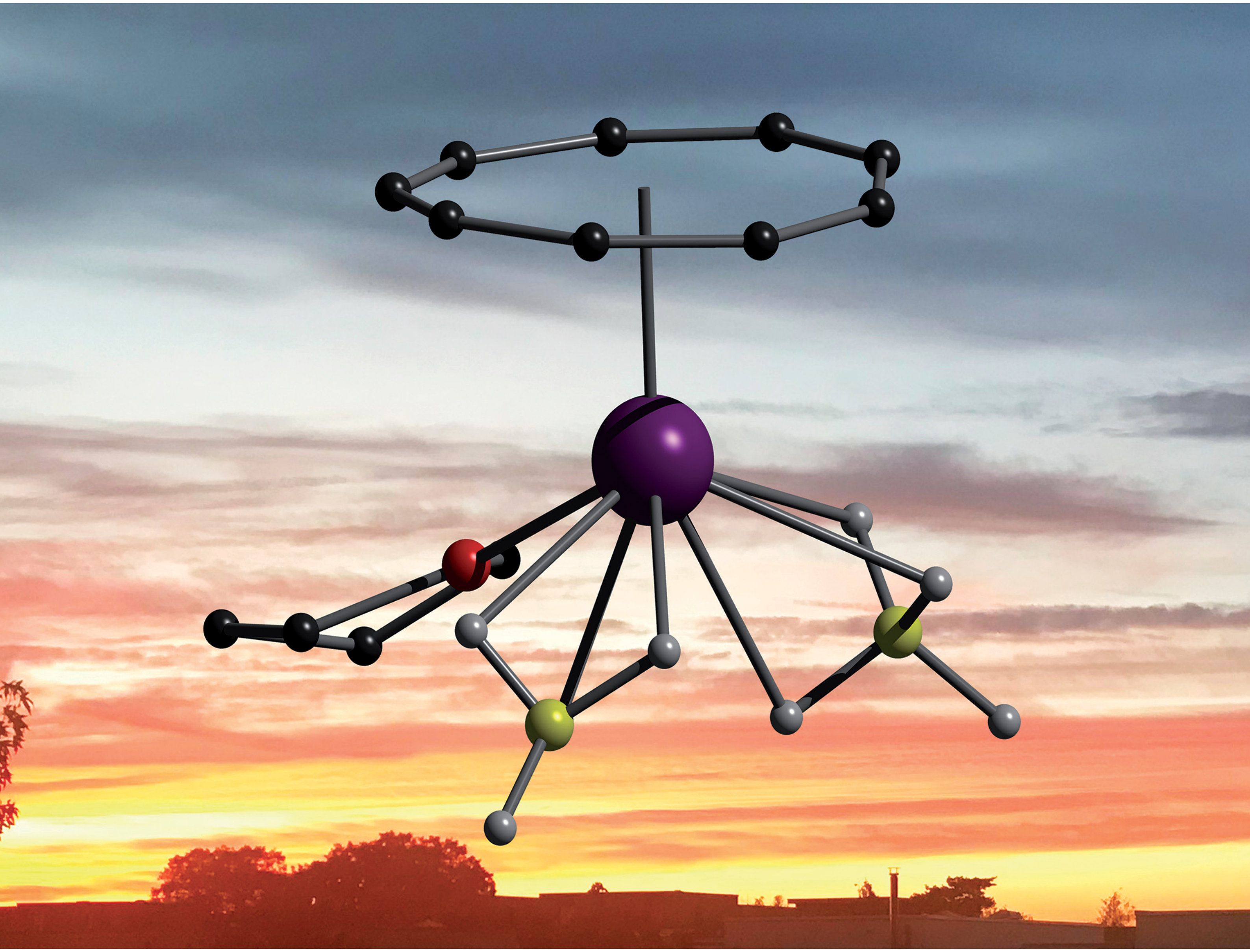

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Mono-cyclononatetraenyl lanthanide complexes†

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The synthesis of the first half-sandwich complexes based on the cyclononatetraenyl (Cnt = $C_9H_9^-$) ligand ($[Ln^{III}(\eta^9\text{-Cnt})(\eta^3\text{-BH}_4)_2(thf)]$ (Ln = La, Ce)) is reported. The title compounds were obtained from the reaction of $[Ln(BH_4)_3(thf)_3]$ and [K(Cnt)]. Further solvation of $[Ln^{III}(\eta^9\text{-Cnt})(\eta^3\text{-BH}_4)_2(thf)]$ with tetrahydrofuran (THF) resulted in a reversible decoordination of the Cnt ring and the formation of the ionic species $[Ln^{III}(\eta^3\text{-BH}_4)_2(thf)_5][Cnt]$. Removal of THF from $[La^{III}(\eta^9\text{-Cnt})(\eta^3\text{-BH}_4)_2(thf)]$ gave the polymeric compound $[La^{III}(\mu\text{-}\eta^2\text{:}\eta^2\text{-BH}_4)_2(\eta^3\text{-BH}_4)(\eta^9\text{-Cnt})]_n$.

