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Simple entry into *N*-*tert*-butyl-iminophosphonamide rare-earth metal alkyl and chlorido complexes†

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In situ protolysis reaction of a highly basic and sterically hindered *N*,*N*′-di-*tert*-butyl-iminophosphonamide ligand $Ph_2P(=N\text{-}tBu)(NH\text{-}tBu)$ = $(NPN^{tBu})H$ (**1**) with equimolar or hemimolar amounts of rare-earth metal tris-alkyls leads to dialkyl $[(NPN^{tBu})Ln(CH_2SiMe_3)_2(THF)_n]$ (Ln = Sc, *n* = 0 (**2**), Ln = Y, *n* = 1 (**3**)) and monoalkyl species $[(NPN^{tBu})_2Ln(CH_2SiMe_3)]$ (Ln = Y (**4**), Nd (**6**), Sm (**7**)). One-pot reaction of $[ScCl_3(THF)_3]$/**1**/MeLi in 1/2/3 eq. ratio gives $[(NPN^{tBu})_2Sc(THF)CH_3]$ **5**. Further reaction of **4** with phenylacetylene resulted in the formation of the Y-alkynyl complex $[(NPN^{tBu})_2Y(-C{\equiv}CPh)]$ **8**. Alkyl abstraction in **2**, **3** and **4** by reaction with $[PhNMe_2H]^+[B(C_6F_5)_4]^-$ resulted in the formation of cationic alkyl complex ion-pairs $[(NPN^{tBu})Ln(CH_2SiMe_3)(THF)_n]^+[B(C_6F_5)_4]^-$ (Ln = Sc (**9**), Y (**10**)) and $[(NPN^{tBu})_2Y(THF)_n]^+[B(C_6F_5)_4]^-$ **11**, as confirmed by NMR data. The reaction of bis-NPN alkyl complexes with $CHCl_3$ is the simplest and most reliable protocol to synthesize bis-NPN-chlorido complexes $[(NPN^{tBu})_2Ln{-}Cl]$ (Ln = Sc (**12**), Y (**13**), Nd (**14**), Sm (**15**), Gd (**16**), Tb (**17**), Yb (**18**) and Lu (**19**)), which can become new post-metallocene alternatives to the prominent organolanthanide building blocks $[Cp^*_2LnX]$. Partial hydrolysis of **12** leads to the formation of the oxido/chlorido-capped trinuclear complex $[\{(NPN^{tBu})Sc(\mu_2\text{-}Cl)\}_3(\mu_3\text{-}O)(\mu_3\text{-}Cl)]$ **20**. Molecular structures of **4**, **6**, **7**, **13**, **19** and **20** were confirmed by X-ray structure analyses.

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Introduction

In the course of our systematic studies of ambident organophosphorus(v) donor ligands of the general type $[R_2P(X)Z]^-$ (X, Z = S, O, NR′, CH_2, CHR′, Cp, Ind, Flu; as for X = Z and X ≠ Z)[1] we turned our attention to the chemistry of iminophosphonamide ligands $[R_2P(NR')_2]^-$ (NPN) and their rare-earth metal complexes. The ligands are isoelectronic analogues of phosphinate anions, in which oxygen atoms are replaced by two imido groups. The influence of nitrogen substituents R′ on ligand properties is definitely stronger than that of R groups at the more remote phosphorus centre.

First reports of rare-earth metal NPN complexes by Edelmann, Schumann and co-workers appeared in the 1980s–1990s using **A**-type ligands (see Chart 1) with $SiMe_3$ (tms) substituents at the nitrogen atoms for the preparation of Pr^{III} and Nd^{III} chlorido complexes I and Ac^{IV} chlorido and oxo complexes (**II** and **III**),[2] yet none of them was structurally characterised. Later, Sm^{III} and Yb^{II}-complexes (**IV** and **V**)[3] as well as a series of Ln-COT NPN-complexes (**VI**)[4] have been reported.

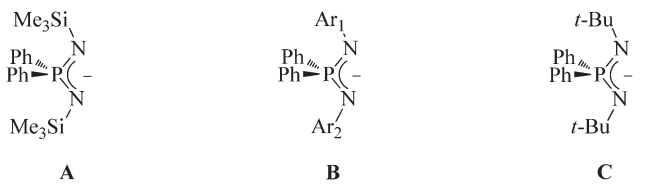

Chart 1 Different types of NPN ligands (**A**–**C**).

In 2006 Hill and co-workers reported several rare-earth metal tms_2N- and dms_2N-complexes (dms: $SiMe_2H$) bearing a chiral {DACH}-bridged bis-NPN ligand regime (**VII**) (DACH = *trans*-diaminocyclohexane),[5] which are highly active one-component catalysts for the stereoselective polymerisation of MMA. Numerous rare-earth metal complexes based on **B**-type NPN-ligands having aromatic moieties on the nitrogen atoms (**VIII**) have been reported by the research groups of Cui and Hou.[6] The catalytic precursors based on rare-earth metal complexes of iminophosphonamide (NPN) skeletons show a high efficiency for 3,4-selective polymerisations of 1,3-conjugated dienes. The regio- and stereoselectivities of these catalytic species are strongly dependent on the *ortho* substituents of the nitrogen bonded aryl ring, of which the sterically demanding ones prefer to show a high 3,4-selectivity.[6a,b] Moreover, a

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borohydrido neodymium (**IX**) and recently 4-methylbenzyl neodymium and lanthanum (**X**) **B**-type NPN-complexes have been reported to act as efficient catalysts for the *trans*-1,4-selective polymerisation of isoprene.[7] Further examples of alkali and alkali-earth metals,[8] Al and Ga,[5,9] Ti and Zr,[10] Cr,[11] Co,[12] Ni,[13] Pd and Pt,[13c,14] Cu,[15] Ag,[16] and Zn,[13d,17] NPN-complexes are know from the literature. Being able to donate up to 6 electrons, anionic NPN ligands can serve as steric and electronic pendants to Cp or Cp* ligands; however in rare-earth metal chemistry only ligands with electron withdrawing *N*-silyl (type **A**, examples **I–VI**) or *N*-aryl (type **B**, examples **VIII–IX**) substituents have been thoroughly investigated so far (Chart 2). The higher the basicity of a ligand, the better its ability to donate electrons and to compensate part of the Lewis acidity of a rare-earth metal centre.

Here we report on the so far unknown rare-earth metal chemistry of the sterically demanding, very basic, easily accessible and perfectly soluble *N*,*N*′-bis-*tert*-butyl-iminophosphonamide ligand (type **C**) $Ph_2P(=N\text{-}tBu)(NH\text{-}tBu)$ = $(NPN^{tBu})H$ (**1**).

Synthesis of mono-(NPN^{tBu}) dialkyl rare-earth metal complexes

Initial attempts to prepare $[(NPN^{tBu})Ln(CH_2SiMe_3)_2(THF)_n]$ complexes using *in situ* prepared rare-earth metal tris-alkyls $[Ln(CH_2SiMe_3)_3(THF)_n]$ from $[LnCl_3(THF)_n]$ and 3 eq. of $LiCH_2SiMe_3$ were fully successful only for the solvent-free Sc-derivative $[(NPN^{tBu})Sc(CH_2SiMe_3)_2]$ **2**. In the case of the larger cation Y^{3+}, formation of the target mono-NPN species $[(NPN^{tBu})Y(CH_2SiMe_3)_2(THF)]$ **3** was accompanied by a small amount of bis-NPN complex $[(NPN^{tBu})_2Y(CH_2SiMe_3)]$ **4** as a by-product in the NMR spectra. Although **4** is less soluble in *n*-pentane or *n*-hexane than **3**, we have not succeeded to separate it and isolate pure **3** by this method (Scheme 1).

Selective and high yield syntheses of very pure **2** and **3** complexes have been achieved using the alkane elimination route

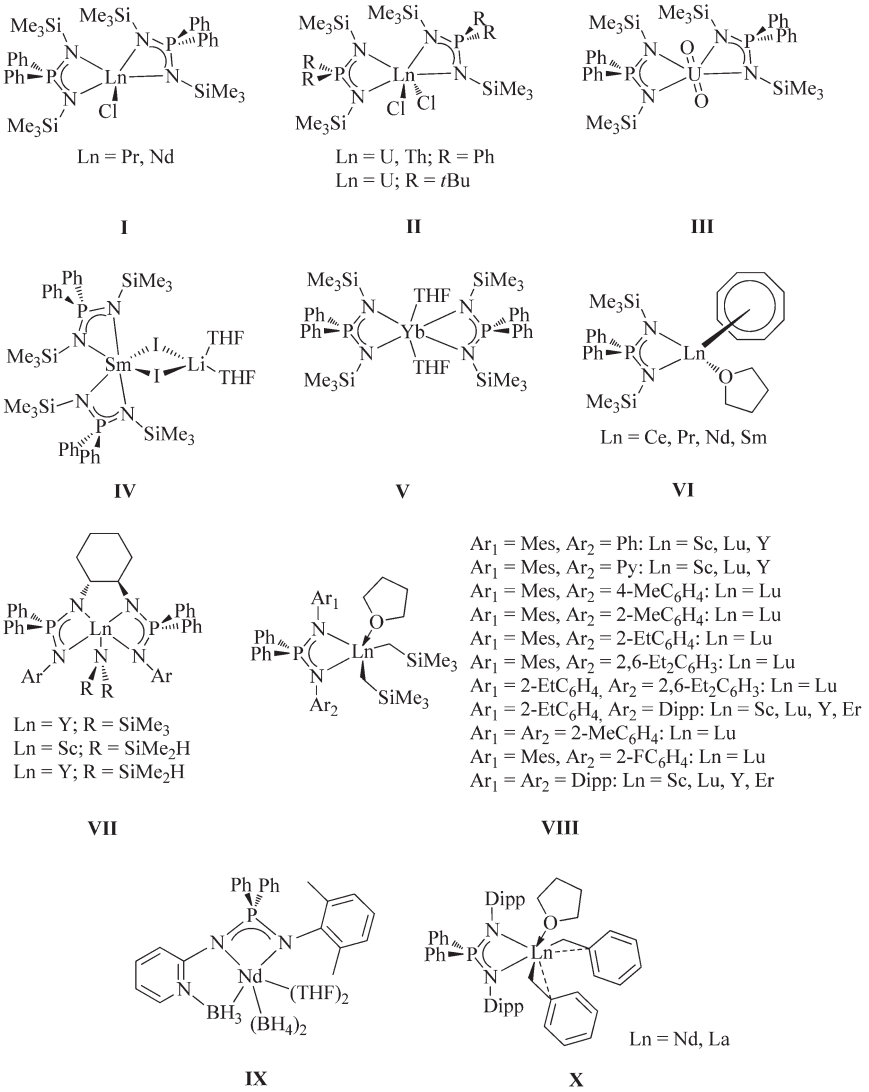
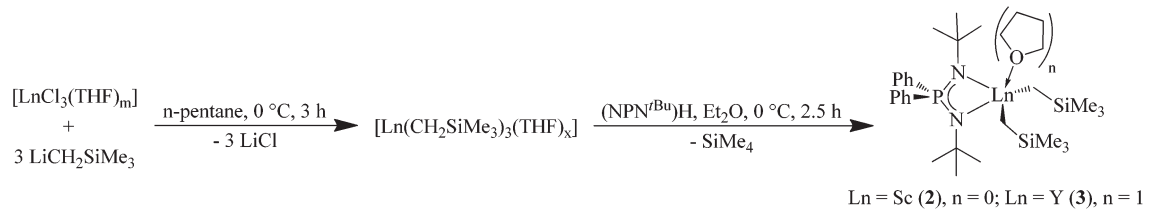


Chart 2 Known rare-earth metal NPN complexes (**I–X**).



