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Rare-Earth Polyhydrides

Rare-Earth Polyhydride Complexes Bearing Bis(phosphinophenyl)amido Pincer Ligands**

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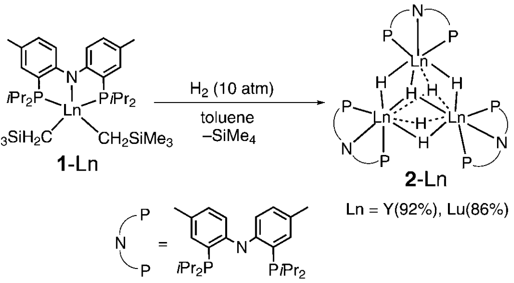
Rare-earth (Group 3 and lanthanide) metal polyhydride complexes consisting of the dihydride species “LLnH$_2$” with one ancillary ligand per metal center are receiving intense current interest because of their fascinating structure and reactivity, which are exquisitely different from their monohydride relatives “L$_2$LnH” with two supporting ligands.[1] The nuclearity of the rare-earth polyhydride complexes is generally dependent on the steric bulk of the ancillary ligands. An increase of ligand hindrance usually leads to a decrease of the nuclearity and increase of the reactivity of the resulting hydride clusters. To date, several hexanuclear,[1a,2a] tetranuclear,[2a,3] and trinuclear[2b,4,5] polyhydride complexes have been reported. However, despite recent progress in this area, the number of well-defined rare-earth polyhydride complexes is still very limited. Most of the ancillary ligands employed to date for rare-earth polyhydride complexes are either sterically demanding cyclopentadienyl derivatives such as $C_5Me_4SiMe_3$[3] or scorpionate tris(pyrazolyl)hydroborate units,[2] although the use of tetraazacycloamido[4] or pyridylamido[5] ligands was also described. Well-defined cationic rare-earth polyhydrides have remained scarce,[6] and a binuclear polyhydride complex consisting of “LLnH$_2$” has not been reported to date. Herein, we report the synthesis and structural characterization of a new family of rare-earth polyhydride complexes supported by the rigid bis(phosphinophenyl)amido (PNP) ligands, including the first examples of cationic trinuclear and binuclear rare-earth polyhydrides.

As a possible precursor to a rare-earth polyhydride complex bearing a PNP ligand, we first chose the yttrium dialkly complex [(PNP^{Ph})Y(CH$_2$SiMe$_3$)$_2$(thf)] (PNP^{Ph} = {2-(Ph$_2$P)-C$_6$H$_4$}$_2$N), which has shown novel polymerization activity.[7] However, the hydrogenolysis reaction of [(PNP^{Ph})Y(CH$_2$SiMe$_3$)$_2$(thf)] with H$_2$ seemed very complicated, and no characterizable product was obtained. In contrast, when an analogous dialkyl complex with a bis(diisopropylphosphinophenyl)amido ligand [(PNP^{iPr})Y(CH$_2$SiMe$_3$)$_2$] (PNP^{iPr} = {2-(*i*Pr$_2$P)-C$_6$H$_4$}$_2$N) was used, clean formation of the trinuclear polyhydride complex [{(PNP^{iPr})YH$_2$}$_3$] was observed, as indicated by the ^{1}H NMR spectrum (6.04 ppm, quartet, $^1J_{Y\text{-}H} = 16.8$ Hz, in C$_6$D$_6$). Unfortunately, however, a single crystal suitable for X-ray structure determination was not obtained because of the high solubility of this hydride compound in all common organic solvents. To make a hydride compound with better crystallinity, the dialkyl complex with a methyl-substituted analogue of the PNP^{iPr} ligand [(Me-PNP^{iPr})Y(CH$_2$SiMe$_3$)$_2$] (**1**-Y, Me-PNP^{iPr} = {4-Me-2-(*i*Pr$_2$P)-C$_6$H$_3$}$_2$N)[8] was then used. To our delight, the hydrogenolysis of **1**-Y in toluene under 10 atm H$_2$ successfully afforded the corresponding trinuclear hexahydride complex [{(Me-PNP^{iPr})YH$_2$}$_3$] (**2**-Y) as pale yellow crystals in 92 % yield of isolated product (Scheme 1). The analogous Lu hydride cluster **2**-Lu was also obtained in a similar way.