The ground-breaking discovery of ferrocene paved the way towards modern organometallic chemistry.[1] The arising family of metallocene and sandwich compounds, *i.e.* complexes where a metal ion or atom is complexed by two cyclic and aromatic ligand moieties, was quickly expanded from d- to f-elements.[2] Although not literally being sandwich compounds, trivalent tris-cyclopentadienyl complexes of the type $[Ln^{III}(\eta^5\text{-}C_5H_5)_3]$ reported by Wilkinson and Birmingham[3] are generally considered to be the starting point of lanthanidocene as well as organolanthanide chemistry.[4] While tris-cyclopentadienyl complexes are rarely used for further derivatization, the rapid development of organolanthanide complexes started when bis(cyclopentadienyl)lanthanide halides became available. Already in 1963 Dubeck *et al.* reported on the synthesis of a variety of thermally stable bis(cyclopentadienyl)lanthanide chlorides.[5] A significant advance was the stabilization of highly reactive organolanthanide species with the pentamethylcyclopentadienyl ligand in the early 1980s.[4a,6] The resulting compounds, which show high solubility in nonpolar solvents, crystallize well, and are stable towards ligand redistribution due to the steric properties of the pentamethylcyclopentadienyl ligand.[4a] In the form of bis(pentamethylcyclopentadienyl) lanthanide σ-alkyl and hydride complexes such as $[(\eta^5\text{-}C_5Me_5)_2Ln^{III}CH(SiMe_3)_2]$ and $[(\eta^5\text{-}C_5Me_5)_2Ln^{III}(\mu\text{-}H)]_2$, this compound class plays a key role in the catalytic σ-bond metathesis.[7]

Similarly, the pentamethylcyclopentadienyl ligand and related systems facilitated the selective synthesis of mono-(cyclopentadienyl) lanthanide complexes (half-sandwich complexes). A number of mono-(cyclopentadienyl) lanthanide bisborohydride compounds were prepared,[8] in which different substitution patterns on the five membered ring have been achieved.[9] The synthesis of the analogue species with an unsubstituted cyclopentadienyl ligand is very difficult because a rearrangement to the thermodynamic more stable bis(cyclopentadienyl) compound is often observed.[10]

Recently, the ‘‘bigger brother’’ of cyclopentadienyl, which is the cyclononatetraenyl anion (Cnt = $C_9H_9^-$), a flat and mono-anionic 10π-electron aromatic ligand,[11] was introduced in coordination chemistry. Inspired by work of Sitzmann *et al.* on barium compounds,[12] Nakajima *et al.*[13] and Nocton *et al.*[14] introduced the Cnt ligand in the coordination sphere of divalent lanthanides forming homoleptic sandwich compounds $[Ln^{II}(\eta^9\text{-Cnt})_2]$ (Ln = Eu, Sm, Tm, Yb). The groups of Nocton and us disclosed the heteroleptic trivalent sandwich compounds $[(Cnt)Ln^{III}(\eta^8\text{-COT})]$ (COT = cyclooctatetraendiid, $C_8H_8^{2-}$)[15] We showed that the Er complex $[(Cnt)Er^{III}(\eta^8\text{-COT})]$ showed interesting single molecular magnet behaviour.[15a] Solvation of $[(Cnt)Ln^{III}(\eta^8\text{-COT})]$ (Ln = La, Ce, Nd, Tb, Er) with THF resulted in neutral $[(\eta^4\text{-Cnt})Ln^{III}(thf)_2(\eta^8\text{-COT})]$ (Ln = La, Ce) and ionic $[Ln^{III}(thf)_x(\eta^8\text{-COT})][Cnt]$ (x = 4 (Ce, Nd, Tb), 3 (Er)) species in a solid-to-solid transformation. The resulting compounds act as switchable luminophores and single-molecule magnets.[16] Nocton and co-workers also reported on the tris(cyclononatetraenyl) rare earth complexes $[Ln^{III}(Cnt)_3]$ (Ln = Y, Gd, Tb, Dy, Ho, Er, Tm).[17] These compounds were obtained by salt metathesis form LnI_3 and [K(Cnt)].[11] In contrast to $[(\eta^5\text{-}C_5H_5)Ln^{III}]$, not all carbon atoms are bound to the lanthanide metal. Instead, the Cnt ligand is significantly bent in order to adapt to the size of the metal ion. For the smaller metals the ligand does not switch away but swings over the metal ion, maximizing electrostatic interactions.[17]

