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Simple Entry into N-tert-Butyl-Iminophosphonamide Rare-Earth Metal Alkyl and Chlorido Complexes

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Abstract

In-situ protolysis reaction of highly basic and sterically hindered N,N’-di-tert-butyl-iminophosphonamide ligand Ph₂P(=N-tBu)(NH-tBu) = (NPN°°°°Bu)H (1) with equimolar or hemimolar amounts of rare-earth metal tris-alkyls leads to dialkyl [(NPN°°°°Bu)Ln(CH₂SiMe₃)₂(THF)ₙ] (Ln = Sc, n = 0 (2), Ln = Y, n = 1 (3)) and monoalkyl species [(NPN°°°°Bu)₂Ln(CH₂SiMe₃)] (Ln = Y (4), Nd (6), Sm (7)). One-pot reaction of [ScCl₃(THF)₃]/1/2/3 eq. ratio gives [(NPN°°°°Bu)₂Sc(THF)CH₃] 5. Further reaction of 4 with phenylacetylene resulted in formation of Y-alkynyl complex [(NPN°°°°Bu)₂Y(C≡CPh)] 8. Alkyl abstraction in 2, 3 and 4 by reaction with [PhNMMe₂H][B(C₆F₅)₄] resulted in formation of cationic alkyl complex ion-pairs [(NPN°°°°Bu)Ln(CH₂SiMe₃)(THF)ₙ][B(C₆F₅)₄] (Ln = Sc (9), Y (10)) and [(NPN°°°°Bu)₂Y(THF)ₙ][B(C₆F₅)₄] 11, as confirmed by NMR data. The reaction of bis-NPN alkyl complexes with CHCl₃ is the most simple and reliable protocol to synthesize bis-NPN-chlorido complexes [(NPN°°°°Bu)₂LnCl] (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 organolanthaneide building blocks [Cp*₂LnX]. Partial hydrolysis of 12 leads to formation of oxido/chlorido-capped trinuclear complex [{(NPN°°°°Bu)Sc(µ₂-Cl)}₃(µ₃-O)(µ₃-Cl)] 20. Molecular structures of 4, 6, 7, 13, 19 and 20 were confirmed by X-ray structure analyses.

Key words: iminophosphonamide ligand, rare-earth metals, lanthanides, alkyl complexes, ion-paired borates, alkyl abstraction, alkynyl complexes, chlorido complexes
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', CH₂, 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 80-90's using A-type ligands (see Chart 1) with SiMe₃ (tms) substituents at the nitrogen atoms for the preparation of Pr¹ΙΙΙ and Nd¹ΙΙΙ chlorido complexes I and Ac⁴ΙV chlorido and oxo complexes (II and III)² yet none of them was structurally characterised. Later, Sm¹ΙΙΙ and Yb¹ΙΙ- complexes (IV and V)³ as well as a series of Ln-COT NPN-complexes (VI)⁴ have been reported.

In 2006 Hill and co-workers reported several rare-earth metal tms₂N- and dms₂N-complexes (dms: SiMe₂H) bearing chiral {DACH}-bridged bis-NPN ligand regime (VII) (DACH = trans-diaminocyclohexane),⁵ that are highly active one-component catalysts for the stereoselective polymerisation of MMA. Numerous rare-earth metals 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 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 high 3,4-selectivity.⁶a,b Moreover, a borohydrido neodymium (IX) and recently 4-methylbenzyl neodymium and lanthanum (X) B-type NPN-complexes has 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,¹²c,¹⁴ Cu,¹⁵ Ag,¹⁶ and Zn¹²d,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 were thoroughly investigated so far (Chart 1). 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.
Chart 1. Different types of NPN ligands (A–C).

