Unusual reactivity of lanthanide borohydride complexes leading to a borane complex†

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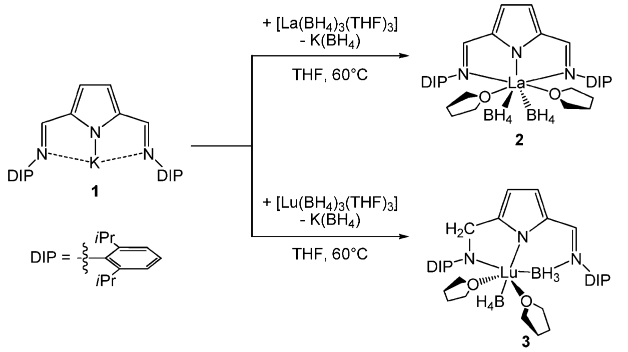
Depending on the ionic radius of the central metal atom the BH_4^- group, which usually reacts in lanthanide chemistry like a pseudo halide, can be involved in redox chemistry and the resulting product contains an N–BH_3 unit, which binds in an unusual η^2-fashion onto the metal atom.

Lanthanide trisborohydrides $[Ln(BH_4)_3(THF)_3]$[1] are efficient catalysts for the polymerization of isoprene[2] and some polar monomers such as ε-caprolactone[3] and trimethylene carbonate.[4] Lanthanide trisborohydrides were originally prepared in the early 1950s by the reaction of lanthanide alkoxides with B_2H_6.[5] A more convenient approach to $[Ln(BH_4)_3(THF)_3]$ is the reaction of $LnCl_3$ (Ln = La, Ce, Pr, Nd, Sm) with $NaBH_4$, which was developed by Mirsaidov *et al.* in the 1970s.[6] Currently borohydrides are being investigated as potential hydrogen storage material.[7] Besides their broad application in catalysis lanthanide trisborohydrides $[Ln(BH_4)_3(THF)_3]$ have also been used as valuable starting materials to prepare a large number of lanthanide borohydride derivatives, which also have a high catalytic potential. To obtain these derivatives $[Ln(BH_4)_3(THF)_3]$ were reacted in a metathetic approach with alkali metal reagents, *e.g.* the reaction of $[Ln(BH_4)_3(THF)_3]$ with alkali metal cyclopentadienyl derivatives resulted in different mono cyclopentadienyl complexes[8] such as $[(\eta^5\text{-}C_5H\mathit{i}Pr_4)Ln(BH_4)_2(THF)]$ (Ln = Sm, Nd)[9] and metallocenes such as $[(\eta^5\text{-}C_5Me_5)_2Ln(BH_4)]$.[10,11] Also post-metallocene complexes[12] and cyclooctatetraene derivatives could be obtained by salt metathesis.[11] To the best of our knowledge in all these metathetic reactions the BH_4^- groups react like a pseudo halide showing no redox reactions. Thus, in the described salt metathesis reactions the BH_4^- groups react as innocent leaving groups forming MBH_4 (M = Li, Na, K) as a byproduct. Based on these considerations we were interested in using ligands which potentially may alter the reactivity of the BH_4^- group. It is well known that Schiff-base ligands such as bis(imino)pyridines are non-innocent ligands, which can be alkylated at the imino function.[13] Since bis(imino)pyridines are neutral compounds, which cannot react *via* a salt metathesis route, we and others recently introduced the compound 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrole $(DIP_2\text{-pyr})H$ as a ligand in lanthanide chemistry.[14,15]

We now report on the reaction of the Schiff-base ligand $(DIP_2\text{-pyr})H$ with lanthanide trisborohydrides $[Ln(BH_4)_3(THF)_3]$. $(DIP_2\text{-pyr})H$ can easily be deprotonated with suitable reagents such as *n*BuLi or KH to form the corresponding alkali metal compounds $[(DIP_2\text{-pyr})Li]$[16] and $[(DIP_2\text{-pyr})K]$ (**1**).[15] Transmetallation of **1** with $[La(BH_4)_3(THF)_3]$ in THF at elevated temperature leads to the expected product $[(DIP_2\text{-pyr})La(BH_4)_2(THF)_2]$ (**2**)‡ (Scheme 1). A similar product, $[(DIP_2\text{-pyr})LnCl_2(THF)_2]$, (Ln = Y, Lu), was observed by the reaction of **1** with anhydrous yttrium and lutetium trichloride in THF.[15] Clearly in the formation of compound **2** the trisborohydride $[La(BH_4)_3(THF)_3]$ reacts like a pseudo halide compound.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of compound **2** show the expected sets of signals. A characteristic splitting of the isopropyl CH_3 signals into two sets of doublets is observed, which is interpreted as a consequence of restricted rotation about the N–C_{ipso} bond. For the protons of the BH_4^- group a broad signal is observed in the ^1H NMR spectrum only, whereas in the ^{11}B NMR spectrum a well resolved quintet is seen at δ −21.3 ppm. In the IR spectrum of compound **2**, two characteristic peaks at 2222 cm^{-1} and 2422 cm^{-1} are observed, which can be assigned to a terminal coordinated $La(\eta^3\text{-}H_3B\text{-}H)$ unit.[1]