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For the intended synthesis of the target compounds the trisborohydrides of the rare earth elements $[\mathrm{Ln^{III}(BH_4)_3(thf)_3}]$[18] were employed as suitable precursors. The $\mathrm{BH_4^-}$ ligand exhibits many advantages over other anionic ligands, especially over chloride because it is much more electron-donating and better soluble in common organic solvents.[19] Although $\mathrm{BH_4^-}$ is isosteric with $\mathrm{Cl^-}$, the electronic properties allow the isolation of otherwise unsaturated and inaccessible species. Moreover, halide derivatives have a significant larger tendency to form ate complexes or bridged derivatives, which are less soluble. The $\mathrm{BH_4^-}$ ligand can also be identified spectroscopically and thus is a suitable probe to monitor reactions by ^{1}H and/or ^{11}B NMR as well as by IR spectroscopy.[8] $[\mathrm{Ln^{III}(BH_4)_3(thf)_3}]$ is conveniently accessible from $\mathrm{LnCl_3}$ and $\mathrm{NaBH_4}$.[18,20]

Reaction of $[\mathrm{Ln^{III}(BH_4)_3(thf)_3}]$ with [K(Cnt)] in a 1 : 1 ratio at 60 °C in toluene led to the anticipated half-sandwich complexes $[\mathrm{Ln^{III}}(\eta^9\text{-Cnt})(\eta^3\text{-BH}_4)_2(\mathrm{thf})]$ (Ln = La (**1**), Ce (**2**)).[21] Crystals of these compounds were isolated from toluene at −10 °C in good yields of 68% and 72%, respectively, after filtration (Scheme 1). Interestingly, in the analogous reaction starting from $[\mathrm{Sm^{III}(BH_4)_3(thf)_3}]$, only the earlier reported divalent sandwich complex $[\mathrm{Sm^{II}}(\eta^9\text{-Cnt})_2]$,[14] was isolated (Scheme 1). A similar reduction was observed by reacting $\mathrm{Sm^{III}I_3}$ with three equivalents of [K(Cnt)].[17] Attempts to synthesize corresponding compounds of the smaller lanthanides $\mathrm{Er^{III}}$ and $\mathrm{Dy^{III}}$ were unsuccessful. Here, no reaction was observed at moderate temperatures, probably due to the smaller ionic radius. Only from about 150 °C in xylene a clear color change and the formation of a colorless precipitate was observable. However, it was not possible to isolate characterizable products from the reaction mixtures.

Both compounds **1** and **2** crystallize in the monoclinic space groups $P2_1/n$ (**1**) and $P2_1/c$ (**2**), respectively and show the expected piano-chair-like coordination motif consisting of an η^9-coordinated Cnt ligand, two terminal η^3-coordinated $\mathrm{BH_4}$ anions and a coordinated THF molecule (Fig. 1). Thus, compounds **1** and **2** represent the first half-sandwich complexes of the Cnt ligand at all. At first glance, this structural motif resembles the silylated cyclooctatetraendiid complexes $[\mathrm{Ln^{III}}(\eta^8\text{-COT}^{\mathrm{TIPS}})\mathrm{BH_4}]$ (Ln = La, Ce, Sm, Er; $\mathrm{COT^{TIPS}}$ = 1,4-bis-triisopropylsilyl-cyclooctatetraendiid)).[22] Only the number of borohydride and THF ligands is inverted for charge balance.