Scheme 1 Preparation of mono-NPN complexes **2** and **3**.

from the purely isolated tris-neosilyl precursors [Sc(CH_2SiMe_3)$_3$(THF)$_2$] and [Y(CH_2SiMe_3)$_3$(THF)$_3$]. A pre-cooled 0 °C diethyl ether solution of **1** was added dropwise to a solution of the trialkyl in *n*-pentane or *n*-hexane at 0 °C. In ^{31}P NMR spectra sharp signals are observed at 12.2 (**2**) and 18.1 (**3**) ppm. ^{1}H NMR spectra of NPN complexes are represented by the signals of the trimethylsilyl and *tert*-butyl groups that appear in both **2** and **3** around 0.45 and 1.11 ppm correspondingly. The methylene groups are observed as singlets at 0.25 ppm for **2** and as doublets at −0.26 ppm with $^2J_{HY}$ = 3.0 Hz for **3**. In the ^{1}H NMR spectrum of scandium complex **2** no signals of the THF molecule are observed. In contrast, in the Y-complex **3** signals at 1.34 and 3.88 ppm with an overall intensity of 8H are clearly seen and undoubtedly assigned to a coordinating THF molecule. The assignment of signals in ^{13}C NMR spectra was carried out by two-dimensional NMR spectroscopy. The signals for phenyl groups are observed in the range of about 130–140 ppm as doublets with different J_{CP} coupling constants.

Synthesis of bis-(NPN^{tBu}) monoalkyl rare-earth metal complexes

Following synthetic protocols described by B. Hessen *et al.* for bis-neosilyl benzamidinate rare-earth metal complexes,[18] we successfully applied them both to the synthesis of bis-(NPN^{tBu}) monoalkyl rare-earth metal complexes [(NPN^{tBu})$_2$Ln(CH_2SiMe_3)] – either starting from *in situ* or from purely isolated tris-neosilyl [Ln(CH_2SiMe_3)$_3$(THF)$_n$] precursors. Both protocols allow us to prepare [(NPN^{tBu})$_2$Y(CH_2SiMe_3)] **4** in high yields (85% – for the *in situ* method and 91% – for the purely isolated one, see Schemes 2 and 4). Purification was achieved by crystallisation from *n*-hexane at −30 °C.

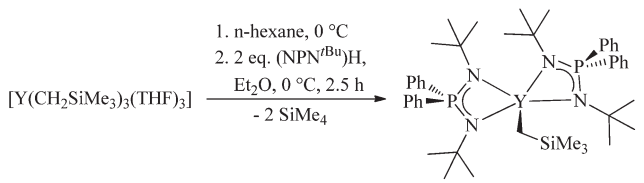
As expected, reaction of 1 eq. of [Sc(CH_2SiMe_3)$_3$(THF)] with 2 eq. of **1** does not allow us to isolate the bis-(NPN^{tBu}) scandium derivative: because of the small ionic radius of the scandium metal centre, it cannot coordinate two bulky (NPN^{tBu})-ligands and further one bulky Me_3SiCH_2-group.

Yet, when instead of the Me_3SiCH_2-group a simple CH_3-group was used, the corresponding bis-NPN scandium derivative can be easily obtained. Thus, a simple one-pot protocol starting from 2 eq. of **1** and 1 eq. of [$ScCl_3$(THF)$_3$] suspended in diethyl ether at 0 °C followed by the addition of 3 eq. of MeLi for 1 h (Scheme 3) led to a new bis-NPN scandium complex [(NPN^{tBu})$_2$Sc(THF)CH_3] **5** that has been isolated as a pure colourless solid in 59% yield.

The ^{31}P NMR spectrum of **5** shows a signal at 19.6 ppm that is very close to that of **4** (see above). The CH_3-group is observed downfield shifted at 0.61 ppm in ^{1}H and at 22.8 ppm in ^{13}C NMR spectra. Co-ordinated THF is also confirmed by both ^{1}H and ^{13}C NMR spectra.

Isolation of tris-alkyl-derivatives of the larger rare-earth metals in a pure form is a serious synthetic task because of their low thermal stability. NPN-complexes of these metals have been synthesized using the described above *in situ* method (Scheme 4). For the completion of tris-alkyl formation from [$LnCl_3$(THF)$_m$] and $LiCH_2SiMe_3$ the reaction mixture was stirred for 1 h at 0 °C, followed by the addition of 2 eq. of **1** in diethyl ether. By this method two new bis-NPN-alkyl complexes, [(NPN^{tBu})$_2$Nd(CH_2SiMe_3)] **6** and [(NPN^{tBu})$_2$Sm(CH_2SiMe_3)] **7**, have been synthesized. Thus-isolated **6** and **7** are slightly (up to 10%) contaminated by another NPN-metallated species presumably by lithiated **1** as confirmed by their NMR spectra.

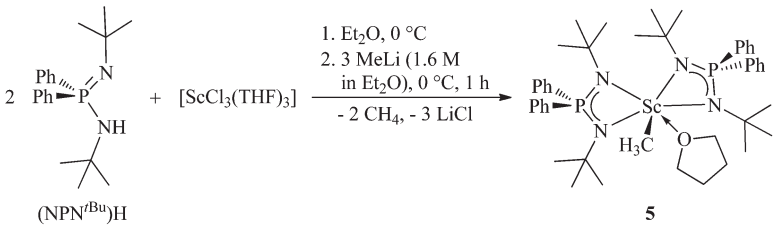
In ^{31}P NMR spectra sharp signals at 19.5 (**4**), 72.4 (**6**) and −133.8 (**7**) ppm have been found. ^{1}H and ^{13}C NMR spectra of **4** are very similar to those of **3** with the exception of THF signals. The ^{1}H NMR spectra of paramagnetic complexes **6** and **7** show sharp signals and can be easily assigned. Thus, *tert*-butyl group signals are upfield-shifted at −2.68 (**6**) and −7.19 (**7**) ppm, whereas trimethylsilyl group signals are slightly high-field-shifted for **6** at −4.34 ppm and downfield-shifted for **7** at 1.53 ppm. The signals of phenyl groups are more or less downfield shifted depending on the distance from the paramagnetic centre. For the samarium complex **7** the signal of the methylene group is observed at 15.98 ppm, yet for the neodymium complex this signal could not be clearly assigned.



Scheme 2 Preparation of [(NPN^{tBu})$_2$Y(CH_2SiMe_3)] **4**.

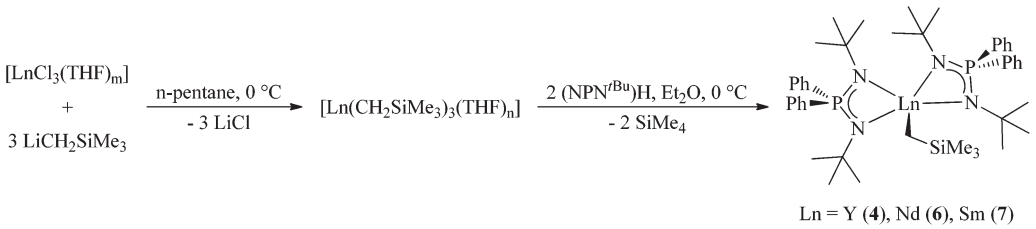
Reaction with phenylacetylene

The reaction of **4** with phenylacetylene was studied in order to prove the possibility of alkyl-abstraction from bis-(NPN)-alkyl



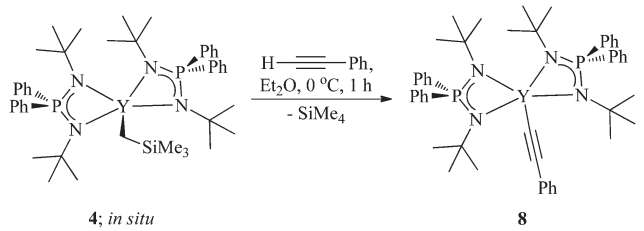
(NPN^{tBu})H 5

Scheme 3 Preparation of [(NPN^{tBu})$_2$Sc(THF)CH$_3$] **5**.



Ln = Y (**4**), Nd (**6**), Sm (**7**)

Scheme 4 Preparation of bis-NPN complexes [(NPN^{tBu})$_2$Ln(CH$_2$SiMe$_3$)] (**4**, **6** and **7**).



4; *in situ* **8**

Scheme 5 Preparation of [(NPN^{tBu})$_2$Y(C≡CPh)] **8**.

complexes by a simple CH-acid. Complex **4** was prepared *in situ* from 1 eq. of [Y(CH$_2$SiMe$_3$)$_3$(THF)$_3$] and 2 eq. of **1** and allowed to react with 1 eq. of phenylacetylene for 1 h at 0 °C. Alkynyl complex **8** forms selectively and has been isolated as a colourless, highly air- and moisture-sensitive solid in a high yield of 78% (Scheme 5).

In the ^{31}P NMR spectrum a singlet is observed at 17.8 ppm that is upfield shifted compared to the starting complex **4** (19.5 ppm). The Ph*C*≡CY signal is found as a doublet at 130.0 ppm with $^{2}J_{CY}$ = 36.2 Hz, the carbon atom bonded to the Y metal centre PhC≡*C*Y is not observed in the ^{13}C NMR spectrum.

Reaction with *N*,*N*-dimethylanilinium tetrakis (pentafluorophenyl) borate

The reaction with the mild protonating [PhNMe$_2$H]$^+$[B(C$_6$F$_5$)$_4$]$^-$ proved to be a highly selective method for the synthesis of cationic species by alkyl abstraction. The most suitable NMR solvent for this study is a 6 : 1 mixture of C$_6$D$_6$: d$_8$-THF.

When mono-NPN dialkyl species **2** and **3** react with 1 eq. of [PhNMe$_2$H]$^+$[B(C$_6$F$_5$)$_4$]$^-$ mono-alkyl cationic species [(NPN^{tBu})-Ln(CH$_2$SiMe$_3$)(THF)$_n$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (Ln = Sc (**9**) and Y (**10**)) are formed (Scheme 6). In the case of bis-NPN mono-alkyl complex **4**, formation of [(NPN^{tBu})$_2$Y(THF)$_n$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ **11** was observed (Scheme 7).

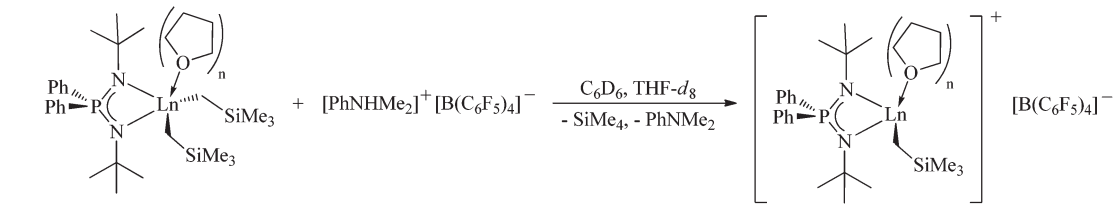
Characterization of the resulting cationic complexes **9–11** was carried out *via* NMR spectroscopy. All three complexes are formed selectively and rapidly as proven by the immediate formation of one equivalent of each of PhNMe$_2$ and SiMe$_4$. Thus-obtained ion-paired complexes are thermally stable and form in non-coordinating solvents insoluble oils.

The tetrakis-pentafluorphenyl borate-anions show as expected very similar NMR characteristics for all complexes. In ^{31}P NMR spectra, the cations show for each complex one signal at 22.3 (**9**), 22.8 (**10**) and 23.5 (**11**) ppm, which in comparison with the starting compounds at 12.2 (**2**), 18.1 (**3**) and 18.1 (**4**) ppm are downfield shifted. ^{1}H and ^{13}C NMR spectra show a similar symmetric set of ligand signals as the precursor NPN-alkyl complexes. Coordination of THF molecules is clearly seen by an additional set of signals next to the signals of deuterated THF residuals.