The solid-state structure of compound **2** was also established by single crystal X-ray crystallography (Fig. 1). The BH_4-hydrogen atoms were freely refined, showing a η^3-coordination of the BH_4^- group. If the BH_4^- group is considered monodentate the structure reveals a seven-fold coordination sphere of the ligands around the lanthanum atom resulting in a distorted pentagonal bipyramidal coordination polyhedron. The two BH_4^- groups are located in the apices in an almost linear setup forming a B1–La–B2 angle of 169.1(2)°,



Scheme 1

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† Electronic supplementary information (ESI) available: Crystallographic data of **2** and **3** and experimental preparations for **2** and **3**. CCDC 689078 (**2**) and 689232 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b907193h

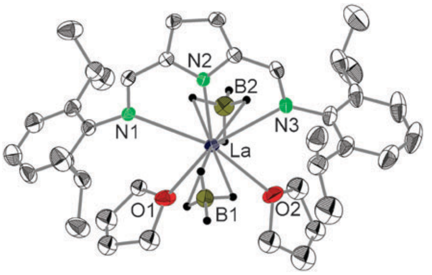

Fig. 1 ORTEP representations of the solid-state structure of **2** at 200 K (50% probability) showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] or angles [°]: La–N1 2.852(3), La–N2 2.453(3), La–N3 2.890(3), La–O1 2.616(3), La–O2 2.604(3), La–B1 2.714(5), La–B2 2.711(6); N1–La–N2 61.37(9), N1–La–N3 122.40(8), N2–La–N3 61.15(9), N1–La–O1 77.43(9), N1–La–O2 160.32(10), N2–La–O1 138.51(9), N2–La–O2 138.30(10), N3–La–O1 160.14(9), N3–La–O2 77.20(10), N1–La–B1 91.21(14), N1–La–B2 96.07(15), N2–La–B1 96.2(2), N2–La–B2 94.40(15), N3–La–B1 91.45(15), N3–La–B2 91.4(2), O1–La–O2 83.03(10), O1–La–B1 89.0(2), O1–La–B2 84.8(2), O2–La–B1 86.11(15), O2–La–B2 84.3(2), B1–La–B2 169.1(2).

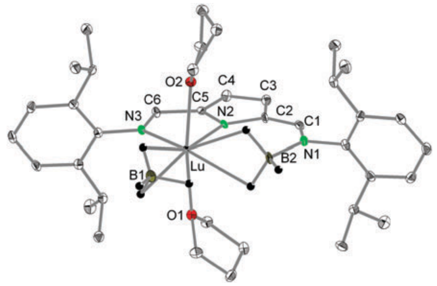

Fig. 2 ORTEP representations of the solid-state structure of **3** (50% probability) at 6 K. Two additional THF solvent molecules and the hydrogen atoms except for the freely refined B–H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu1–N2 2.284(3), Lu1–N3 2.168(3), Lu1–O1 2.356(3), Lu1–O2 2.358(3), Lu1–B1 2.486(5), Lu1–B2 2.853(5), N1–C1 1.317(5), N3–C6 1.465(5), N2–Lu1–N3 76.03(12), N2–Lu1–O1 88.38(10), N2–Lu1–O2 82.85(10), O1–Lu1–B1 93.50(13), O1–Lu1–B2 88.06(12), O2–Lu1–B1 94.96(13), O2–Lu1–B2 86.45(12), N2–Lu1–B1 174.67(13), N2–Lu1–B2 74.26(12), N3–Lu1–B1 108.86(14), N3–Lu1–B2 150.27(13), B1–Lu1–B2 100.79(14).

whereas the (DIP$_2$-pyr)$^-$ ligand and both THF molecules are located in the molecular plane. The almost planar arrangement of the LaN$_3$O$_2$ fragment is reflected by the sum of the corresponding five valence angles of 360.18°. The two phenyl rings are oriented perpendicular to the plane of the pyrrolyl moiety. The structural model of compound **2** is very similar to the one of [(DIP$_2$-pyr)YCl$_2$(THF)$_2$],[15] which also shows a pentagonal bipyramidal coordination with two chlorine atoms located in apical positions. This again clearly supports the pseudo halide character of the BH$_4$$^-$ groups in lanthanide chemistry.