Within **1** and **2** the Ln–Ct (Ct = ring centroid) distances account for 2.1149(2) Å (**1**) and 2.0739(4) Å (**2**), with Ln–C distances from 2.906(4)-2.985(3) Å (**1**) and 2.869(7)-2.929(7) Å (**2**), respectively. There is a tiny shift of the Cnt-ring from the ideal η^9-coordination in **2**, that however is still within the error range. The positions of all hydride atom could be localized and freely refined, confirming beyond doubt the coordination mode of the borohydride ligands in the solid state (Fig. 1). Moreover, Raman spectra of the two compounds show bands at 2231 cm^{-1} and 2453 cm^{-1} for **1** and 2234 cm^{-1} and 2452 cm^{-1} for **2**, which are characteristic for this binding mode.[23] As described earlier Raman spectroscopy is a valuable tool for the characterization of Cnt complexes.[15a] The characteristic ring vibrations of the Cnt ring ($\nu_{\mathrm{asym}}(\eta^9\text{-Cnt})$ = 1520 cm^{-1} (**1**), 1522 cm^{-1} (**2**); $\nu_{\mathrm{sym}}(\eta^9\text{-Cnt})$ = 678 cm^{-1} (**1**), 679 cm^{-1} (**2**)) and Ln–Cnt vibration (ν(Ln-Cnt) = 145 cm^{-1} (**1**), 140 cm^{-1} (**2**)), can be clearly assigned. The remaining, less intense bands between 800 cm^{-1} and 1500 cm^{-1} were attributed to the THF ligand, respectively.[24]

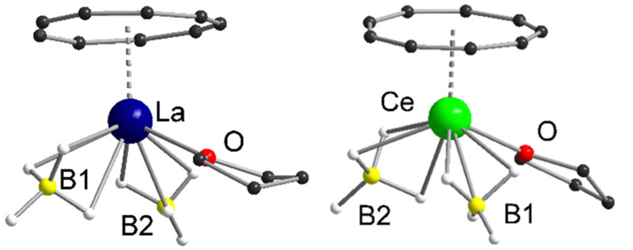
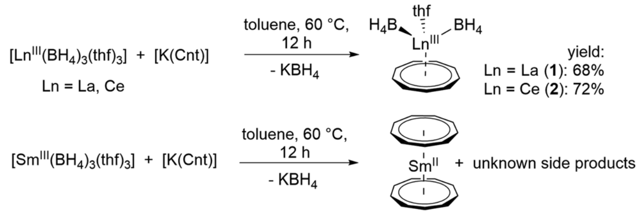


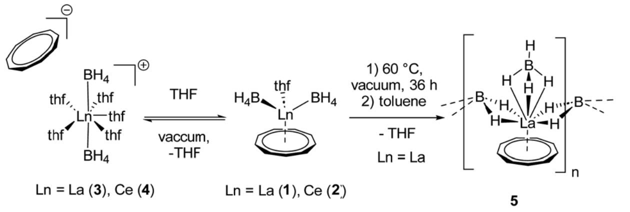
Fig. 1 Left: Molecular structure of $[\mathrm{La^{III}}(\eta^9\text{-Cnt})(\eta^3\text{-BH}_4)_2(\mathrm{thf})]$ (**1**) in the solid-state. Right: Molecular structure of $[\mathrm{Ce^{III}}(\eta^9\text{-Cnt})(\eta^3\text{-BH}_4)_2(\mathrm{thf})]$ (**2**) in the solid-state. Carbon bound hydrogen atoms are omitted for clarity. For detailed bond lengths and angles see Fig. S15 and S16 (ESI†).



Scheme 1 Synthesis of **1** and **2** (top), and reaction of [K(Cnt)] with $[\mathrm{Sm^{III}(BH_4)_3(thf)_3}]$ (bottom).

As expected, the ^{1}H NMR spectra of **1** and **2** in solution show a singlet that can be assigned to the nine isochronous aromatic protons of the η^9-Cnt ligand. In the case of the diamagnetic species **1**, the signal is localized at δ = 7.01 ppm in THF-d$_8$. In the case of the paramagnetic compound **2**, the corresponding signal is shifted as expected and is located at δ = 5.41 ppm. At δ = 1.26–0.61 ppm for **1** in THF-d$_8$ and δ = 39.4 ppm for **2**, the broad resonances of the hydridic $\mathrm{BH_4}$ protons were detected. The corresponding signals in the ^{11}B NMR spectra were observed at δ = 19.8 ppm for **1** and δ = 35.2 ppm for **2**. However, it should be noted here that in some cases the resonances in the proton spectra of the diamagnetic compound **1** did not show the expected integral ratio. In these cases, the integrals over the borohydride resonances were too large. A contamination of the samples with the precursor $[\mathrm{Ln^{III}(BH_4)_3(THF)_3}]$ is unlikely since the precursor signals have different chemical shifts. Therefore, we suggest that solubility equilibria may lead to a changed chemical composition of the species in solution, because the deviations changes with concentration.