Chart 2. Known rare-earth metal NPN complexes (I–X).
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) \( \text{Ph}_2\text{P(=N-tBu)(NH-tBu) = (NPN}^{\text{tBu}}\text{)H (1).} \)

**Synthesis of mono-(NPN\textsuperscript{tBu}) dialkyl rare-earth metal complexes**

Initial attempts to prepare \([(NPN}^{\text{tBu}})\text{Ln(CH}_2\text{SiMe}_3)_2(\text{THF})_n] \) complexes using *in situ* prepared rare-earth metal tris-alkyls \([\text{Ln(CH}_2\text{SiMe}_3)_3(\text{THF})_n]\) from \([\text{LnCl}_3(\text{THF})_n]\) and 3 eq. of \( \text{LiCH}_2\text{SiMe}_3 \) was fully successful only for the solvent-free Sc-derivative \([(NPN}^{\text{tBu}})\text{Sc(CH}_2\text{SiMe}_3)_2] \text{ 2. In the case of the larger cation Y}^{3+}, \text{ formation of the target mono-NPN species } [(NPN}^{\text{tBu}})\text{Y(CH}_2\text{SiMe}_3)_2(\text{THF})] \text{ 3 was accompanied by a small amount of bis-NPN complex } [(NPN}^{\text{tBu}})_2\text{Y(CH}_2\text{SiMe}_3)] \text{ 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 succeed to separate it and isolate pure 3 by this method.}

![Scheme 1](image_url)

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

Selective and high yield syntheses of very pure 2 and 3 complexes have been achieved using the alkane elimination route from the *purely isolated* tris-neosilyl precursors \([\text{Sc(CH}_2\text{SiMe}_3)_3(\text{THF})_2]\) and \([\text{Y(CH}_2\text{SiMe}_3)_3(\text{THF})_3]\). A pre-cooled 0 °C diethyl ether solution of 1 was added drop-wise to a solution of the trialkyl in n-pentane or n-hexane at 0 °C. In \( ^{31}\text{P} \) NMR spectra sharp signals are observed at 12.2 (2) and 18.1 (3) ppm. \( ^1\text{H} \) 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 singlet at 0.25 ppm for 2 and as doublet at –0.26 ppm with \( ^2J_{HY} = 3.0 \) Hz for 3. In the \( ^1\text{H} \) 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 \( ^{13}\text{C} \) 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 $[(NPN^{tBu})_2Ln(CH_2SiMe_3)]$ - either starting from in situ or from purely isolated tris-neosilyl $[Ln(CH_2SiMe_3)_3(THF)_n]$ precursors. Both protocols allow to prepare $[(NPN^{tBu})_2Y(CH_2SiMe_3)]$ 4 in high yields (85% – for 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.

![Scheme 2. Preparation of $[(NPN^{tBu})_2Y(CH_2SiMe_3)]$ 4.](image)

As expected reaction of 1 eq. of $[Sc(CH_2SiMe_3)_3(THF)]$ with 2 eq. of 1 doesn't allow to isolate bis-(NPN$^{tBu}$) scandium derivative: because of the small ionic radius of scandium metal centre it cannot coordinate two bulky (NPN$^{tBu}$)-ligands and further one bulky Me$_3$SiCH$_2$-group.

Yet, when instead of Me$_3$SiCH$_2$-group a simple CH$_3$-group was used 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 $[ScCl_3(THF)]$ suspended in diethyl ether at 0 °C followed by addition of 3 eq. of MeLi for 1 h (Scheme 3) leads to a new bis-NPN scandium complex $[(NPN^{tBu})_2Sc(THF)CH_3]$ 5 that has been isolated as a pure colourless solid in 59% yield.

![Scheme 3. Preparation of $[(NPN^{tBu})_2Sc(THF)CH_3]$ 5.](image)
The $^{31}\text{P}$ 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 $^1\text{H}$ and at 22.8 ppm in $^{13}\text{C}$ NMR spectra. Co-ordinated THF is also confirmed by both $^1\text{H}$ and $^{13}\text{C}$ 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 described above in situ method (Scheme 4). For completion of tris-alkyls' formation from [LnCl$_3$(THF)$_m$] and LiCH$_2$SiMe$_3$ the reaction mixture was stirred for 1 h at 0 °C, followed by addition of 2 eq. of 1 in diethyl ether. By this method two new bis-NPN-alkyl complexes [(NPN$^{\text{tBu}}$)$_2$Nd(CH$_2$SiMe$_3$)] 6 and [(NPN$^{\text{tBu}}$)$_2$Sm(CH$_2$SiMe$_3$)] 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.