Reacting compound **1** with [Lu(BH$_4$)$_3$(THF)$_3$] under the same reaction conditions used for the preparation of compound **2** does not result in an analogous complex. Instead, a reduction of one imino function by one BH$_4$$^-$ group takes place and compound **3** is formed‡ (Scheme 1). The resulting BH$_3$ unit is bound to the nitrogen atom of the remaining imino function of the ligand. Thus, the resulting formally dinegatively charged ligand is coordinated to a Lu–BH$_4$ unit *via* the nitrogen atoms of the amido and the pyrrolyl function and the two hydrogen atoms of the newly formed =N–BH$_3$ group (Scheme 1). To the best of our knowledge a comparable reactivity of the BH$_4$$^-$ group was not observed previously in lanthanide chemistry. It can be clearly seen from the ^{1}H and ^{13}C{^{1}H} NMR spectra of compound **3** that the symmetry of the ligand is broken due to the reduction process. Thus, the four isopropyl CH$_3$ groups are all in chemically different environments and display four doublets and two septets in the ^{1}H NMR spectrum while the hydrogen atoms of the pyrrolyl ring show two doublets. The ^{13}C{^{1}H} NMR is consistent with these observations. In the ^{11}B NMR a quintet for the BH$_4$$^-$ group ($\delta = -25.2$ ppm) and a broad signal for the =N–BH$_3$ moiety ($\delta = -14.9$ ppm) is seen.

The solid-state structural model of compound **3** was established by single crystal X-ray diffraction at low temperatures (6 K) to minimize the smearing of the electron density due to thermal motion and to overcome the structural disorder observed above 200 K. Subsequent structural refinements allowed us to resolve the position of the B–H hydrogen atoms in close proximity to the lutetium atom in difference Fourier maps (Fig. 2). The obtained solid-state model is consistent with the NMR data of **3** in solution and as a result of the reduction process the ligand displays one imino and one amido functionality. Accordingly, the C–N bond lengths of both groups differ significantly (N1–C1 1.317(5) Å *vs.* N3–C6 1.465(5) Å) and clearly reveal the single bond character of the amino C–N moiety. Furthermore, as a result of this ligand reduction, the remaining BH$_3$ group is coordinated to the imino function featuring a covalent B–N bond length of 1.562(6) Å. The distorted pentagonal bipyramidal coordination polyhedron of **3** is completed by two THF ligands in axial positions and a η^3-coordinated BH$_4$$^-$ group. In contrast to complex **2** both borohydride groups are now situated in the molecular plane spanning a B1–Lu–B2 angle of 100.79(14)°. The different chemical nature of the coordinating BH$_4$$^-$ ligand and the =N–BH$_3$ moiety is reflected in significantly different Lu–B contacts of 2.486(5) and 2.853(5) Å, respectively.

Moreover, the coordination mode of both borohydride moieties differs (Fig. 2). Accordingly, the =N–BH$_3$ moiety coordinates in a η^2-fashion to the lutetium atom resulting in Lu–H distances of 2.38(6) Å and 2.47(7) Å. The B–H bond distances of these two hydrogen atoms (1.24(7) and 1.18(7) Å, respectively) are significantly longer than that one of the non-coordinated B–H hydrogen atom (1.01(6) Å). In contrast, the BH$_4$$^-$ ligand binds in an asymmetric η^3-fashion and displays one shorter and two longer Lu–H bond lengths of 2.24(6) Å, 2.33(6) Å, and 2.35(7) Å, respectively. The observed reactivity and the simultaneous coordination of a BH$_4$$^-$ and a BH$_3$ unit are to the best of our knowledge unique in lanthanide chemistry. The only other structurally characterized rare-earth complex, featuring a N–BH$_3$ moiety in the ligand sphere, is a scandium compound, which is coordinated by four anionic 3-borane-1-alkylimidazol-2-ylidene ligands.[17] This ligand is an *N*-heterocyclic carbene having one BH$_3$ group attached onto one of the two nitrogen atoms. In contrast to compound **3**, this complex was obtained by a standard salt metathesis reaction starting from ScCl$_3$. In the scandium complex one hydrogen atom of each N–BH$_3$ coordinates to the metal center.