Therefore, we investigated this issue in more detail by performing solvation experiments of compounds **1** and **2** in THF. Both **1** and **2** are readily soluble in warm THF, and single crystals can be isolated after separation of insoluble residues by filtration and slow cooling to room temperature (Scheme 2) (note compounds **1** and **2** were crystallized from toluene). Single crystal X-ray structural analysis revealed the formation of ionic compounds $[\mathrm{Ln^{III}}(\eta^3\text{-BH}_4)_2(\mathrm{thf})_5][\mathrm{Cnt}]$ (Ln = La (**3**), Ce (**4**)) featuring structural motifs with fully displaced Cnt ligands



Scheme 2 Possible structural transformations of compounds **1** and **2** by varying crystallization conditions. Left: Ionic complexes **3** and **4** after THF solvation and crystallization. Middle: Neutral parent compounds **1** and **2** after crystallization from toluene. Right: Polymeric and solvent-free species **5** after drying in high vacuum and crystallization from toluene.

in both cases (Fig. 2).[21] A similar displacement of the Cnt ligand by THF was observed for the sandwich complexes [(Cnt)Ln^{III}(η^8-COT)] (Ln = Ce, Nd, Tb, Er) with THF.[16] Among others the ionic species [Ln^{III}(thf)$_x$(η^8-COT)][Cnt] (x = 4 (Ce, Nd, Tb), 3 (Er)) with a non-coordinated Cnt anion were isolated. This clearly shows that the Cnt anion is significantly weaker bound to the lanthanide ions than the smaller cyclopentadienyl ligand.

Compounds **3** and **4** crystallize with one cation, two half-occupied anions and two half-occupied non-coordinating THF molecules in the asymmetric unit. Furthermore, one of the THF ligands of **4** is statistically disordered. Since crystals of the two compounds were reproducibly twinned, structural refinement was performed after twin integration with X-area.[25] The cationic units in both cases are pentagonal-bipyramidal coordinated [Ln^{III}(η^3-BH$_4$)$_2$(thf)$_5$]$^+$ fragments, with the axial positions occupied by two BH$_4^-$ anions and the equatorial positions by five neutral THF ligands each. A similar structural motif is already known in the form of [Nd^{III}(η^3-BH$_4$)$_2$(thf)$_5$][BPh$_4$], which was prepared by protolysis of a borohydride ligand in [Nd^{III}(BH$_4$)$_3$(thf)$_3$] with [NH(Et)$_3$][BPh$_4$] in THF.[26] Since the binding metric of the central cationic fragment of **3** and **4** are almost identical to that [Nd^{III}(η^3-BH$_4$)$_2$(thf)$_5$][BPh$_4$], a detailed discussion will not be given here (see Fig. S17 and S18 for selected bond lengths and angles, ESI†).

Since the related full displacement of the Cnt ring with THF in the ionic compounds [Ln^{III}(thf)$_x$(η^8-COT)][CNT] (x = 4 (Ce, Nd, Tb), 3 (Er)) is fully reversible,[16] we were interested to study the back reaction of **3** and **4** to compounds **1** and **2**. After drying the crystals of the THF adducts **3** and **4** in high vacuum, Raman spectra of the isolated solids were obtained analogous to those of the unsolvated compounds **1** and **2**. In particular, the Ln-Cnt vibrational bands are clearly observable (see above). As seen for [(η^9-CNT)Ln^{III}(η^8-COT)] (Ln = Ce, Nd, Tb, Er),[16] this effect offers some potential with respect to switchable materials.

Besides coordinating more THF molecules to the metal atom in compounds **1** and **2**, it is also possible to remove the THF ligand from the coordination sphere in compound **1** by drying this substance in high vacuum at 60 °C for several days. As result a polymeric species [La^{III}(μ-η^2:η^2-BH$_4$)$_2$(η^3-BH$_4$)(η^9-Cnt)]$_n$ (**5**) (Scheme 2) is formed.[21] It should be noted, however, that much of the originally used compound **1** seems to be decomposed in this process, or the polymeric species is only very poorly soluble in toluene and benzene. Thus, only a few single crystals of **5** could be isolated after extraction of the dried compound **1** with hot toluene and evaporation of the solvent at room temperature. In case of compound **2** no crystalline product could be obtained.