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

In $^{31}\text{P}$ NMR spectra sharp signals at 19.5 (4), 72.4 (6) and −133.8 (7) ppm have been found. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of 4 are very similar to those ones of 3 with exception of THF signals. The $^1\text{H}$ NMR spectra of paramagnetic complexes 6 and 7 show sharp signals and can be easily assigned. Thus, tert-butyl groups signals are upfield-shifted at −2.68 (6) and −7.19 (7) ppm, whereas trimethylsilyl groups 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 signal of methylene group is observed at 15.98 ppm, yet, for neodymium complex this signal could not be clearly assigned.

**Reaction with phenylacetylene**

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

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{H} & \quad \text{Ph} \\
\text{Et}_2\text{O}, 0 \degree \text{C}, 1 \text{ h} & \quad \text{SiMe}_3 \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

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

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

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

The reaction with the mild protonating [PhNMe\(_2\text{H}\)]\(^+\)[B(C\(_6\text{F}_5\))\(_4\)]\(^-\) proved to be 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\(_6\text{D}_6\):d\(_8\)-THF.

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

\[
\begin{align*}
\text{Ln} = \text{Sc (2), } n = 0, \text{Ln} = \text{Y (3), } n = 1
\end{align*}
\]

Scheme 6. Preparation of \([(\text{NPN}^{\text{tBu}})\text{Ln(CH}_2\text{SiMe}_3)(\text{THF})_n]^+[\text{B(C}_6\text{F}_5\text{)}_4]^-(9 \text{ and } 10)\).

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

Scheme 7. Preparation of [(NPN$^{tBu}$)$_2$Y(THF)$_n$]$^+$$\text{[B(C}_6\text{F}_5)_4]$^-$ 11.

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, that in comparison to 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 similar symmetric set of ligand signals as the precursor NPN-alkyl complexes. Coordination of THF molecules is clearly seen by 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 $^1J_{CY}$ coupling constants: 42.3 Hz in 10 vs. 38.7 Hz in 3 and downfield shifted Ln-CH$_2$: 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 highly pure form due to their crystallisation from n-pentane. In contrast, our initial attempts to synthesize chlorido complexes by 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-metallocene [(NPN$^{tBu}$)$_2$Ln-Cl]complexes. They offer reaction patterns complementary to those of the alkyls [(NPN$^{tBu}$)$_2$Ln-R]. We found the simplest synthetic approach to these chlorido complexes. This protocol includes *in-situ* formation of [(NPN$^{tBu}$)$_2$Ln-CH$_2$SiMe$_3$] 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$^{tBu}$)$_2$Ln-CH$_2$SiMe$_3$] complexes are highly soluble in alkanes, whereas [(NPN$^{tBu}$)$_2$Ln-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 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.

Scheme 8. Preparation of [(NPN$_{t}$Bu)$_2$LnCl] (12–19).

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.

**Molecular structures of bis-(NPN$_{t}$Bu) 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 P21/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-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\textsuperscript{19} and donor-acceptor\textsuperscript{20} bonds. They are also in the same range as for other type A and B monok- and bis-NPN complexes, for example: in [{Ph\textsubscript{2}P(NMes)(NPh)}\textsubscript{2}Y(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{2}(THF)]: d(Y–N) = 2.335(3) and 2.349(4) Å\textsuperscript{6ab} in [{Ph\textsubscript{2}P(NSiMe\textsubscript{3})\textsubscript{2}}\textsubscript{2}Sm(μ\textsubscript{2}-I)\textsubscript{2}]Li(THF): d(Sm–N) = 2.384(3)–2.506(4) Å\textsuperscript{3} or in [{Ph\textsubscript{2}P(NSiMe\textsubscript{3})\textsubscript{2}}Nd(COT)(THF)]: d(Nd–N) = 2.472(3) and 2.473(3) Å.\textsuperscript{4} The Ln–C bond lengths are within the expected range for Ln-CH\textsubscript{2}SiMe\textsubscript{3} derivatives.\textsuperscript{21}

As expected Y–N bond lengths in chlorido complex 13 with more electron-poor central atom are significantly shorter than in corresponding alkyl complex 4. 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, [Cp₂Ln(THF)Cl] complexes lose coordinated THF to form dimeric species with two µ-Cl ligands [(Cp₂Ln-Cl₂)].²² Similar behavior is observed in the case of Cp* complexes,²³ yet [(Cp*₂YCl)₂] species does exist as asymmetric dimer with only one µ-Cl ligand.²⁴ For the smallest among rare-earth metals, scandium, formation of monomeric [Cp*₂ScCl] was described.²⁵ The fact, that we isolated ether-free penta-coordinate corresponding [(NPN₄Bu)₂LnCl] complexes from solution containing the probe ligands - diethyl ether and THF - indicates the very strong donor character of this NPN₄Bu ligand. Despite of 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 [C₅Me₅, Cp*].