Scheme 1. Synthesis of PNP-ligated trinuclear polyhydride complexes.

X-ray crystallographic studies revealed that the complexes **2**-Y and **2**-Lu are isostructural. The ORTEP drawing of **2**-Y is shown in Figure 1; selected interatomic distances are listed in Table 1. Each Y atom in **2**-Y is bonded to a PNP

Table 1: Selected interatomic distances [Å] for **2**-Y and **3**-Y.

	2-Y	**3**-Y
Y1···Y2	3.4829(6)	3.4789(6)
Y1···Y3	3.4678(6)	3.4411(6)
Y2···Y3	3.1648(7)	3.4812(6)
Y(1,2,3)–H1	2.31(4), 2.22(4), 2.32(4)	2.37(4), 2.30(4), 2.43(4)
Y(1,2,3)–H2	2.06(4), 2.37(4), 2.34(4)	2.37(4), 2.30(4), 2.33(4)
Y(1,3)–H3	2.12(4), 2,27(4)	2.11(3), 2.07(3)
Y(1,2)–H4	2.12(4), 2.21(4)	2.08(3), 2.11(3)
Y(2,3)–H5	2.07(4), 2.11(4)	2.03(4), 2.05(4)
Y(2,3)–H6	2.07(4), 2.24(4)	
Y–N (av.)	2.367(3)	2.309(3)
Y–P (av.)	2.948(1)	2.900(1)

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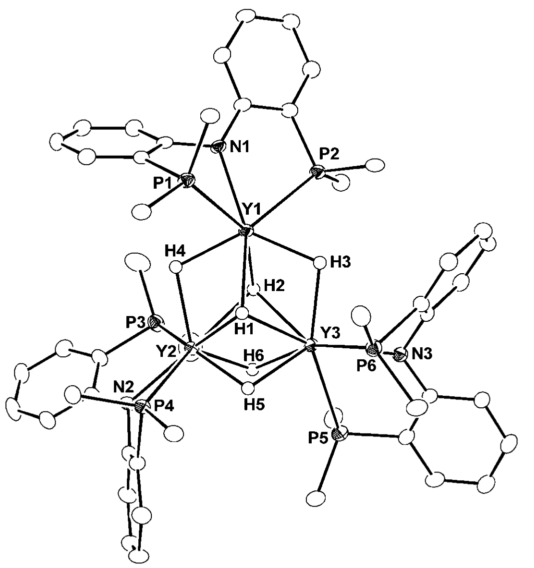
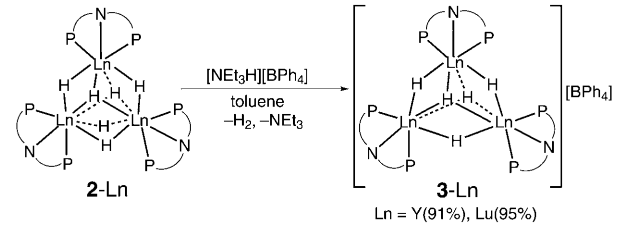


Figure 1. ORTEP plot of **2**-Y with thermal ellipsoids at the 30% probability level. The methyl groups and hydrogen atoms in the PNP ligands have been omitted for clarity.



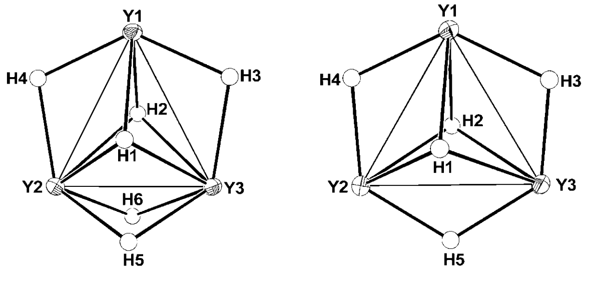
Scheme 2. Synthesis of cationic trinuclear pentahydride complexes.