Stronger and shorter Ln–C bond character in cationic mono-alkyl NPN-complexes compared to their bis-alkyl neutral precursors manifests in ^{13}C NMR spectra larger $^{1}J_{CY}$ coupling constants: 42.3 Hz in **10** *vs.* 38.7 Hz in **3** and downfield shifted Ln-*C*H$_2$: 47.5 ppm for **9** *vs.* 39.7 ppm for **2** and 34.4 ppm for **10** *vs.* 32.4 ppm for **3**.

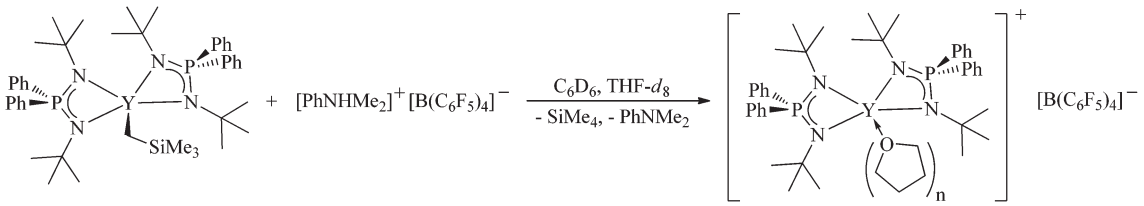
Synthesis of bis-(NPN^{tBu}) chlorido rare-earth metal complexes

As shown above, bis-(NPN^{tBu}) rare-earth metal alkyl complexes are easily accessible in a highly pure form due to their crystallisation from *n*-pentane. In contrast, our initial attempts to synthesize chlorido complexes by the reaction of 2 eq. of lithiated **1** with 1 eq. of [LnCl$_3$(THF)$_m$] led to product mixtures difficult to separate rather than to the desired pure chlorido post-metal-



Ln = Sc (**2**), n = 0; Ln = Y (**3**), n = 1 Ln = Sc (**9**), Y (**10**)

Scheme 6 Preparation of $[(NPN^{tBu})Ln(CH_2SiMe_3)(THF)_n]^+[B(C_6F_5)_4]^-$ (**9** and **10**).



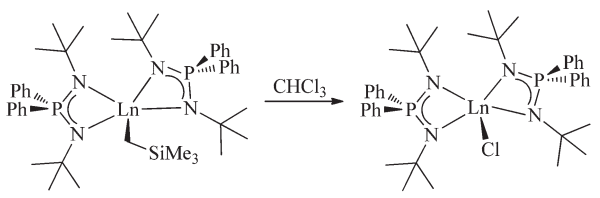
4 **11**

Scheme 7 Preparation of $[(NPN^{tBu})_2Y(THF)_n]^+[B(C_6F_5)_4]^-$ **11**.

locene $[(NPN^{tBu})_2Ln–Cl]$ complexes. They offer reaction patterns complementary to those of the alkyls $[(NPN^{tBu})_2Ln–R]$. We found the simplest synthetic approach to these chlorido complexes. This protocol includes *in situ* formation of $[(NPN^{tBu})_2Ln–CH_2SiMe_3]$ complexes as described above for **4**, **6** and **7**, their extraction into *n*-pentane or *n*-hexane, followed by quenching with dry chloroform. This leads to alkyl/Cl exchange (Scheme 8). As all $[(NPN^{tBu})_2Ln–CH_2SiMe_3]$ complexes are highly soluble in alkanes, whereas $[(NPN^{tBu})_2Ln–Cl]$ complexes are not, the latter precipitate from alkanes. They are collected *via* centrifugation, decantation or filtration. Following this protocol rare-earth metal complexes of early lanthanides with relatively large atomic radii: Nd (**14**) and Sm (**15**), of the middle range lanthanides and yttrium: Gd (**16**), Tb (**17**) and Y (**13**), as well as late lanthanides with smaller atomic radii and scandium: Yb (**18**), Lu (**19**) and Sc (**12**) were obtained in high purity and in 33–85% yields.

Being easily accessible in pure form now all these complexes represent a convenient platform for further investigation of a manifold of reactivity patterns, as they are soluble in benzene, toluene and ethers, crystalline and relatively stable against hydrolysis.

In the ^{31}P NMR spectra of diamagnetic complexes sharp signals at 19.6 (**12**), 18.5 (**13**) and 20.0 (**19**) ppm are observed. These signals are in the same range as for bis-NPN alkyl complexes of yttrium, 19.5 ppm (**4**) and scandium 19.6 (**5**). The paramagnetic complexes of Nd and Sm exhibit ^{31}P NMR signals at −113.9 (**14**) and 81.8 (**15**) ppm, which are both downfield shifted compared to their NPN-alkyl analogues −133.8 (**6**) and 72.4 (**7**) ppm.



Ln = Sc, Y (**4**), Nd (**6**), Sm (**7**) Gd, Tb, Yb, Lu; *in situ* Ln = Sc (**12**), Y (**13**), Nd (**14**), Sm (**15**), Gd (**16**), Tb (**17**), Yb (**18**), Lu (**19**)

Scheme 8 Preparation of $[(NPN^{tBu})_2Ln–Cl]$ (**12–19**).

Molecular structures of bis-(NPN^{tBu}) rare-earth metal alkyl and chlorido complexes

Single crystals of **4** (Y), **6** (Nd) and **7** (Sm) suitable for X-ray crystallography were obtained from a saturated *n*-pentane solution at −30 °C. All these alkyl-complexes are isostructural and crystallise in the monoclinic space group $P2_1/n$ with four molecular units per cell unit (Fig. 1). Selected bond lengths and angles of the compounds are presented in Table 1.

Crystallisation of chlorido complexes of Y (**13**) and Lu (**19**) was achieved from a saturated diethyl ether solution at room temperature. These complexes are isostructural and crystallise in the triclinic space group $P\bar{1}$ with two molecular units per cell unit (Fig. 2). Selected bond lengths and angles of the compounds are presented in Table 1.

Ln–N bond lengths 2.307(3)–2.407(3) Å for **4**, 2.400(3)–2.501 (3) Å for **6** and 2.370(3)–2.476(3) Å for **7** lie between representative covalent[19] and donor–acceptor[20] bonds. They are also in the same range as for other type **A** and **B** mono- and bis-NPN complexes, for example: in $[\{Ph_2P(NMes)(NPh)\}Y(CH_2SiMe_3)_2(THF)]$: d(Y–N) = 2.335(3) and 2.349(4) Å,[6a,b] in $[\{Ph_2P(NSiMe_3)_2\}_2Sm(\mu_2\text{-}I)_2]Li(THF)$: d(Sm–N) = 2.384(3)–2.506(4) Å[3]

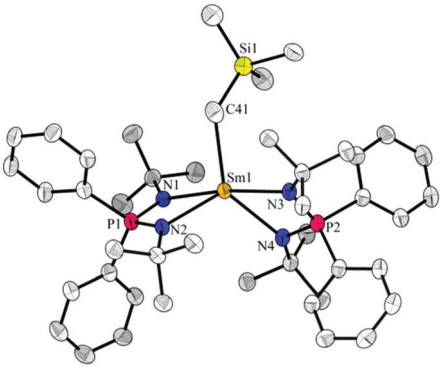


Fig. 1 Molecular structure of **7**, one of the series of isostructural bis-NPN alkyl complexes [(NPN$^{t\mathrm{Bu}}$)$_2$Ln(CH$_2$SiMe$_3$)] (**4**, **6** and **7**). The hydrogen atoms are omitted for clarity.

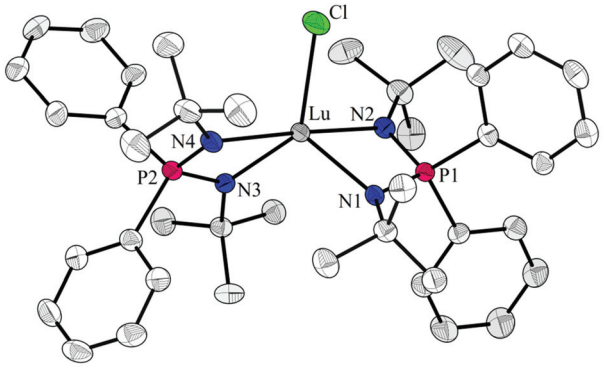


Fig. 2 Molecular structure of **19**, one of the two isostructural bis-NPN chlorido complexes [(NPN$^{t\mathrm{Bu}}$)$_2$Ln–Cl] (Ln = Y **13** and Lu **19**). The hydrogen atoms are omitted for clarity.

or in [{Ph$_2$P(NSiMe$_3$)$_2$}Nd(COT)(THF)]: d(Nd–N) = 2.472(3) and 2.473(3) Å.[4] The Ln–C bond lengths are within the expected range for Ln–CH$_2$SiMe$_3$ derivatives.[21]

As expected, Y–N bond lengths in chlorido complex **13** with a more electron-poor central atom are significantly shorter than in the corresponding alkyl complex **4**. The Y–N distance range in alkyl complex **4** is 2.307(3)–2.407(3) Å and only 2.291(2)–2.385(2) Å in chlorido complex **13**.

It is well known that upon sublimation, [Cp$_2$Ln(THF)Cl] complexes lose coordinated THF to form dimeric species with two μ-Cl ligands [(Cp$_2$Ln–Cl)$_2$].[22] A similar behavior is observed in the case of Cp* complexes,[23] yet the [(Cp*$_2$YCl)$_2$] species does exist as an asymmetric dimer with only one μ-Cl ligand.[24] For the smallest among rare-earth metals, scandium, the formation of monomeric [Cp*$_2$ScCl] was described.[25] The fact that we isolated ether-free penta-coordinate corresponding [(NPN$^{t\mathrm{Bu}}$)$_2$LnCl] complexes from a solution containing the probe ligands – diethyl ether and THF – indicates the very strong donor character of this NPN$^{t\mathrm{Bu}}$ ligand. Despite its different steric shielding, the title ligand electron donating ability is probably best compared to (or even higher than) the most prominent ligand in lanthanocene chemistry [C$_5$Me$_5$, Cp*].

The strong similarity between the N–P bond lengths in alkyl complexes (Δ = 0.005(3) Å for **4**, Δ = 0.004(3) Å for **6** and Δ = 0.007(4) Å for **7**) indicates perfect electron delocalization within the N–P–N ligand fragment. Yet, in chlorido complexes these differences are significantly larger (Δ = 0.023(2) Å for **13**, Δ = 0.019(4) Å for **19**), indicating less pronounced delocalization.

In all complexes, N–Ln–N bond angles within each pair of coordinated NPN ligands differ insignificantly and are in a similar range to other structurally characterised complexes.[6a,b]

Our attempt to obtain suitable single crystals of scandium derivative **12** by crystallisation from the C$_6$D$_6$ solution in the NMR tube at room temperature resulted in the determination of the molecular structure of a new trinuclear complex [{(NPN$^{t\mathrm{Bu}}$)Sc(μ$_2$-Cl)}$_3$(μ$_3$-O)(μ$_3$-Cl)] **20** (Fig. 3) as the product of partial hydrolysis of **12** by water traces. One NPN$^{t\mathrm{Bu}}$ ligand per scandium summing up to three negative charges per trinuclear unit are replaced by three negative charges of capping oxido and chlorido ligands.

Complex **20** crystallises in the triclinic space group $P\bar{1}$ with two formula units and six benzene molecules incorporated per unit cell. A representative set of bond lengths (Å) and angles (°) for complex **20** is given in Table 2.