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 N–P–N ligand fragment. Yet, in chlorido complexes these difference 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 as for other structurally characterised complexes.⁶a,b
Table 1: Selected bond lengths (Å) and angles (°) of complexes 4, 6, 7, 13 and 19.

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<th></th>
<th>4 (Y)</th>
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<th>7 (Sm)</th>
<th>13 (Y)</th>
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<td>2.438(3)</td>
<td>2.511(4)</td>
<td>2.471(5)</td>
<td>---</td>
<td>---</td>
<td>C1–Ln–N1</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>91.6(1)</td>
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<tr>
<td>Ln–Cl</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>2.575(1)</td>
<td>2.529(2)</td>
<td>Ln–C41–Si</td>
<td>133.7(2)</td>
<td>133.2(2)</td>
<td>134.3(2)</td>
<td>---</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>20</th>
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<tbody>
<tr>
<td>Sc1–N1</td>
<td>2.177(3)</td>
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<tr>
<td>Sc1–N2</td>
<td>2.106(3)</td>
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<tr>
<td>Sc1–O1</td>
<td>2.032(3)</td>
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<tr>
<td>Sc3–O1</td>
<td>2.024(2)</td>
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<td>Sc1–Cl2</td>
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<td>Sc1–Cl3</td>
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<td>Sc1–Sc2</td>
<td>2.761(1)</td>
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<td>Sc1–Sc3</td>
<td>3.200(1)</td>
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<tr>
<td>P1–N1</td>
<td>1.606(3)</td>
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<tr>
<td>P1–N2</td>
<td>1.619(4)</td>
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</table>
Our attempt to get 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 $\{\{(NPN^\text{Bu})\text{Sc}(\mu_2-\text{Cl})\}_3(\mu_3-\text{O})(\mu_3-\text{Cl})\}$ 20 (Fig. 3) as the product of partial hydrolysis of 12 by water traces. One NPN$^\text{Bu}$ 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 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 $\mu_3$-O capping structural motif have been described in the literature. Examples are shown in Chart 3.\textsuperscript{26}

The basic framework of this structure is formed by the three scandium atoms, that are above and below capped via a $\mu_3$-O and $\mu_3$-Cl atoms. Other three chlorido atoms are $\mu_2$-bridging the edges of the Sc$_3$-triangle so that a highly distorted six-membered ring is formed.
Thus, the shortest Sc–µ3-Cl distance (2.717(1) Å) is even longer than the longest Sc–µ2-Cl one (2.565(1) Å). The Sc–Cl bond distances are similar to those of other scandium complexes, bearing µ2-Cl atoms, e.g. in \[ \{N(SiMe_2H)_2\}_2Sc(µ_2-Cl)(THF)\] \(_2\) \( d(Sc–Cl) = 2.559 \) Å \(^{27}\) and in \[ [Cp_2Sc(µ_2-Cl)]_2 \] \( d(Sc–Cl) = 2.573 \) Å \(^{28}\). No crystallographically characterised molecular scandium compound with a µ3-Cl motif is known to date. The Sc–O distance lies in the range of 2.024(2) - 2.034(3) Å and significantly shorter than that one in XIV (2.066 Å).

Due to the shorter Sc–µ3 compared to Sc–µ3-Cl distances corresponding Sc–(µ3-Cl)–Sc angles (69.8(1) - 72.4(1)°) become smaller than Sc–(µ3-O)–Sc ones (104.2(1) - 105.4(1)°).