ligand in a typical κ^3-(*P*,*N*,*P*) mode. Two of the six hydride ligands adopt a μ$_3$ bonding mode, each of which caps one side of the Y$_3$ plane. The remaining four hydride ligands bridge the three edges of the Y$_3$ triangle in a μ$_2$ fashion, and therefore, one the of the three Y···Y edges is bridged by two μ$_2$-H ligands, while the other two Y···Y edges are each bridged by only one μ$_2$-H ligand, in addition to the μ$_3$-H capping ligands. As a consequence, the Y2···Y3 edge (3.1648(7) Å) bridged by two μ$_2$-H ligands is significantly shorter than the other two Y···Y edges (3.4829(6) and 3.4678(6) Å, Table 1). This Y2···Y3 edge represents the shortest Y···Y distance ever reported, as far as we are aware. The Y$_3$H$_6$ core structure in **2**-Y is thus in contrast to those of other reported trinuclear hexahydrides, such as [{(Tp^{iPr2})YH$_2$}$_3$] (Tp^{iPr2} = tris(3,5-diisopropyl-1-pyrazolyl)hydroborate), which possesses one μ$_3$-H and five μ$_2$-H ligands,[2b] and [{(Me$_3$TACD)YH$_2$}$_3$] (Me$_3$TACD-H = 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane),[4] in which all six hydride ligands adopted the same μ$_2$-H bonding mode. The Y···Y distances in these previous examples range from 3.3423(3) to 3.6841(2) Å.

The ^{1}H NMR spectrum of **2**-Y in C$_6$D$_6$ showed a quartet ($^1J_{\text{Y-H}} = 17.0$ Hz) at $\delta = 6.08$ ppm corresponding to the hydride ligands, thus suggesting that the structure is fluxional and that all six hydrides are equivalent on the time scale of NMR spectroscopy. The hydrides in **2**-Lu showed a broad singlet at $\delta = 9.70$ ppm. These results are comparable with those observed in other trinuclear polyhydride complexes.[2b,4]

On treatment with an equivalent of [NEt$_3$H][BPh$_4$] in toluene (or THF) at room temperature, both **2**-Y and **2**-Lu gave the corresponding cationic pentahydrides [(Me-PNP^{iPr})$_3$Y$_3$H$_5$][BPh$_4$] (**3**-Ln; Ln = Y, Lu) in high yields, with concomitant release of H$_2$ and NEt$_3$ (Scheme 2).

The cationic complexes **3**-Y and **3**-Lu are soluble in THF and C$_6$H$_5$Cl and partly soluble in toluene and benzene but almost insoluble in hexane. Single crystals suitable for X-ray diffraction studies were obtained from saturated toluene solutions. Similar to the neutral precursors **2**-Ln, the cationic hydride clusters **3**-Ln are also isostructural. The {Ln$_3$H$_5$} core structure of **3**-Y is shown in Figure 2 (right) together with its neutral counterpart **2**-Y (left) for comparison. Some selected interatomic distances are summarized in Table 1. All three Y atoms in the cationic complex **3**-Y are almost equally connected by the hydride ligands. Two of the five hydride ligands adopt a μ$_3$ bonding mode, and the remaining three hydride ligands are bonded in a μ$_2$ fashion, each bridging one Y···Y edge. Therefore, the three Y···Y edges in **3**-Y are almost equal, in contrast with its neutral precursor **2**-Y, in which one of the Y···Y edges is much shorter than the other two because of the additional bridging hydride ligand (Figure 2 and Table 1). The hexagon formed by the three Y atoms and the three μ$_2$-H atoms in **3**-Y is almost planar, with a maximum deviation of 0.129 Å. The two μ$_3$-H atoms are located 1.213 and 1.248 Å above and below the hexagonal plane. The Y–(μ$_3$-H) bonds in **3**-Y (av. 2.35(4) Å) are longer than the Y–(μ$_2$-H) bonds (av. 2.08(4) Å), similar to the situation in **2**-Y. The Y–N and Y–P bonds in the cationic complex **3**-Y are significantly shorter than those in the neutral precursor **2**-Y (Table 1).