In the ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of compound **5**, the expected peak for the CNT ligand is seen at δ = 7.44 ppm (^{1}H) and δ = 113.4 ppm (^{13}C{^{1}H}). The integral of the BH$_4$ groups in the ^{1}H NMR spectrum (δ = 0.96–0.38 ppm) is higher than expected (*vide supra*). Compound **5** crystallizes with three units of the polymeric chain and two molecules of toluene in the asymmetric unit. With respect to the monomeric units, a piano-chair-like structural motif with an η^9-coordinated Cnt ligand is formed similar to the parent compound **1**, with the THF ligand of **1** replaced by a bridging μ-η^2:η^2-BH$_4$ ligand of one of the neighboring molecules (Fig. 3). The second borohydride ligand remains in the original terminal η^3-coordination mode. The assignment of the binding modes is based on freely refined BH$_4$ hydrogen atoms. The polymeric structure as a whole can be described as a coordination polymer of the type [La^{III}(μ-η^2:η^2-BH$_4$)$_2$(η^3-BH$_4$)(η^9-Cnt)]$_n$ with trigonal prism as chain links. The average La-Ct$_{Cnt}$ and La-B(η^3-BH$_4$) distances are in good agreement with those of the monomeric compound **1**, averaging to 2.03 Å and 2.74 Å, respectively. The La-B(η^2-BH$_4$) distances of the bridging borohydride ligands average 2.97 Å, slightly longer than those of the terminal η^3-BH$_4$ ligands, as expected. In general, μ-η^2:η^2-bridging BH$_4$ groups are very rare and to the best of our knowledge not reported for lanthanum.

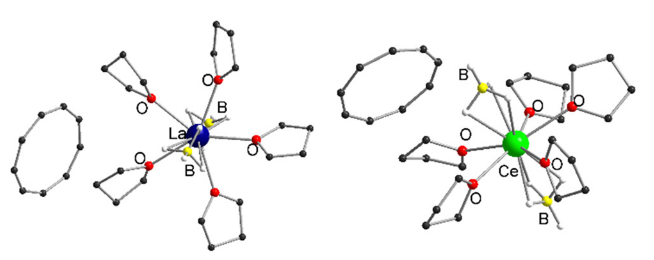


Fig. 2 Left: Molecular structure of [La^{III}(η^3-BH$_4$)$_2$(thf)$_5$][Cnt] (**3**) in the solid-state. Left: Molecular structure of [Ce^{III}(η^3-BH$_4$)$_2$(thf)$_5$][Cnt] (**4**) in the solid-state. B For detailed bond lengths and angles see Fig. S17 and S18 (ESI†).

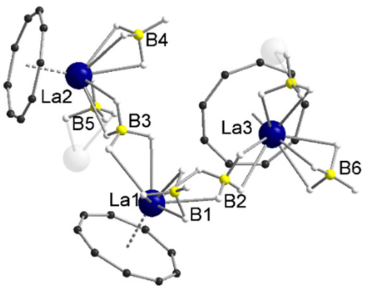


Fig. 3 Molecular structure of the asymmetric unit of [La^{III}(μ-η^2:η^2-BH$_4$)$_2$(η^3-BH$_4$)(η^9-Cnt)]$_n$ (**5**) in the solid-state. Carbon bound hydrogen atoms and toluene molecules are omitted for clarity. For detailed bond lengths and angles see Fig. S19 (ESI†).

However, bridging BH_4 groups with different coordination modes have been previously observed for lanthanum,[27] *e.g.*, in $[La^{III}(Htp)_2(\mu\text{-}BH_4)]_2$ (Htp = 2,5-di-*tert*-butylphospholyl)[28] and $[La^{III}(Cp^{ttt})(BH_4)_2(thf)_2]$ ($Cp^{ttt} = C_5H_2{}^tBu_3$-1,2,4).[29]

In summary, we report the synthesis of the first Cnt half sandwich complexes. The use of the borohydrides $[Ln^{III}(BH_4)_3(thf)_3]$ of the early lanthanides La and Ce allowed the access to the desired complexes $[Ln^{III}(\eta^9\text{-Cnt})(\eta^3\text{-}BH_4)_2(thf)]$ (Ln = La (**1**), Ce (**2**)) in good yields. Both compounds form piano stool coordination polyhedra in the solid state. Depending on amount of coordinated THF molecules a rich diversity of compounds could be obtained, ranging from ionic pentagonal-bipyramidal species (**3** and **4**) with a non-coordinated Cnt ligand over monomeric half-sandwich complexes (**1** and **2**) to a trigonal-prismatic coordination polymer (**5**).