Trinuclear rare-earth metal complexes with a similar μ$_3$-O capping structural motif have been described in the literature. Examples are shown in Chart 3.[26]

Table 1 Selected bond lengths (Å) and angles (°) of complexes **4**, **6**, **7**, **13** and **19**

	4 (Y)	**6** (Nd)	**7** (Sm)	**13** (Y)	**19** (Lu)		**4** (Y)	**6** (Nd)	**7** (Sm)	**13** (Y)	**19** (Lu)
Ln–N1	2.350(3)	2.501(3)	2.476(3)	2.348(2)	2.245(4)	N1–P1–N2	101.1(1)	100.8(2)	100.9(2)	100.1 (1)	100.2(2)
Ln–N2	2.388(3)	2.400(3)	2.370(3)	2.291(2)	2.305(4)	N3–P2–N4	100.6(1)	101.6(2)	101.2(2)	100.7 (1)	100.1(2)
Ln–N3	2.307(3)	2.458(3)	2.458(3)	2.385(2)	2.274(4)	N1–Ln–N3	113.3(1)	110.8(1)	171.6(1)	174.9 (1)	111.7(1)
Ln–N4	2.407(3)	2.485(3)	2.416(3)	2.319(2)	2.333(4)	N2–Ln–N4	172.2(1)	119.5(1)	113.5(1)	111.6(1)	175.5(1)
P1–N1	1.612(3)	1.608(3)	1.600(3)	1.598(2)	1.629(4)	N1–Ln–N2	63.3(1)	60.7(1)	61.2(1)	64.2(1)	66.2(1)
P1–N2	1.608(3)	1.610(3)	1.603(3)	1.619(2)	1.610(4)	C41–Ln–N4	91.4(1)	96.4(1)	135.0(1)	—	—
P2–N3	1.612(3)	1.609(3)	1.607(4)	1.607(3)	1.624(4)	C41–Ln–N2	95.5(1)	111.2(1)	111.5(1)	—	—
P2–N4	1.607(3)	1.606(3)	1.607(3)	1.621(2)	1.617(4)	Cl–Ln–N4	—	—	—	135.8(1)	92.7(1)
Ln–C41	2.438(3)	2.511(4)	2.471(5)	—	—	Cl–Ln–N1	—	—	—	91.6(1)	113.3(1)
Ln–Cl	—	—	—	2.575(1)	2.529(2)	Ln–C41–Si	133.7(2)	133.2(2)	134.3(2)	—	—

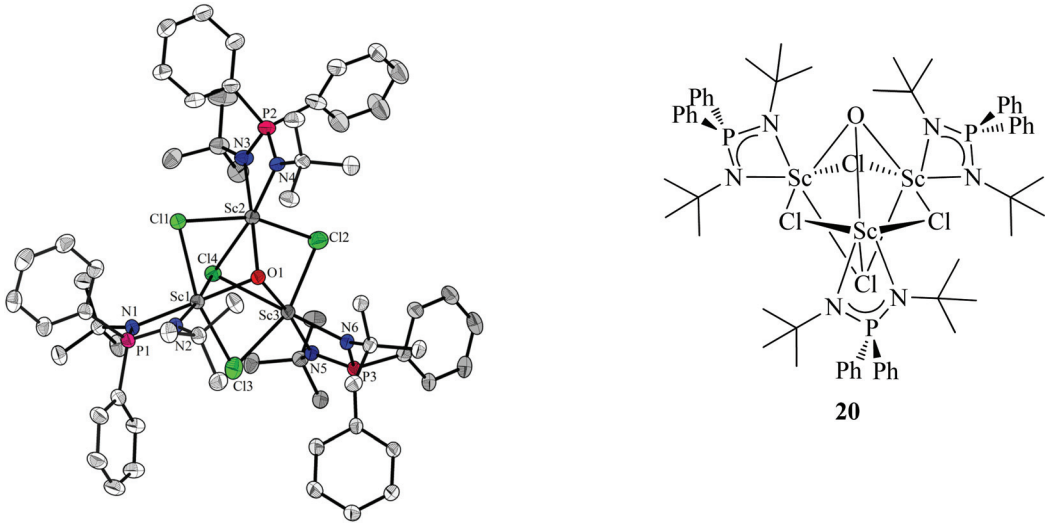


Fig. 3 Molecular structure (left) and valence-bond formula (right) of compound **20**. Hydrogen atoms and the solvent molecules are omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) of complex **20**

20			
Sc1–N1	2.177(3)	N1–Sc1–N2	69.7(1)
Sc1–N2	2.106(3)	Cl1–Sc1–Cl3	160.0(1)
Sc1–O1	2.032(3)	O1–Sc1–Cl4	72.2(1)
Sc3-O1	2.024(2)	N2–Sc1–Cl4	170.8(1)
Sc1–Cl3	2.491(2)	N1–Sc1–O1	173.2(1)
Sc1–Cl1	2.560(1)	N2–Sc1–Cl1	100.2(1)
Sc1–Cl4	2.761(1)	N2–Sc1–Cl3	98.4(1)
Sc1–Sc2	3.200(1)	Sc1–Cl4–Sc3	69.8(1)
P1–N1	1.606(3)	Sc1–Cl1–Sc3	79.7(1)
P1–N2	1.619(4)	Sc1–O1–Sc3	104.2(1)

The basic framework of this structure is formed by the three scandium atoms that are, above and below, capped *via* μ_3-O and μ_3-Cl atoms. The other three chlorido atoms are μ_2-bridging the edges of the Sc_3-triangle so that a highly distorted six-membered ring is formed (Fig. 3, left). Thus, the shortest Sc–μ_3-Cl distance (2.717(1) Å) is even longer than the longest Sc–μ_2-Cl one (2.565(1) Å). The Sc–Cl bond distances are similar to those of other scandium complexes, bearing μ_2-Cl atoms, *e.g.* in $[\{N(SiMe_2H)_2\}_2Sc(\mu_2\text{-}Cl)(THF)]_2$ *d*(Sc–Cl) = 2.559 Å (ref. 27) and in $[Cp_2Sc(\mu_2\text{-}Cl)]_2$ *d*(Sc–Cl) = 2.573 Å.[28] No crystallographically characterised molecular scandium compound with a μ_3-Cl motif is known to date. The Sc–O distance lies in the range of 2.024(2)–2.034(3) Å and is significantly shorter than that in **XIV** (2.066 Å). Due to the shorter Sc–μ_3-O distances compared to Sc–μ_3-Cl distances, the corresponding Sc–(μ_3-Cl)–Sc angles (69.8(1)–72.4(1)°) become smaller than the Sc–(μ_3-O)–Sc ones (104.2(1)–105.4(1)°).

Conclusions

So far iminophosphonamido complexes of the rare-earth metals have been limited to derivatives with two electron withdrawing *N*-silyl or *N*-aryl substituents; no such *N*,*N*′-dialkyl derivatives have been studied in detail. The relative stability of *tert*-butyl azide used in Staudinger type ligand synthesis prompted us to investigate bis-*tert*-butyl derivatives NPN^{tBu} and their potential to act as easily accessible, crystalline and sterically most demanding ligands with so far the highest NPN donor strength within this class of complexes. We are con-

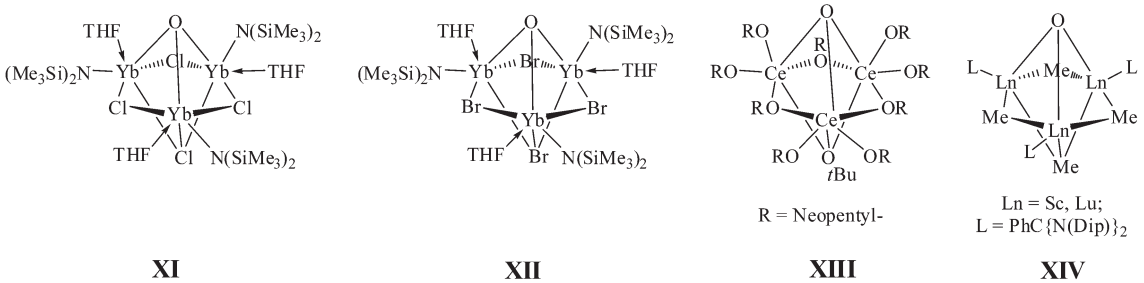


Chart 3 Examples of trinuclear rare-earth metal complexes (**XI**,[26a] **XII**,[26b] **XIII**,[26c] **XIV**[26d]).

vinced that the prominent donor strength, the steric demand as well as the favourable solubility and NMR spectroscopic features make these post-metallocene complexes [$(NPN^{tBu})_2$Ln–X] building blocks as useful as the lanthanocenes [$(C_5Me_5)_2$Ln–X] in their further exploration.

Experimental part

General remarks

All syntheses were performed using Schlenk equipment under argon (grade 5.0) that was additionally freed of oxygen traces at an Al_2O_3/Na SOLVONA column and dried of water traces at a P_4O_{10} column. Weighing and sample preparation for analytical characterization, as well as materials storage, were performed in a glove box under an atmosphere of dry nitrogen. Drying of the solvents and reagents used was carried out by general methods under an inert atmosphere. The solvents were, after drying, stored in absorption columns over BASF alumina molecular sieve 3 Å/R3-11G catalyst. The solvent and all the chemicals used in the syntheses were, unless mentioned separately, purchased from Fluka, Aldrich, Acros, Sigma or Merck. Rare-earth metal salts or the corresponding oxides were purchased from Chempur. The following starting materials were synthesized by literature methods: $tBuN_3$,[29] [$LnCl_3(THF)_n$] (Ln = Sc, Y, Nd and Sm) and [$LnCl_3$] (Ln = Gd, Tb, Yb and Lu),[30] [$Ln(CH_2SiMe_3)_3(THF)_2$]: Ln = Sc,[31] Lu[32] and [$Y(CH_2SiMe_3)_3(THF)_3$].[33] The concentrations of the solutions used by organolithium and Grignard reagents were determined by titration with *sec*-butanol and 1,10-phenanthroline as indicators. Because of the strong paramagnetic behaviour, measuring ^{13}C NMR spectra of **6**, **7**, and **14–18** and ^{1}H NMR spectra of **16** and **18** did not make sense. Additional metal titration (with Xylenol orange as an indicator) for **16–19** was fulfilled.

Synthesis of $Ph_2P(=N\text{-}tBu)(NH\text{-}tBu)$ (1). For working with gram quantities of $tBuN_3$ an extra safety shield is recommended. Despite its relatively high stability compared to highly explosive primary and secondary alkyl azides, only glass and plastic needles were used.

To an ice-cooled solution of dry $tBuNH_2$ (13.1 mL, 125 mmol, 2.5 eq.) in dry CH_2Cl_2 (200 mL), under vigorous stirring and argon overflow, a solution of Ph_2PCl (9 mL, 50 mmol, 1.0 eq.) in dry CH_2Cl_2 (50 mL) was added dropwise and then allowed to warm up to ambient temperature. After stirring for 4 h the reaction solvent with excess $tBuNH_2$ was removed and an oily residue was extracted with dry toluene (300 mL) followed by filtration of $tBuNH_3Cl$ salt precipitate (D4), solvent removal and drying under high vacuum to obtain crude $Ph_2PNHtBu$ as a light-coloured viscous oil, which was purified by quick bulb-to-bulb distillation under dynamic high vacuum giving a pure semi-product $Ph_2PNHtBu$ (9 g, 35 mmol) in 70% yield. The latter was dissolved in THF (100 mL) followed by the addition of $tBuN_3$ (5 g, 50 mmol, 1.5 eq.) at ambient temperature and allowed to stir overnight. The next day, the formation of a fine, voluminous solid was observed. The reaction mixture was heated to reflux under stirring whereupon the precipitate goes into solution with gas evolution. Once, after about 4 h the latter ceased, the reaction mixture was cooled and the solvent was removed under high vacuum (**Caution!** Thus-removed solvent still contains some $tBuN_3$. For its decomposition it should be treated with triethylphosphite before disposal). The solid was suspended in 100 ml of *n*-hexane, the solution was decanted and the solid was dried under high vacuum to give 9.7 g of **1** as a white solid in 85% (overall ~60%) yield. **1** was sparingly soluble in *n*-pentane and *n*-hexane, but soluble in benzene, toluene and ethers.