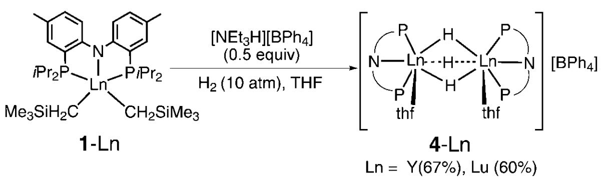
2-Y **3**-Y

Figure 2. The metal hydride core structures of **2**-Y and **3**-Y.

It is also noteworthy that no direct bonding interaction was observed between the cation [((Me-PNP^{iPr})$_3$Ln$_3$H$_5$] and the anion [BPh$_4$] in **3**-Y despite steric and electronic unsaturation (compared to **2**-Y) at the metal center. Moreover, the incorporation of a thf ligand into **3**-Y was not observed even when the complex was mixed with THF. These results are in sharp contrast with what was observed in the tetranuclear cationic polyhydride complex [(C$_5$Me$_4$SiMe$_3$)$_4$Y$_4$H$_7$][B(C$_6$F$_5$)$_4$], which adopted a contact-ion-pair structure in the THF-free form and gave the solventseparated ion pair $[(C_5Me_4SiMe_3)_4Y_4H_7(thf)_2][B(C_6F_5)_4]$, upon reaction with THF.[6] Complex **3**-Y (as well as **3**-Lu) represents the first example of a structurally characterized cationic trinuclear rare-earth polyhydride complex and also the first example of a cationic rare-earth polyhydride complex bearing a non-cyclopentadienyl ligand.

The five hydride ligands of the cationic complex **3**-Y showed two sets of ^1H NMR signals in C_6D_5Cl, with a broad singlet at $\delta = 5.53$ ppm for the two μ_3-H ligands and a triplet at $\delta = 6.52$ ppm ($^1J_{Y\text{-}H} = 31.7$ Hz) for the three μ_2-H ligands, in contrast with its neutral precursor **2**-Y, which exhibited only a quartet ($\delta = 5.97$ ppm, $^1J_{Y\text{-}H} = 16.9$ Hz) for all six hydrides under similar conditions. Similarly, the hydrides in **3**-Lu showed two broad signals at $\delta = 8.43$ and 11.85 ppm. These results suggest that the Ln_3H_5 core structure in the cationic complexes **3**-Ln is more rigid than the Ln_3H_6 unit in the neutral complexes **2**-Ln. Similar phenomena were also observed in the $C_5Me_4SiMe_3$-ligated tetranuclear polyhydride analogues.[6]

Surprisingly to us, when the hydrogenolysis reaction of the dialkyl complexes **1**-Ln was carried out in the presence of 0.5 equivalent $[NEt_3H][BPh_4]$ in THF, the binuclear cationic trihydride complexes $[(Me\text{-}PNP^{iPr})_2Y_2H_3(thf)_2][BPh_4]$ (**4**-Ln; Ln = Y, Lu) were obtained in 60–67% yields of isolated product (Scheme 3), in sharp contrast with the reaction in the absence of $[NEt_3H][BPh_4]$, which yielded selectively the trinuclear polyhydrides **2**-Ln as described above.[9] The three hydride ligands in **4**-Y showed a triplet at $\delta = 5.72$ ppm with $^1J_{Y\text{-}H} = 23.1$ Hz in the ^1H NMR spectrum in $[D_8]$THF. Complex **4**-Lu gave a singlet at $\delta = 8.45$ ppm.



Scheme 3. One-pot synthesis of cationic binuclear trihydride complexes.