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Conflicts of interest

There are no conflicts to declare.

References

1 (*a*) T. J. Kealy and P. L. Pauson, *Nature*, 1951, **168**, 1039; (*b*) G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *J. Am. Chem. Soc.*, 1952, **74**, 2125; (*c*) E. O. Fischer and W. Pfab, *Z. Naturforsch., B: Chem. Sci.*, 1952, **7**, 377; (*d*) P. Štěpnička, *Ferrocenes: Ligands, Materials and Biomolecules*, John Wiley & Sons, Ltd, Chichester, 2008; (*e*) P. Štěpnička, *Dalton Trans.*, 2022, **51**, 8085.

2 C. Elschenbroich, *Organometallics*, Wiley-VCH, Weinheim, 3 edn, 2006.

3 (*a*) G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, 1954, **76**, 6210; (*b*) J. M. Birmingham and G. Wilkinson, *J. Am. Chem. Soc.*, 1956, **78**, 42.

4 (*a*) H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95**, 865; (*b*) H. Schumann, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 474.

5 R. E. Maginn, S. Manastyrskyj and M. Dubeck, *J. Am. Chem. Soc.*, 1963, **85**, 672.

6 (*a*) P. L. Watson, J. F. Whitney and R. L. Harlow, *Inorg. Chem.*, 1981, **20**, 3271; (*b*) L. Gong, A. Streitwieser and A. Zalkin, *J. Chem. Soc., Chem. Commun.*, 1987, 460; (*c*) S. Schäfer, S. Kaufmann, E. S. Rösch and P. W. Roesky, *Chem. Soc. Rev.*, 2023, **52**, 4006.

7 (*a*) F. T. Edelmann, *Organolanthoid Chemistry: Synthesis, Structure, Catalysis*, Springer Berlin Heidelberg, Berlin, Heidelberg, 1996, p. 247; (*b*) P. L. Watson and G. W. Parshall, *Acc. Chem. Res.*, 1985, **18**, 51; (*c*) W. J. Evans, I. Bloom, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc.*, 1983, **105**, 1401; (*d*) G. Jeske, H. Lauke, H. Mauermann, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 8111; (*e*) G. A. Molander and J. O. Hoberg, *J. Org. Chem.*, 1992, **57**, 3266; (*f*) M. A. Giardello, V. P. Conticello, L. Brard, M. R. Gagne and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10241; (*g*) P. L. Watson, *J. Am. Chem. Soc.*, 1982, **104**, 337; (*h*) P. L. Watson and D. C. Roe, *J. Am. Chem. Soc.*, 1982, **104**, 6471; (*i*) M. R. Gagne and T. J. Marks, *J. Am. Chem. Soc.*, 1989, **111**, 4108; (*j*) M. R. Gagne, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 275; (*k*) M. R. Gagne, S. P. Nolan and T. J. Marks, *Organometallics*, 1990, **9**, 1716; (*l*) G. A. Molander and M. Julius, *J. Org. Chem.*, 1992, **57**, 6347; (*m*) P.-F. Fu and T. J. Marks, *J. Am. Chem. Soc.*, 1995, **117**, 10747; (*n*) K. N. Harrison and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 9220; (*o*) E. A. Bijpost, R. Duchateau and J. H. Teuben, *J. Mol. Catal. A: Chem.*, 1995, **95**, 121; (*p*) G. A. Molander and J. O. Hoberg, *J. Am. Chem. Soc.*, 1992, **114**, 3123.

8 S. M. Guillaume, L. Maron and P. W. Roesky, in *Handbook on the Physics and Chemistry of Rare Earths*, eds. J.-C. G. Bünzli and V. K. Pecharsky, Elsevier, 2014, vol. 44, pp. 1.

9 (*a*) D. Barbier-Baudry, F. Bouyer, A. S. Madureira Bruno and M. Visseaux, *Appl. Organomet. Chem.*, 2006, **20**, 24; (*b*) F. Bonnet, M. Visseaux, D. Barbier-Baudry, A. Hafid, E. Vigier and M. M. Kubicki, *Inorg. Chem.*, 2004, **43**, 3682.