CHN: ($C_{20}H_{29}N_2P$, M_W: 328.43): found (calcd): C: 73.01% (73.14%), H: 9.02% (8.90%), N: 8.39% (8.53%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = 1.35 (br s, 18H, *t*Bu*H*), 2.53 (br s, 1H, N*H*), 7.06–7.11 (m, 6H, *m*-/*p*-Ph*H*), 7.83–7.90 (m, 4H, *o*-Ph*H*) ppm.

^{13}C NMR (75.5 MHz, C_6D_6): δ = 33.9 (br s, *t*BuC_{Me}), 51.8 (d, $^2J_{CP}$ = 3.7 Hz, *t*BuC_q), 127.9 (d, overlapped with residual C_6D_6 signal, *p*-Ph*C*), 133.0 (d, $^3J_{CP}$ = 2.7 Hz, *m*-Ph*C*), 132.5 (d, $^2J_{CP}$ = 9.4 Hz, *o*-Ph*C*), 139.4 (d, $^1J_{CP}$ = 125.3 Hz, *ipso*-Ph*C*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): δ = −21.9 (s) ppm.

General synthetic protocols of rare-earth metal NPN-alkyl complexes.

A1: [$Ln(CH_2SiMe_3)_3(THF)_n$] (0.5 mmol, 1 eq.) was dissolved in *n*-hexane (10 mL). A pre-cooled 0 °C solution of **1** (0.5 mmol, 1.0 eq. or 1.0 mmol, 2 eq.) in diethyl ether (10 mL) was slowly added dropwise at 0 °C and stirred for 2.5 h.

A2: [$LnCl_3(THF)_n$] (0.5 mmol, 1 eq.) was suspended in *n*-hexane (10 mL), cooled to 0 °C followed by dropwise addition of $LiCH_2SiMe_3$ (1.5 mmol, 3 eq.) solution in *n*-hexane (3 mL) *via* a syringe. After stirring for 3 h at 0 °C a solution of **1** (0.5 mmol, 1.0 eq. or 1.0 mmol, 2 eq.) in diethyl ether (20 mL) was slowly added. After stirring for 2.5 h the reaction mixture was concentrated to one-half, treated with 10 mL of *n*-pentane and filtered through Celite®. The work-up was carried out differently and is additionally detailed below for each case. The solids are moderately soluble in *n*-hexane, but soluble in benzene, toluene and ethers.

Synthesis of [$(NPN^{tBu})Sc(CH_2SiMe_3)_2$] (2). According to **A1**: from [$Sc(CH_2SiMe_3)_3(THF)_2$] (225 mg, 0.50 mmol, 1 eq.) with **1** (164 mg, 0.50 mmol, 1 eq.).

According to **A2**: from [$ScCl_3(THF)_3$] (186 mg, 0.50 mmol, 1 eq.) with $LiCH_2SiMe_3$ (140 mg, 1.49 mmol, 2.98 eq.) and **1** (163 mg, 0.49 mmol, 0.99 eq.).

Work-up is the same for **A1** and **A2**: thus-obtained solution was concentrated under high vacuum to a volume of *ca.* 1.5–2 mL and allowed to crystallise overnight at −30 °C, the supernatant in the cold was decanted and the residue was dried under high vacuum to give **2** as a colourless, powdery solid. Yields: (**A1**) 219 mg (80%), (**A2**) 190 mg (70%).

CHN: ($C_{28}H_{50}N_2PScSi_2$, M_W: 546.81): found (calcd): C: 60.49% (61.50%), H: 9.01% (9.22%), N: 5.14% (5.12%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = 0.25 (s, 4H, Sc–CH_2), 0.45 (s, 18H, SiMe_3), 1.11 (d, $^4J_{HP}$ = 1.2 Hz, 18H, *t*Bu*H*), 7.05–7.08 (m, 6H, *m*-/*p*-Ph*H*), 7.84–7.91 (m, 4H, *o*-Ph*H*) ppm.

^{13}C NMR (75.5 MHz, C_6D_6): δ = 4.2 (s, Si*Me*$_3$), 34.3 (d, $^3J_{CP}$ = 8.1 Hz, *t*Bu*C*$_{Me}$), 39.7 (br s, Sc–*C*H$_2$), 54.3 (d, $^2J_{CP}$ = 1.6 Hz, *t*Bu*C*$_q$), 128.5 (d, overlapped with residual C_6D_6 signal, *p*-Ph*C*), 131.9 (d, $^3J_{CP}$ = 2.9 Hz, *m*–Ph*C*), 133.1 (d, $^1J_{CP}$ = 90.1 Hz, *ipso*-Ph*C*), 133.3 (d, $^2J_{CP}$ = 10.5 Hz, *o*-Ph*C*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): δ = 12.2 (s) ppm.

IR: $\tilde{\nu}$ = 432 (s), 532 (s), 553 (s), 607 (s), 618 (s), 678 (s), 698 (s), 718 (s), 743 (s), 772 (s), 834 (s), 1027 (s), 1089 (s), 1109 (s), 1195 (s), 1217 (s), 1237 (m), 1251 (m), 1311 (w), 1360 (s), 1387 (m), 1436 (m), 1465 (w), 1483 (w), 2801 (w), 2859 (m), 2894 (m), 2945 (s), 3055 (w), 3076 (w) cm^{-1}.

Synthesis of [(NPN^{tBu})Y(CH$_2$SiMe$_3$)$_2$(THF)] (3). According to **A1**: from [Y(CH$_2$SiMe$_3$)$_3$(THF)$_3$] (283 mg, 0.5 mmol, 1 eq.) with **1** (164 mg, 0.5 mmol, 1 eq.). Work-up: the solvent was completely removed under high vacuum. The colourless residue was treated with *n*-hexane (3 mL), crystallised at −30 °C overnight and the solution was decanted in the cold. The solid was washed with pre-cooled *n*-hexane at −30 °C (5 mL) and dried under high vacuum to give **3** as a colourless solid. Yield: 97 mg (29%).

CHN: ($C_{32}H_{58}N_2OPSi_2Y$, M_W: 662.87): found (calcd): C: 53.68% (57.98%), H: 8.36% (8.82%), N: 4.34% (4.23%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = −0.26 (d, $^2J_{HY}$ = 3.0 Hz, 4H, Y–C*H*$_2$), 0.45 (s, 18H, Si*Me*$_3$), 1.12 (d, $^4J_{HP}$ = 0.9 Hz, 18H, *t*Bu*H*), 1.32–1.36 (br m, 4H, thf-C*H*$_2$), 3.90–3.95 (br m, 4H, thf-OC*H*$_2$), 7.10–7.23 (m, 6H, *m*-/*p*-Ph*H*), 8.12–8.19 (m, 4H, *o*-Ph*H*) ppm.

^{13}C NMR (1k, 75.5 MHz, C_6D_6): δ = 5.1 (s, Si*Me*$_3$), 25.2 (s, thf-*C*H$_2$), 32.4 (d, $^1J_{CY}$ = 38.7 Hz, Y–*C*H$_2$), 34.9 (d, $^3J_{CP}$ = 8.9 Hz, *t*Bu*C*$_{Me}$), 52.9 (d, $^2J_{CP}$ = 0.9 Hz, *t*Bu*C*$_q$), 70.2 (s, thf-O*C*H$_2$), 128.2 (d, $^4J_{CP}$ = 11.0 Hz, *p*–Ph*C*), 130.8 (d, $^3J_{CP}$ = 2.9 Hz, *m*-Ph*C*), 133.4 (d, $^2J_{CP}$ = 9.7 Hz, *o*-Ph*C*), 137.0 (d, $^1J_{CP}$ = 84.9 Hz, *ipso*–Ph*C*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): δ = 18.1 (s) ppm.

IR: $\tilde{\nu}$ = 497 (s), 530 (s), 597 (s), 672 (s), 698 (s), 712 (s), 743 (s), 762 (s), 833 (s), 1020 (s), 1094 (s), 1193 (s), 1234 (s), 1248 (s), 1312 (w), 1359 (s), 1387 (m), 1436 (s), 1462 (w), 1482 (w), 2898 (m), 2943 (s), 3055 (w) cm^{-1}.

Synthesis of [(NPN^{tBu})$_2$Y(CH$_2$SiMe$_3$)] (4). According to **A1**: from [Y(CH$_2$SiMe$_3$)$_3$(THF)$_3$] (283 mg, 0.5 mmol, 1 eq.) with **1** (328 mg, 1 mmol, 2 eq.).

According to **A2**: from [YCl$_3$(THF)$_{3.5}$] (206 mg, 0.5 mmol, 1 eq.) with LiCH$_2$SiMe$_3$ (141 mg, 1.5 mmol, 3 eq.) and **1** (328 mg, 1 mmol, 2 eq.).

Work-up is the same for **A1** and **A2**: the solvent was removed under high vacuum, the colourless residue was dissolved in *n*-hexane (3 mL) and crystallised at −30 °C overnight and the solution was decanted in the cold. The residue was washed with pre-cooled at −30 °C *n*–hexane (5 mL) and dried under high vacuum to give **4** as a microcrystalline, colourless solid. Single crystals were obtained from a concentrated *n*-pentane solution at −30 °C. Yields: (**A1**) 379 mg (91%), (**A2**) 353 mg (85%).

CHN ($C_{44}H_{67}N_4P_2SiY$, M_W: 830.97): found (calcd): C: 63.33% (63.60%), H: 8.79% (8.13%), N: 6.61% (6.74%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = 0.19 (d, $^2J_{HY}$ = 3.0 Hz, 2H, Y–C*H*$_2$), 0.58 (s, 9H, Si*Me*$_3$), 1.30 (s, 36H, *t*Bu*H*), 7.14–7.24 (m, 12H, *m*-/*p*-Ph*H*), 8.21–8.28 (m, 8H, *o*-Ph*H*) ppm.

^{13}C NMR (75.5 MHz, C_6D_6): δ = 5.7 (s, Si*Me*$_3$), 29.6 (d, $^1J_{CY}$ = 40.4 Hz, Y–*C*H$_2$), 35.6 (d, $^3J_{CP}$ = 9.0 Hz, *t*Bu*C*$_{Me}$), 53.2 (s, *t*Bu*C*$_q$), 128.3 (d, overlapped with residual C_6D_6 signal, *p*-Ph*C*), 130.8 (d, $^3J_{CP}$ = 2.7 Hz, *m*-Ph*C*), 133.8 (d, $^2J_{CP}$ = 9.6 Hz, *o*-Ph*C*), 137.4 (d, $^1J_{CP}$ = 83.5 Hz, *ipso*-Ph*C*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): δ = 19.5 (s) ppm.

IR: $\tilde{\nu}$ = 467 (s), 531 (s), 595 (s), 671 (s), 697 (s), 711 (s), 744 (s), 833 (s), 863 (s), 1026 (s), 1086 (s), 1192 (s), 1226 (m), 1260 (m), 1311 (w), 1359 (m), 1387 (m), 1435 (m), 1462 (w), 1482 (w), 2860 (m), 2955 (m), 3053 (w) cm^{-1}.

Synthesis of [(NPN^{tBu})$_2$Sc(CH$_3$)(THF)] (5). [ScCl$_3$(THF)$_3$] (184 mg, 0.5 mmol, 1 eq.) and **1** (328 mg, 1 mmol, 2 eq.) were dissolved in diethyl ether (15 mL) and cooled to 0 °C and MeLi (0.94 mL as 1.6 M diethyl ether solution, 1.5 mmol, 3 eq.) was added *via* a syringe. After stirring for 1 h at 0 °C the mixture was filtered through Celite®. Upon solvent removal the residue was dried under vacuum, and washed with *n*-pentane (3 mL) to give **5** as a colourless solid. Yield: 233 mg (59%).