In conclusion, we have shown that the BH_4^- group, which usually reacts in lanthanide chemistry like a pseudo halide, can be involved in a redox reaction. By reacting compound **1** with $[Lu(BH_4)_3(THF)_3]$ one of the two Schiff-base functions of the ligand is reduced.[18] The byproduct BH_3 of this reduction was trapped by the remaining imino nitrogen atom. The resulting N–BH_3 unit binds in a η^2-fashion *via* two three-center-two-electron bonds onto the lutetium atom. To the best of our knowledge this kind of coordination has not been observed previously in lanthanide chemistry. It should also be noted that under the same reaction conditions the BH_4^- groups in $[La(BH_4)_3(THF)_3]$ do not show any redox reaction. Maybe as a result of the smaller ion radius of lutetium a compound of composition $[(DIP_2\text{-pyr})Lu(BH_4)_2(THF)_2]$ cannot be formed because of steric reasons. The resulting steric strain may cause the unusual reactivity.

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Notes and references

‡ *Preparation of* **2–3**: All manipulations were carried out under anaerobic and anhydrous conditions. **2**: THF (10 ml) was condensed at −78 °C onto a mixture of $[La(BH_4)_3(THF)_3]$ (0.40 g, 1.0 mmol) and (0.48 g, 1.0 mmol) $[(DIP_2\text{-pyr})K]$ (**1**) and the resulting yellow reaction mixture was stirred for 16 h at 60 °C. The yellow solution was filtered off and concentrated until a white precipitate appears. The mixture was heated carefully until the solution became clear. The solution was allowed to stand at ambient temperature to obtain the product as yellow crystals after 16 h. Yield: 0.55 g, 0.7 mmol, 70%. ^{1}H-NMR (THF-d_8, 400 MHz, 25 °C): $\delta = 0.62$–0.84 (br, 8H, BH_4), 1.03 (d, 12H, $CH(CH_3)_2$, $J_{H,H} = 6.7$ Hz), 1.20 (d, 12H, $CH(CH_3)_2$, $J_{H,H} = 6.7$ Hz), 3.57 (sept, 4H, $CH(CH_3)_2$, $J_{H,H} = 6.7$ Hz), 6.62 (s, 2H, 3,4-pyr), 7.07–7.14 (m, 6H, Ph), 8.05 (s, 2H, N=CH). $^{13}C\{^1H\}$ NMR (THF-d_8, 100.4 MHz, 25 °C): $\delta = 22.1$ ($CH(CH_3)_2$), 25.6 ($CH(CH_3)_2$), 27.4 ($CH(CH_3)_2$), 117.1 (3,4-pyr), 123.2 (Ph), 126.4 (Ph), 141.0 (2,5-pyr), 142.9 (Ph), 148.7 (Ph), 163.3 (N=CH). ^{11}B NMR (THF-d_8, 128.15 MHz, 25 °C): $\delta = -21.3$ (br qt, $J_{H,B} = 89.1$ Hz). IR (KBr, ν/cm^{-1}): 871(m), 1049(m), 1099(m), 1161(s), 1327(s), 1450(m), 1566(vs), 2171(w), 2222(s), 2330(w), 2422(m), 2874(s), 2962(vs). $C_{38}H_{62}B_2N_3O_2La$ (753.45): calcd C, 60.58, H, 8.29, N, 5.58%; found C, 59.63, H, 8.84, N, 5.40%. **3**: THF (10 ml) was condensed at −78 °C onto a mixture of $[Lu(BH_4)_3(THF)_3]$ (0.63 g, 1.4 mmol) and $[(DIP_2\text{-pyr})K]$ (**1**) (0.67 g, 1.4 mmol) and the resulting yellow reaction mixture was stirred for 16 h at 60 °C. The yellow solution was filtered off and concentrated until a white precipitate appears. The mixture was heated carefully until the solution became clear. The solution was allowed to stand at ambient temperature to obtain the product as yellow crystals after several hours. Yield 0.45 g, 0.6 mmol, 43%. ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): $\delta = 0.82$–0.90 (br, 4H, BH_4), 1.12 (d, 6H, $CH(CH_3)_2$, $J_{H,H} = 7.0$ Hz), 1.14 (d, 6H, $CH(CH_3)_2$, $J_{H,H} = 7.0$ Hz), 1.15 (d, 6H, $CH(CH_3)_2$, $J_{H,H} = 7.0$ Hz), 1.21 (d, 6H, $CH(CH_3)_2$, $J_{H,H} = 7.0$ Hz), 2.42 (br, 3H, BH_3), 3.05 (sept, 2H, $CH(CH_3)_2$, $J_{H,H} = 7.0$ Hz), 3.73 (sept, 2H, $CH(CH_3)_2$, $J_{H,H} = 7.0$ Hz), 4.51 (s, 2H, N–CH_2), 6.21 (d, 1H, pyr, $J_{H,H} = 3.8$ Hz), 6.85 (t, 1H, Ph, $J_{H,H} = 7.3$ Hz), 6.95 (d, 2H, Ph, $J_{H,H} = 7.3$ Hz), 7.04 (d, 1H, pyr, $J_{H,H} = 3.8$ Hz), 7.14–7.22 (m, 3H, Ph), 7.56 (s, 1H, N=CH). $^{13}C\{^1H\}$ NMR (THF-d_8, 100.4 MHz, 25 °C): $\delta = 23.2$ ($CH(CH_3)_2$), 23.5 ($CH(CH_3)_2$), 24.8 ($CH(CH_3)_2$), 25.7 ($CH(CH_3)_2$), 26.4 ($CH(CH_3)_2$), 28.4 ($CH(CH_3)_2$), 58.6 (N–CH_2), 110.3 (pyr), 122.6, 122.9, 123.6, 127.0, 129.6, 133.2, 142.6, 146.0, 149.6, 153.0, 153.3, 165.7 (N=CH). ^{11}B NMR (THF-d_8, 128.15 MHz, 25 °C): $\delta = -25.2$ (br qt, BH_4, $J_{H,B} = 71.3$ Hz), −14.8 (br, BH_3). IR (KBr, ν/cm^{-1}): 865(m), 906(w), 1056(s), 1103(m), 1139(m), 1198(s), 1246(s), 1289(s), 1322(s), 1382(m), 1462(s), 1538(w), 1584(s), 1607(vs), 2180(w), 2230(m), 2295(m), 2423(m), 2467(m), 2867(s), 2963(vs). $C_{38}H_{62}B_2N_3O_2Lu$ (789.51): calcd C, 57.81, H, 7.92, N, 5.32%; found C, 57.62, H, 8.09, N, 5.38%.