10 S. Arndt and J. Okuda, *Chem. Rev.*, 2002, **102**, 1953.

11 T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, 1964, **86**, 5194.

12 M. D. Walter, G. Wolmershäuser and H. Sitzmann, *J. Am. Chem. Soc.*, 2005, **127**, 17494.

13 K. Kawasaki, R. Sugiyama, T. Tsuji, T. Iwasa, H. Tsunoyama, Y. Mizuhata, N. Tokitoh and A. Nakajima, *Chem. Commun.*, 2017, **53**, 6557.

14 M. Xémard, S. Zimmer, M. Cordier, V. Goudy, L. Ricard, C. Clavaguéra and G. Nocton, *J. Am. Chem. Soc.*, 2018, **140**, 14433.

15 (*a*) L. Münzfeld, C. Schoo, S. Bestgen, E. Moreno-Pineda, R. Köppe, M. Ruben and P. W. Roesky, *Nat. Commun.*, 2019, **10**, 3135; (*b*) M. Tricoire, L. Münzfeld, J. Moutet, N. Mahieu, L. La Droitte, E. Moreno-Pineda, F. Gendron, J. D. Hilgar, J. D. Rinehart, M. Ruben, O. Cador, B. Le Guennic, P. W. Roesky and G. Nocton, *Chem. – Eur. J.*, 2021, 13558.

16 L. Münzfeld, M. Dahlen, A. Hauser, N. Mahieu, S. K. Kuppusamy, J. Moutet, M. Tricoire, R. Köppe, L. La Droitte, O. Cador, B. Le Guennic, G. Nocton, E. Moreno-Pineda, M. Ruben and P. W. Roesky, *Angew. Chem., Int. Ed.*, 2023, **62**, e202218107.

17 O. Stetsiuk, L. La Droitte, V. Goudy, B. Le Guennic, O. Cador and G. Nocton, *Organometallics*, 2022, **41**, 133.

18 S. M. Cendrowski-Guillaume, M. Nierlich, M. Lance and M. Ephritikhine, *Organometallics*, 1998, **17**, 786.

19 Z. Xu and Z. Lin, *Coord. Chem. Rev.*, 1996, **156**, 139.

20 (*a*) U. Mirsaidov, G. N. Boiko, A. Kurbonbekov and A. Rakhimova, *Dokl. Akad. Nauk Tadzh. SSR*, 1986, **29**, 608; (*b*) U. Mirsaidov and A. Kurbonbekov, *Dokl. Akad. Nauk Tadzh. SSR*, 1985, **28**, 219; (*c*) U. Mirsaidov, I. B. Shaimuradov and M. Khikmatov, *Zh. Neorg. Khim.*, 1986, **31**, 1321; (*d*) S. M. Cendrowski-Guillaume, G. Le Gland, M. Nierlich and M. Ephritikhine, *Organometallics*, 2000, **19**, 5654.

21 L. Münzfeld, Dissertation, Karlsruher Institut für Technologie, 2022.

22 L. Münzfeld, X. Sun, S. Schlittenhardt, C. Schoo, A. Hauser, S. Gillhuber, F. Weigend, M. Ruben and P. W. Roesky, *Chem. Sci.*, 2022, **13**, 945.

23 M. Ephritikhine, *Chem. Rev.*, 1997, **97**, 2193.

24 B. Cadioli, E. Gallinella, C. Coulombeau, H. Jobic and G. Berthier, *J. Phys. Chem.*, 1993, **97**, 7844.

25 *X-AREA: Program for the Acquisition and Analysis of Data*, Stoe & Cie GmbH, Darmstadt, German, 2018.

26 (*a*) D. Robert, M. Kondracka and J. Okuda, *Dalton Trans.*, 2008, 2667; (*b*) T. Arliguie, L. Belkhiri, S.-E. Bouaoud, P. Thuéry, C. Villiers, A. Boucekkine and M. Ephritikhine, *Inorg. Chem.*, 2009, **48**, 221.

27 F. Ortu, *Chem. Rev.*, 2022, **122**, 6040.

28 J. Liu, L. E. Nodaraki, P. J. Cobb, M. J. Giansiracusa, F. Ortu, F. Tuna and D. P. Mills, *Dalton Trans.*, 2020, **49**, 6504.

29 F. Ortu, D. Packer, J. Liu, M. Burton, A. Formanuik and D. P. Mills, *J. Organomet. Chem.*, 2018, **857**, 45.