CHN: ($C_{45}H_{67}N_4OP_2Sc$, M_W: 786.94): found (calcd): C: 62.96% (68.68%), H: 7.98% (8.58%), N: 6.75% (7.12%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = 0.61 (s, 3H, Sc–C*H*$_3$), 1.37 (s, 40H, *t*Bu*H* + thf-C*H*$_2$), 3.54–3.59 (s, 4H, thf-OC*H*$_2$), 7.15–7.19 (m, 12H, *m*-/*p*-Ph*H*), 8.26–8.34 (m, 8H, *o*-Ph*H*) ppm.

^{13}C NMR (4k, 62.9 MHz, C_6D_6): δ = 22.8 (s, Sc–*C*H$_3$), 25.7 (s, thf-*C*H$_2$), 35.2 (d, $^3J_{CP}$ = 8.7 Hz, *t*Bu*C*$_{Me}$), 53.8 (d, $^2J_{CP}$ = 0.9 Hz, *t*Bu*C*$_q$), 68.0 (s, thf-O*C*H$_2$), 127.9 (d, overlapped with residual C_6D_6 signal, *p*-Ph*C*), 130.8 (d, $^3J_{CP}$ = 2.9 Hz, *m*-Ph*C*), 134.2 (d, $^2J_{CP}$ = 9.7 Hz, *o*-Ph*C*), 137.1 (d, $^1J_{CP}$ = 83.4 Hz, *ipso*-Ph*C*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): δ = 19.6 (s) ppm.

IR: $\tilde{\nu}$ = 407 (s), 433 (s), 466 (s), 531 (s), 598 (s), 619 (w), 672 (s), 697 (s), 712 (s), 744 (s), 759 (s), 833 (s), 914 (w), 998 (m), 1027 (m), 1084 (s), 1192 (s), 1219 (m), 1310 (w), 1357 (m), 1386 (m), 1434 (m), 1459 (w), 1481 (w), 2952 (m), 3053 (w) cm^{-1}.

Synthesis of [(NPN^{tBu})$_2$Nd(CH$_2$SiMe$_3$)] (6). According to **A2**: from [NdCl$_3$THF)$_2$] (197 mg, 0.5 mmol, 1 eq.) with LiCH$_2$SiMe$_3$ (141 mg, 1.5 mmol, 3 eq.) and **1** (328 mg, 1 mmol, 2 eq.). Since the low stability of the Nd tris-alkyl complex is known, the ligand was added already after 1 h. Work-up: the solvent was removed under high vacuum and the residue was washed with cold *n*-pentane (3 mL) to give **6** as a blue solid. Single crystals were obtained from a concentrated *n*-pentane solution at −30 °C. Yield: 93 mg (21%).

CHN: ($C_{44}H_{67}N_4NdP_2Si$, M_W: 886.30): found (calcd): C: 61.30% (59.63%), H: 8.20% (7.62%), N: 6.72% (6.32%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = −7.19 (br s, 36H, *t*Bu*H*), −4.34 (s, 9H, Si*Me*$_3$), 9.84 (t, $^3J_{HH}$ = 6.7 Hz, 4H, *p*-Ph*H*), 10.59 (m, 8H, *m*-Ph*H*), 19.66 (d, $^3J_{HH}$ = 3.8 Hz, 8H, *o*-Ph*H*) ppm. The signal of Nd–CH$_2$ hydrogen atoms could not be clearly identified.

^{31}P NMR (121.5 MHz, C_6D_6): δ = −133.8 (br s) ppm.

Synthesis of [(NPN^{tBu})$_2$Sm(CH$_2$SiMe$_3$)] (7). According to **A2**: from [SmCl$_3$(THF)$_2$] (200 mg, 0.5 mmol, 1 eq.) with LiCH$_2$SiMe$_3$ (141 mg, 1.5 mmol, 3 eq.) and **1** (328 mg, 1 mmol, 2 eq.). Since the low stability of the Sm tris-alkyl complex is known, the ligand was added already after 1 h. Work-up: the solvent was

removed under high vacuum and the residue was washed with cold *n*-pentane (3 mL) to give **7** as a yellow solid. Single crystals were obtained from a concentrated *n*-pentane solution at −30 °C. Yield: 186 mg (42%).

CHN: ($C_{44}H_{67}N_4P_2SiSm$, M_W: 892.42): found (calcd): C: 58.73% (59.22%), H: 7.67% (7.57%), N: 6.02% (6.28%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = −2.68 (s, 36H, *t*Bu*H*), 1.53 (s, 9H, Si*Me*$_3$), 8.02 (br t, $^3J_{HH}$ = 7.3 Hz, 4H, *p*-Ph*H*), 8.27 (br t, $^3J_{HH}$ = 7.3 Hz, 8H, *m*-Ph*H*), 11.79 (d, $^3J_{HH}$ = 6.7 Hz, 8H, *o*-Ph*H*), 15.98 (br s, 2H, Sm–C*H*$_2$) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): δ = 72.4 (br s) ppm.

IR: $\tilde{\nu}$ = 466 (m), 530 (s), 594 (s), 669 (s), 697 (s), 711 (s), 743 (s), 831 (s), 859 (s), 953 (w), 1027 (s), 1092 (s), 1194 (s), 1261 (s), 1310 (s), 1359 (s), 1386 (s), 1434 (s), 1461 (s), 1481 (s), 2860 (s), 2900 (s), 2954 (s), 3053 (s) cm^{-1}.

Synthesis of [(NPN^{tBu})$_2$Y–C≡CPh] (8). To [Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (0.5 mmol, 1 eq.), a solution of **1** (0.5 mmol, 1.0 eq. or 1.0 mmol, 2 eq.) in diethyl ether (10 mL) was slowly added dropwise at 0 °C and stirred for 2.5 h. [Y(CH$_2$SiMe$_3$)$_3$(THF)$_3$] (283 mg, 0.5 mmol, 1 eq.) was suspended in *n*-pentane (10 mL) at 0 °C followed by the addition of **1** (328 mg, 1 mmol, 2 eq.) as a solution in diethyl ether (5 mL).

The reaction mixture was stirred at 0 °C for 3 h. Subsequently, phenylacetylene (54.9 μL, 0.5 mmol, 1 eq.) was added *via* a syringe at 0 °C. The solution turned yellow and after 1 h at 0 °C was allowed to stand overnight at −30 °C for crystallisation. After decanting, the product was washed with pre-cooled *n*-pentane (2 × 4 mL). Drying in a high vacuum gave **8** as a colourless, powdery solid. Yield: 330 mg (78%).

CHN: ($C_{48}H_{61}N_4P_2Y$, M_W: 844.34): found (calcd): C: 68.24% (67.57%), H: 7.28% (7.53%), N: 6.63% (5.78%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = 1.40 (s, 36H, C(C*H*$_3$)$_3$), 7.00–7.13 (m, 12H, *m*-/*p*-Ph*H* and *m*-/*p*-Ph*H*-Alkynyl), 7.77 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, *o*-Ph*H*-Alkynyl), 8.26–8.33 (m, 8H, *o*-Ph*H*) ppm.

^{13}C NMR (4k, 62.9 MHz, C_6D_6): δ = 35.2 (d, $^3J_{CP}$ = 8.8 Hz, *t*BuC_{Me}), 53.4 (d, $^2J_{CP}$ = 1.2 Hz, *t*BuC_q), 108.2 (s, *ipso*-Ph*C*-Alkynyl), 125.8 (s, *p*-Ph*C*-Alkynyl), 127.9 (s, *m*-Ph*C*-Alkynyl), 128.4 (d, $^4J_{CP}$ = 16.6 Hz, *p*–Ph*C*), 130.0 (d, $^2J_{CY}$ = 36.2 Hz, Ph*C*≡CY), 130.8 (d, $^3J_{CP}$ = 2.8 Hz, *m*-Ph*C*), 132.6 (s, *o*-Ph*C*-Alkynyl), 133.8 (d, $^2J_{CP}$ = 9.9 Hz, *o*-Ph*C*), 136.9 (d, $^1J_{CP}$ = 84.0 Hz, *ipso*-Ph*C*) ppm. No signal of the PhC≡*C*Y can be observed.

^{31}P NMR (121.5 MHz, C_6D_6): δ = 17.8 (s) ppm.

IR: $\tilde{\nu}$ = 2959 (w), 1483 (w), 1435 (w), 1358 (m), 1192 (m), 1089 (m), 832 (m), 823 (s), 745 (s), 729 (s), 714 (s), 698 (s), 672 (m), 598 (m), 530 (s) cm^{-1}.

General protocol of reactions of alkyl complexes with [PhNMe$_2$H]$^+$[B(C$_6$F$_5$)$_4$]$^-$

A3: In the glove box a solution of [PhNHMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (~50 μmol, 1.00 eq.) in 0.1 mL C_6D_6 and 0.1 mL of THF-d^8 was added dropwise *via* a syringe to a solution of rare-earth metal NPN alkyl complexes (~50 μmol, 1 eq.) in 0.3 mL of C_6D_6. The reaction solution was transferred to a NMR tube, the reaction vessel was rinsed with 0.2 mL C_6D_6, combined with the thus transferred reaction solution and then analyzed by NMR spectroscopy.

Synthesis of [(NPN^{tBu})Sc(CH$_2$SiMe$_3$)(THF)$_n$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (9). According to **A3:** from **2** (30.73 mg 56.2 μmol, 1.00 eq.) with [PhNHMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (44.06 mg, 55.0 μmol, 0.98 eq.).

^{1}H NMR (400.0 MHz, C_6D_6/THF-d_8, 6 : 1): δ = 0.00 (s, 12H, Si*Me*$_4$), 0.17 (s, 9H, Si*Me*$_3$), 0.23 (s, 2H, Sc–C*H*$_2$), 0.89 (s, 18H, *t*Bu*H*), 2.63 (s, 6H, aniline-*Me*$_2$), 6.64 (d, $^3J_{HH}$ = 8.2 Hz, 2H, aniline-*m*-Ph*H*), 6.72 (t, $^3J_{HH}$ = 7.1 Hz, 1H, aniline-*p*-Ph*H*), 7.18 (d, overlapping with residual C_6D_6 signal, 2H, aniline-*o*–Ph*H*), 7.32–7.37 (m, 6H, *o*-/*p*-Ph*H*), 7.86–7.91 (m, 4H, *m*–Ph*H*) ppm.

^{13}C NMR (100.6 MHz, C_6D_6/THF-d_8, 6 : 1): δ = −0.1 (s, Si*Me*$_4$), 3.7 (s, Si*Me*$_3$), 33.8 (d, $^3J_{CP}$ = 7.9 Hz, *t*BuC_{Me}), 40.2 (s, aniline-*Me*$_2$), 47.5 (br s, Sc–*C*H$_2$), 55.0 (d, $^2J_{CP}$ = 1.10 Hz, *t*BuC_q), 113.0 (s, aniline-*m*-Ph*C*), 116.9 (s, aniline-*p*-Ph*C*), 125.2 (br m, *ipso*–C_6F_5), 128.9 (d, $^4J_{CP}$ = 11.7 Hz, *p*-Ph*C*), 129.3 (s, aniline-*o*–Ph*C*), 132.2 (d, $^1J_{CP}$ = 89.5 Hz, *ipso*–Ph*C*), 132.8 (d, $^3J_{CP}$ = 2.8 Hz, *m*-Ph*C*), 133.5 (d, $^2J_{CP}$ = 10.3 Hz, *o*-Ph*C*), 137.1 (dm, $^1J_{CF}$ = 247.8 Hz, *m*–C_6F_5), 139.0 (dm, $^1J_{CF}$ = 244.7 Hz, *p*–C_6F_5), 149.15 (dm, $^1J_{CF}$ = 241.1 Hz, *o*–C_6F_5), 151.1 (s, aniline–*ipso*–Ph*C*) ppm.