Crystal data for **2–3**: **2**: Stoe IPDS2T diffractometer, MoKα radiation ($\lambda = 0.71073$ Å): space group *Pbca* (no. 61) with $a = 16.0927(8)$ Å, $b = 25.137(2)$ Å, $c = 19.9083(10)$ Å, at 200(1) K, $Z = 8$, $V = 8053.4(8)$ Å^3, $\mu = 1.094$ mm^{-1}, $2\theta_{max} = 54.3°$, 28 300 reflections collected, 7100 independent reflections ($R_{int} = 0.0573$). The structure was solved by Patterson methods and refined by full-matrix least-square techniques using 4451 reflections with $I > 2\sigma(I)$ to $R_1 = 0.0340$ and $wR_2 = 0.0723$. **3**: MAR345 imaging plate detector system (MARRESEARCH) mounted on a four-circle goniometer with Eulerian geometry (HUBER) with a rotating anode generator (Bruker FR591, MoKα radiation $\lambda = 0.71073$ Å). The crystal was cooled to 6 K employing a closed-cycle helium cryostat (ARS-4K). Details of the data reduction and refinement: space group *Pn* (no. 7) with $a = 9.5587(9)$ Å, $b = 15.1757(17)$ Å, $c = 16.1030(19)$ Å, $\beta = 100.420(9)°$ at 6(2) K, $Z = 2$, $V = 2297.4(4)$ Å^3, $\mu = 2.192$ mm^{-1}, $2\theta_{max} = 60.84°$, 13 834 reflections collected, 8265 independent reflections ($R_{int} = 0.0282$). The data set was corrected for beam inhomogeneity and absorption effects ($T_{min}/T_{max} = 0.688(4)/0.814(4)$). The structure was solved by Patterson methods and refined by full-matrix least-square techniques using 8047 reflections with $I > 2\sigma(I)$ to $R_1 = 0.0271$, $wR_2 = 0.0618$, goodness of fit 1.141, largest diff. peak and hole 1.091 and −0.848 e Å^{-3}. All hydrogenatom positions could be located in the difference fourier map but were put to calculated positions (except for the BH_3 and the BH_4 group) in the final structural model to achieve faster convergence of the least-square refinement.

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