Single crystals of **4**-Y and **4**-Lu were grown from THF/hexane. These two complexes are isostructural. Figure 3 depicts the ORTEP structure of the cation part of **4**-Y. The two Y atoms are bridged by three hydride ligands, and each Y atom is also bonded to a κ^3-PNP ligand and a thf ligand. The Y_2H_3 core adopts a slightly distorted triangular bipyramid geometry, with the three hydride ligands occupying the equatorial positions and the two Y atoms in the apical sites. The Y−H bond lengths vary from 2.08(5) to 2.21(5) Å, but fall in the range of typical Y-(μ_2-H) distances. The Y⋯Y distance in **4**-Y (3.3297(5) Å) is significantly shorter than those in the trinuclear cationic complex **3**-Y (av. 3.4671(6) Å). Complexes **4**-Y and **4**-Lu represent the first examples of structurally characterized cationic binuclear rare-earth polyhydride complexes.

The present formation of **4**-Ln could formally be viewed as a combination of a neutral dihydride species such as $[(Me\text{-}PNP^{iPr})LnH_2(thf)_x]$, formed by the hydrogenolysis of the dialkyl complex **1**-Ln, with a cationic monohydride species $[(Me\text{-}PNP^{iPr})\ LnH(thf)_x][BPh_4]$ resulting from the hydrogenolysis of the cationic monoalkyl species $[(Me\text{-}PNP^{iPr})Ln(CH_2SiMe_3)(thf)_x][BPh_4]$ that could be formed by reaction of **1**-Ln with $[NEt_3H][BPh_4]$ in THF.

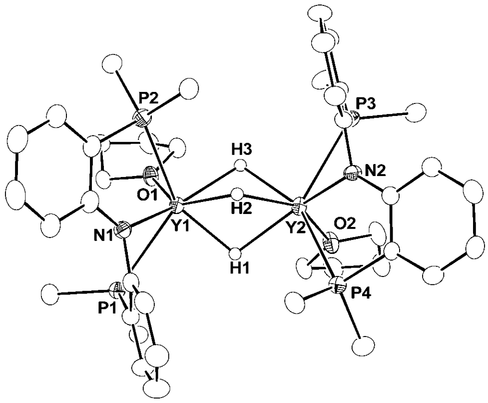


Figure 3. ORTEP plot of the cationic part of **4**-Y with thermal ellipsoids at the 30% probability level. The methyl groups and hydrogen atoms in the PNP ligands have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Y1–H1 2.08(5), Y1–H2 2.14(4), Y1–H3 2.17(4), Y1–N1 2.314(3), Y1–P1 2.9492(12), Y1–P2 2.9293(11), Y1–O1 2.372(2), Y2–H1 2.21(4), Y2–H2 2.09(4), Y2–H3 2.12(4), Y2–N2 3.321(3), Y2–P3 2.9349(12), Y2–P4 2.9266(12), Y2–O2 2.351(3), Y1⋯Y2 3.3297(5); Y1-H1-Y2 102.0(12), Y1-H2-Y2 104.0(12), Y1-H3-Y2 102.1(12).

In summary, we have demonstrated that the rigid bis(phosphinophenyl)amido moiety $\{4\text{-Me-2-}(iPr_2P)\text{-}C_6H_3\}_2N$ can serve as an excellent supporting ligand for rare-earth polyhydride complexes, leading to formation of a new family of structurally characterizable trinuclear and binuclear polyhydride complexes, including the first examples of cationic trinuclear and binuclear rare-earth polyhydrides. Studies on the reactivity of these hydride clusters and on the analogous rare-earth polyhydride complexes with other non-cyclopentadienyl ancillary ligands are in progress.[10]

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[9] The hydrogenolysis of **1**-Y in THF in the absence of $[\text{NEt}_3\text{H}][\text{BPh}_4]$ did not give a characterizable product. Neither did that of **1**-Y in toluene in the presence of $[\text{NEt}_3\text{H}][\text{BPh}_4]$.

[10] Structurally characterizable cationic binuclear trihydrides bearing amidinate ancillary ligands, such as $[(\text{PhC(NAr*)}_2)_2\text{Y}_2\text{H}_3(\text{thf})_4][\text{BPh}_4]$ (Ar* = 2,6-diisopropylphenyl), were also obtained by the hydrogenolysis of $[\{\text{PhC(NAr*)}_2\}\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})]$ with 0.5 equivalents of $[\text{NEt}_3\text{H}][\text{BPh}_4]$ in a THF solution.