^{31}P NMR (161.9 MHz, C_6D_6/THF-d_8, 6 : 1): δ = 22.3 (s) ppm.

^{19}F NMR (376.3 MHz, C_6D_6/THF-d_8, 6 : 1): δ = −166.7 (br s, 8F, *m*-Ph*F*), −163.0 (t, $^3J_{FF}$ = 20.5 Hz, 4F, *p*-Ph*F*), −131.8 (br s, 8F, *o*-Ph*F*) ppm.

^{11}B NMR (128.3 MHz, C_6D_6/THF-d_8, 6 : 1): δ = −16.3 (s) ppm.

Synthesis of [(NPN^{tBu})Y(CH$_2$SiMe$_3$)(THF)$_n$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (10). According to **A3:** from **3** (36.370 mg, 54.9 μmol, 1.00 eq.) with [PhNHMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (43.949 mg 54.9 μmol, 1.00 eq.).

^{1}H NMR (300.1 MHz, C_6D_6/THF-d_8, 6 : 1): δ = −0.49 (d, $^2J_{HY}$ = 3.3 Hz, 2H, Y–C*H*$_2$), 0.00 (s, 12H, Si*Me*$_4$), 0.19 (s, 9H, Si*Me*$_3$), 0.96 (d, $^4J_{HP}$ = 0.7 Hz, 18H, *t*Bu*H*), 2.66 (s, 6H, aniline-*Me*$_2$), 6.64 (d, $^3J_{HH}$ = 8.5 Hz, 2H, aniline-*m*-Ph*H*), 6.70 (t, $^3J_{HH}$ = 7.3 Hz, 1H, aniline-*p*-Ph*H*), 7.15–7.21 (overlapping with residual C_6D_6 signal, 2H, aniline-*o*-Ph*H*), 7.27–7.39 (m, 6H, *m*-/*p*-Ph*H*), 7.88–8.00 (m, 4H, *o*-Ph*H*) ppm.

^{13}C NMR (62.9 MHz, C_6D_6/THF-d_8, 6 : 1): δ = 0.0 (s, Si*Me*$_4$), 4.6 (s, Si*Me*$_3$), 34.4 (d, $^1J_{CY}$ = 42.3 Hz, Y–*C*H$_2$), 34.6 (d, $^3J_{CP}$ = 8.6 Hz, *t*BuC_{Me}), 40.4 (s, aniline-*Me*$_2$), 53.5 (s, *t*BuC_q), 113.1 (s, aniline-*m*-Ph*C*), 117.0 (s, aniline-*p*-Ph*C*), 125.2 (br m, *ipso*–C_6F_5), 128.4 (d, $^4J_{CP}$ = 11.4 Hz, *p*-Ph*C*), 129.4 (s, aniline-*o*–Ph*C*), 132.1 (d, $^3J_{CP}$ = 2.8 Hz, *m*-Ph*C*), 134.0 (d, $^2J_{CP}$ = 10.1 Hz, *o*-Ph*C*), 135.0 (d, $^1J_{CP}$ = 86.8 Hz, *ipso*-Ph*C*), 137.1 (dm, $^1J_{CF}$ = 248.3 Hz, *m*–C_6F_5), 139.0 (dm, $^1J_{CF}$ = 245.8 Hz, *p*-C_6F_5), 149.2 (dm, $^1J_{CF}$ = 239.8 Hz, *o*–C_6F_5), 151.3 (s, aniline–*ipso*–Ph*C*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6/THF-d_8, 6 : 1): δ = 22.8 (s) ppm.

^{19}F NMR (376.3 MHz, C_6D_6/THF-d_8, 6 : 1): δ = −167.4 (br m, 8F, *m*-Ph*F*), −163.6 (br m, 4F, *p*-Ph*F*), −132.3 (br s, 8F, *o*-Ph*F*) ppm.

^{11}B NMR (128.3 MHz, C_6D_6/THF-d_8, 6 : 1): δ = −16.3 (s) ppm.

Synthesis of [(NPN^{tBu})$_2$Y(THF)$_n$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (11). According to **A3:** from **4** (16.71 mg, 20.1 μmol, 1 eq.) with [PhNHMe$_2$]$^+$-[B(C$_6$F$_5$)$_4$]$^-$ (16.60 mg, 20.7 μmol, 1 eq.).

^{1}H NMR (400.0 MHz, C_6D_6/THF-d_8, 6 : 1): δ = 0.00 (s, 12H, Si*Me*$_4$), 1.02 (s, 36H, *t*Bu*H*), 2.62 (s, 6H, aniline-*Me*$_2$), 6.64 (d, $^3J_{HH}$ = 8.3 Hz, 2H, aniline-*m*-Ph*H*), 6.73 (t, $^3J_{HH}$ = 7.3 Hz, 1H, aniline-*p*-Ph*H*), 7.19–7.21 (overlapping with residual C_6D_6

signal, 2H, aniline-*o*–Ph*H*), 7.29–7.32 (m, 8H, *m*-Ph*H*), 7.34–7.36 (m, 4H, *p*-Ph*H*), 7.90–7.94 (m, 8H, *o*-Ph*H*) ppm.

^{13}C NMR (100.6 MHz, C_6D_6/THF-d_8, 6 : 1): δ = −0.1 (s, Si*Me*$_4$), 35.0 (d, $^3J_{CP}$ = 8.5 Hz, *t*Bu*C*$_{Me}$), 40.2 (s, aniline-*Me*$_2$), 53.9 (d, $^2J_{CP}$ = 1.8 Hz, *t*Bu*C*$_q$), 113.0 (s, aniline-*m*-Ph*C*), 116.9 (s, aniline-*p*-Ph*C*), 128.7 (d, $^4J_{CP}$ = 11.4 Hz, *p*-Ph*C*), 129.3 (s, aniline-*o*–Ph*C*), 132.4 (d, $^4J_{CP}$ = 5.3 Hz, *m*-Ph*C*), 133.6 (d, $^2J_{CP}$ = 10.1 Hz, *o*-Ph*C*), 150.1 (s, aniline–*ipso*–Ph*C*) ppm. No signals of C_6F_5-groups and of *ipso*–Ph*C* are observed.

^{31}P NMR (161.9 MHz, C_6D_6/THF-d_8, 6 : 1): δ = 23.5 (s) ppm.

^{19}F NMR (376.3 MHz, C_6D_6/THF-d_8, 6 : 1): δ = −167.2 (t, $^3J_{FF}$ = 17.8 Hz, 8F, *m*-Ph*F*), −163.5 (t, $^3J_{FF}$ = 20.7 Hz, 4F, *p*-Ph*F*), −132.1 (d, $^3J_{FF}$ = 10.4 Hz, 8F, *o*-Ph*F*) ppm.

^{11}B NMR (128.3 MHz, C_6D_6/THF-d_8, 6 : 1): δ = −16.3 (s) ppm.

General synthetic protocol of rare-earth metal bis-NPN-chlorido complexes

A4: For $[ScCl_3(THF)_3]$, $[YCl_3(THF)_{3.5}]$, $[NdCl_3(THF)_2]$ and $[SmCl_3(THF)_2]$ simple suspensions of 0.50 mmol, 1 eq. in *n*-hexane (10 mL) were used. For anhydrous $[LnCl_3]$: Ln = Gd, Tb, Yb, Lu (0.50 mmol, 1 eq.), stirring with 20% THF in *n*-hexane (20 mL) overnight was used instead, followed by solvent removal and suspending the residue in *n*-hexane (10 mL). To the thus obtained $[LnCl_3(THF)_n]$ suspensions kept at 0 °C a solution of $LiCH_2SiMe_3$ (141 mg, 1.5 mmol, 3 eq.) in *n*-hexane (10 mL) was added dropwise *via* a syringe. After 3 hours (Sc, Y, Gd, Lu) or 1 h (Nd, Sm, Tb, Yb) stirring at 0 °C, assuming approx. 80% yield of tris-alkyl species, a solution of **1** (262 mg, 0.8 mmol, 2 eq.) in diethyl ether (10 mL) was added *via* a syringe. After stirring for 2.5 h the reaction mixture was concentrated to one-half its initial volume, treated with *n*-pentane (10 mL), filtered through Celite® and washed with *n*-pentane (10 mL). The solvent was removed under vacuum and the residue was extracted with *n*–pentane (20 mL) and treated with freshly dried over basic Al_2O_3 chloroform (0.5 mL) and stirred overnight. Fine microcrystalline solids formed. The solvent was decanted and the solid was washed with 5 ml of *n*–pentane and dried under high vacuum. The solids are nearly insoluble in *n*–pentane, sparingly soluble in hot *n*-hexane, and soluble in benzene, toluene and ethers. Yields are calculated assuming the fact that only 80% (*i.e.* 0.4 mmol) of tris-alkyl species took part in the reaction with **1**.

Synthesis of [(NPN^{tBu})$_2$Sc–Cl] (12). According to **A4**: from 184 mg of $[ScCl_3(THF)_3]$ as a light-brown solid.

Yield: 97 mg (33%).

CHNCl: ($C_{40}H_{56}ClN_4P_2Sc$, M_W: 735.26): found (calcd): C: 63.32% (65.34%), H: 7.86% (7.68%), N: 7.33% (7.62%), Cl: 5.82% (4.82%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = 1.41 (s, 36H, *t*Bu*H*), 7.14–7.19 (m, 12H, *m*-/*p*-Ph*H*), 8.30–8.36 (m, 8H, *o*-Ph*H*) ppm.

^{13}C NMR (75.5 MHz, C_6D_6): δ = 34.9 (d, $^3J_{CP}$ = 8.4 Hz, *t*Bu*C*$_{Me}$), 54.5 (d, $^2J_{CP}$ = 1.2 Hz, *t*BuC_q), 128.0 (d, overlapped with residual C_6D_6 signal, *p*-Ph*C*), 131.1 (d, $^3J_{CP}$ = 2.8 Hz, *m*-Ph*C*), 134.4 (d, $^2J_{CP}$ = 10.0 Hz, *o*-Ph*C*), 135.8 (d, $^1J_{CP}$ = 85.0 Hz, *ipso*-Ph*C*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): δ = 19.6 (s) ppm.

IR: $\tilde{\nu}$ = 414 (s), 469 (s), 533 (s), 600 (s), 672 (s), 699 (s), 713 (s), 745 (s), 761 (s), 834 (s), 998 (m), 1029 (s), 1068 (s), 1104 (s), 1190 (s), 1217 (m), 1358 (m), 1386 (m), 1435 (m), 1470 (w), 1482 (w), 2861 (m), 2899 (m), 2952 (m), 3052 (w) cm^{-1}.

Synthesis of [(NPN^{tBu})$_2$Y–Cl] (13). According to **A4**: from 224 mg of $[YCl_3(thf)_{3.5}]$ as a light-brown solid. Yield: 150 mg (48%).

CHNCl: ($C_{40}H_{56}ClN_4P_2Y$, M_W: 779.21): found (calcd): C: 59.44% (61.66%), H: 7.33% (7.24%), N: 6.74% (7.19%), Cl: 4.93% (4.55%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = 1.34 (s, 36H, *t*Bu*H*), 7.14–7.20 (m, 12H, *m*-/*p*-Ph*H*), 8.22–8.29 (m, 8H, *o*-Ph*H*) ppm.

^{13}C NMR (75.5 MHz, C_6D_6): δ = 35.1 (d, $^3J_{CP}$ = 8.7 Hz, *t*Bu*C*$_{Me}$), 53.4 (s, *t*BuC_q), 128.3 (d, overlapped with residual C_6D_6 signal, *p*-Ph*C*), 130.9 (d, $^3J_{CP}$ = 2.7 Hz, *m*-Ph*C*), 133.7 (d, $^2J_{CP}$ = 9.8 Hz, *o*-Ph*C*), 136.6 (d, $^1J_{CP}$ = 84.8 Hz, *ipso*-Ph*C*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): δ = 18.5 (s) ppm.

IR-Spektroskopie: $\tilde{\nu}$ = 467 (s), 531 (s), 597 (s), 672 (s), 697 (s), 713 (s), 745 (s), 758 (s), 832 (s), 890 (w), 997 (m), 1027 (m), 1082 (s), 1103 (s), 1192 (s), 1216 (m), 1359 (m), 1386 (m), 1434 (m), 1468 (w), 1482 (w), 2860 (m), 2899 (m), 2950 (m), 3052 (w) cm^{-1}.

Synthesis of [(NPN^{tBu})$_2$Nd–Cl] (14). According to **A4**: from 197 mg of $[NdCl_3(thf)_2]$ as a light-blue solid. Yield: 134 mg (40%).

CHNCl: ($C_{40}H_{56}ClN_4P_2Nd$, M_W: 834.54): found (calcd): C: 55.01% (57.57%), H: 7.13% (6.76%), N: 6.20% (6.71%), Cl: 4.61% (4.25%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = −6.40 (s br s, 36H, *t*Bu*H*), 10.21 (br s, 4H, *p*-Ph*H*), 10.91 (br s, 8H, *m*–Ph*H*), 22.92 (s br s, 8H, *o*-Ph*H*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): δ = −113.9 (br s) ppm.

IR: $\tilde{\nu}$ = 466 (s), 529 (s), 555 (s), 597 (s), 670 (s), 697 (s), 713 (s), 743 (s), 754 (s), 830 (s), 996 (m), 1027 (m), 1092 (s), 1194 (s), 1217 (s), 1308 (w), 1360 (s), 1385 (m), 1434 (m), 1467 (w), 1481 (w), 2860 (m), 2899 (m), 2949 (m), 3053 (w) cm^{-1}.

Synthesis of [(NPN^{tBu})$_2$Sm–Cl] (15). According to **A4**: from 200 mg of $[SmCl_3(thf)_2]$ as a yellow solid. Yield: 188 mg (56%).

CHNCl ($C_{40}H_{56}ClN_4P_2Sm$, M_W: 840.66): found (calcd): C: 55.14% (57.15%), H: 6.94% (6.71%), N: 6.55% (6.66%), Cl: 5.19% (4.22%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = −2.28 (s, 36H, *t*Bu*H*), 7.93–7.98 (m, 4H, *p*-Ph*H*), 8.11–8.13 (m, 8H, *m*–Ph*H*), 11.69 (s, 8H, *o*-Ph*H*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): δ = 81.8 (br s) ppm.

IR-Spektroskopie: $\tilde{\nu}$ = 464 (s), 529 (s), 556 (m), 593 (s), 670 (s), 697 (s), 740 (s), 831 (s), 998 (w), 1027 (m), 1079 (s), 1093 (s), 1116 (s), 1190 (s), 1312 (w), 1360 (m), 1389 (m), 1435 (m), 1468 (w), 1482 (w), 2862 (w), 2959 (m), 3051 (w) cm^{-1}.

Synthesis of [(NPN^{tBu})$_2$Gd–Cl] (16). According to **A4**: from 132 mg of $[GdCl_3]$ as a colourless solid. Yield: 236 mg (69%).

CHNClGd: ($C_{40}H_{56}ClN_4P_2Gd$, M_W: 847.55): found (calcd): C: 56.04% (56.69%), H: 7.00% (6.66%), N: 6.61% (6.61%), Cl: 4.48% (4.18%). Gd: 18.45% (18.55%).

Synthesis of [(NPN^{tBu})$_2$Tb–Cl] (17). According to **A4**: from 133 mg of $[TbCl_3]$ as a colourless solid. Yield: 272 mg (80%).

CHNClTb: ($C_{40}H_{56}ClN_4P_2Tb$, M_W: 849.24): found (calcd): C: 55.97% (56.57%), H: 7.06% (6.66%), N: 6.51% (6.60%), Cl: 4.39% (4.17%). Tb: 18.61% (18.71%).

Table 3 Details of the X-ray structure determination of complexes **4**, **6**, **7**, **13**, **19** and **20*3C$_6$D$_6$**

	4	**6**	**7**	**13**	**19**	**20*3C$_6$D$_6$**
Empirical formula	$C_{44}H_{67}N_4P_2SiY$	$C_{44}H_{67}N_4NdP_2Si$	$C_{44}H_{67}N_4P_2SiSm$	$C_{40}H_{56}ClN_4P_2Y$	$C_{40}H_{56}ClLuN_4P_2$	$C_{78}H_{84}Cl_4D_{18}N_6OP_3Sc_3$
Formula weight	830.96	886.29	892.40	779.19	865.25	1527.35
Temperature, K	100(2)	100(2)	100(2)	200(2)	180(2)	100(2)
Wavelength, Å	0.71069	0.71073	0.71073	0.71073	0.71073	0.71069
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions: a, Å	18.4804(6)	18.4969(14)	8.4815(7)	11.291(2)	11.255(3)	12.8438(4)
b, Å	10.7054(3)	10.7302(5)	10.6977(3)	12.957(3)	12.900(3)	14.0230(5)
c, Å	22.8125(8)	23.1856(16)	23.0704(9)	15.213(3)	15.145(4)	24.5137(8)
α, °	90	90	90	104.56(3)	104.05(3)	80.619(3)
β, °	92.651(3)	92.751(6)	92.641(3)	103.59(3)	103.39(3)	79.875(3)
γ, °	90	90	90°	95.79(3)	95.60(3)	70.044(3)
Volume, Å^3	4508.4(2)	4596.5(5)	4556.4(3)	2063.3(7)	2047.4(9)	4060.0(2)
Z	4	4	4	2	2	2
Density (calculated) Mg m^{-3}	1.224	1.281	1.301	1.254	1.404	1.249
μ, mm^{-1}	1.425	1.258	1.418	1.587	2.586	0.479
F(000)	1768	1852	1860	820	884	1592
Crystal size, mm	0.39 × 0.08 × 0.05	0.13 × 0.09 × 0.08	0.45 × 0.16 × 0.03	0.5 × 0.4 × 0.3	0.48 × 0.40 × 0.24	0.32 × 0.20 × 0.16
Theta range for data collection, °	4.66 to 26.73	1.44 to 25.00	1.44 to 26.73	1.85 to 26.19	2.57 to 25.50	1.554 to 26.732
Index ranges	$-23 \le h \le 23$, $-13 \le k \le 12$, $-28 \le l \le 25$	$-21 \le h \le 21$ $-12 \le k \le 10$, $-27 \le l \le 22$	$-23 \le h \le 23$, $-13 \le k \le 13$ $-28 \le l \le 29$	$-13 \le h \le 13$, $-16 \le k \le 15$ $0 \le l \le 18$	$-13 \le h \le 13$, $-15 \le k \le 15$ $-18 \le l \le 18$	$-16 \le h \le 15$, $-17 \le k \le 17$, $-30 \le l \le 30$
Reflections collected	24 581	14 843	31 218	16 180	21 039	59 927
Independent reflections	9447	7138	9656	7588	7154	17 184
R_{int}	0.0679	0.0476	0.0702	0.0577	0.0549	0.0780
Completeness to θ = 25.00°	98.7%	88.0%	100.0%	91.8%	93.7%	99.7%
Data/restraints/parameters	9447/0/484	7138/0/484	9656/0/484	7588/0/433	7154/0/433	17 184/84/875
Goodness-of-fit on F^2	0.936	0.960	0.761	0.852	1.038	0.808
Final R indices[a] [$I > 2\sigma(I)$]	R_1 = 0.0483, wR_2 = 0.0882	R_1 = 0.0340, wR_2 = 0.0838	R_1 = 0.0362, wR_2 = 0.0685	R_1 = 0.0353, wR_2 = 0.0645	R_1 = 0.0398, wR_2 = 0.0971	R_1 = 0.0605 wR_2 = 0.1432
R indices (all data)	R_1 = 0.0846, wR_2 = 0.0976	R_1 = 0.0427, wR_2 = 0.0856	R_1 = 0.0734, wR_2 = 0.0746	R_1 = 0.0685, wR_2 = 0.0729	R_1 = 0.0447, wR_2 = 0.0991	R_1 = 0.1070 wR_2 = 0.1557
$\Delta\rho_{max,\ min}$, e Å^{-3}	0.479 and −0.652	0.812 and −0.850	0.618 and −0.844	0.309 and −0.494	3.273 and −1.099	1.321 and −0.820

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

Synthesis of [(NPN^{tBu})$_2$Yb–Cl] (18). According to **A4**: from 140 mg of [YbCl$_3$] as a yellow solid. Yield: 121 mg (35%).

CHNClYb ($C_{40}H_{56}ClN_4P_2Yb$, M_W: 863.36): found (calcd): C: 55.04% (55.65%), H: 6.99% (6.54%), N: 6.51% (6.49%), Cl: 4.31% (4.11%). Yb: 19.60% (20.04%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = −18 (br s, 36H, *t*Bu*H*), 6.5 (br m, 20H, Ph*H*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): δ = −142.5 (br s) ppm.

Synthesis of [(NPN^{tBu})$_2$Lu–Cl] (19). According to **A4**: from 224 mg of [LuCl$_3$] as a colourless solid. Yield: 294 mg (85%).

CHNClLu: ($C_{40}H_{56}ClN_4P_2Lu$, M_W: 865.29): found (calcd): C: 54.98% (55.52%), H: 6.69% (6.52%), N: 6.62% (6.47%), Cl: 4.40% (4.10%). Lu: 20.00% (20.22%).

^{1}H NMR (300.1 MHz, C_6D_6): δ = 1.30 (s, 36H, *t*Bu*H*), 7.12–7.16 (m, 12H, *m*-/*p*-Ph*H*), 8.22–8.23 (m, 8H, *o*-Ph*H*) ppm.

^{13}C NMR (75.5 MHz, C_6D_6): δ = 35.0 (d, $^3J_{CP}$ = 8.6 Hz, *t*BuC_{Me}), 53.4 (s, *t*BuC_q), 128.1 (d, overlapped with residual C_6D_6 signal, *p*-Ph*C*), 130.9 (d, $^4J_{CP}$ = 2.5 Hz, *m*-Ph*C*), 133.7 (d, $^2J_{CP}$ = 10 Hz, *o*-Ph*C*), 136.5 (d, $^1J_{CP}$ = 85 Hz, *ipso*-Ph*C*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): δ = 20.0 (s) ppm.

X-ray crystallography

Crystal data were collected with different area-detector diffractometers using graphite-monochromatised Mo-Kα-radiation (λ = 0.71073 Å), namely: for **4** and **6** with IPDS-2T at 100 K, for **7** and **20** with IPDS-II at 100 K, and for **13** and **19** with IPDS-I at 200 K and 180 K correspondingly. Data reduction was carried out using the IPDSI software or X-Area (Stoe).[34] Single crystals of complexes **4**, **6**, **7**, **13**, **19** and **20** were respectively mounted in Lindemann capillaries under nitrogen. The structures were solved by direct methods using SHELXS-97,[35] Sir-92,[36] and Sir-2004[37] programs and refined against F_o^2 by full-matrix least squares using SHELXL-97.[38] Details of the X-ray structure determination are given in Table 3. CCDC no. 1414805 (**4**), 1414808 (**6**), 1414807 (**7**), 901056 (**13**), 901055 (**19**) and 1414806 (**20*3C$_6$D$_6$**) contain the supplementary crystallographic data for this paper.

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