Conclusions

So far iminophosphonamido complexes of the rare-earth metals were 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 the Staudinger type of 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 highest NPN donor strength within this class of complexes. We are convinced, that the prominent donor strength, the steric demand as well as favourable solubility and NMR spectroscopic features make these post-metallocene complexes [(NPN\(^{tBu}\))\(_2Ln-X\)] to building blocks as useful as the lanthanocenes [(C\(_5\)Me\(_5\))\(_2Ln-X\)] 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 Al\(_2\)O\(_3\)/Na SOLVONA column and dried of water traces at P\(_4\)O\(_{10}\) column. Weighing and sample preparation for analytical characterization, as well as materials storage was performed in a glove box under atmosphere of dry nitrogen. Drying of solvents and reagents used was carried out by the general methods under an inert atmosphere. The solvents were after drying stored in absorption columns over BASF alumina molecular sieve 3Å/R3-11G catalyst. Solvent and all chemicals used in the syntheses were, unless mentioned separately purchased from Fluka, Aldrich, Acros, Sigma or Merck. Rare-earth metal salts or 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),\textsuperscript{30} [Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$]: Ln = Sc,\textsuperscript{31} Lu\textsuperscript{32} and [Y(CH$_2$SiMe$_3$)$_3$(THF)$_3$].\textsuperscript{33} The concentrations of the solutions used by organolithium and Grignard reagents were determined by titration with sec-butanol and 1,10-phenanthroline as indicator. Because of the strong paramagnetic behaviour measuring of $^{13}$C NMR spectra of 6, 7, 14–18 and $^1$H NMR spectra for 16 and 18 did not make sense. Additional metal titration (with Xylenol orange as indicator) for 16–19 was fulfilled.

**Synthesis of Ph$_2$P(=N-tBu)(NH-tBu) (1)**

*For working with gram quantities of tBuN$_3$ an extra safety shield is recommended. Despite of its relative 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$_2$Cl$_2$ (200 mL), under vigorous stirring and argon overflow a solution of Ph$_2$PCl (9 mL, 50 mmol, 1.0 eq.) in dry CH$_2$Cl$_2$ (50 mL) was added drop-wise and then allowed to warm up to ambient temperature. After stirring for 4 h the reaction solvent with some excess of tBuNH$_2$ was removed and an oily residue was extracted with dry toluene (300 mL) followed by filtration of tBuNH$_3$Cl salt precipitate (D4), solvent removal and drying under high vacuum to get crude Ph$_2$PNHtBu as light-coloured viscous oil, that was purified by quick bulb-to-bulb distillation under dynamic high vacuum giving pure semi-product Ph$_2$PNHtBu (9 g, 35 mmol) in 70\% yield. The latter was dissolved in THF (100 mL) followed by addition of tBuN$_3$ (5 g, 50 mmol, 1.5 eq.) at ambient temperature and allowed to stir over night. Next day 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 by triethylphosphite before disposal*). The solid was suspended in 100 ml of n-hexane, the solution was decanted and the solid dried under high vacuum to give 9.7 g of 1 as a white solid in 85\% (overall ~60\%) yield. 1 sparingly soluble in n-pentane and n-hexane, but soluble in benzene, toluene and ethers.

**CHN:** (C$_{20}$H$_{29}$N$_2$P, MW: 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$_6$D$_6$): $\delta = 1.35$ (br s, 18H, tBuH), 2.53 (br s, 1H, NH), 7.06–7.11 (m, 6H, m-/p-PhH), 7.83–7.90 (m, 4H, o-PhH) ppm.

$^{13}$C NMR (75.5 MHz, C$_6$D$_6$): $\delta = 33.9$ (br s, tBuC$_3$), 51.8 (d, $^2$J$_{CP}$ = 3.7 Hz, tBuC$_3$), 127.9 (d, overlapped with residual C$_6$D$_6$ signal, p-PhC), 133.0 (d, $^2$J$_{CP}$ = 2.7 Hz, m-PhC), 132.5 (d, $^2$J$_{CP}$ = 9.4 Hz, o-PhC), 139.4 (d, $^1$J$_{CP}$ = 125.3 Hz, ipso-PhC) ppm.

$^{31}$P NMR (121.5 MHz, C$_6$D$_6$): $\delta = -21.9$ (s) ppm.

**General synthetic protocols to rare-earth metal NPN-alkyl complexes**

**A1**: [Ln(CH$_2$SiMe$_3$)$_3$(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 drop-wise 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 and followed by drop-wise addition of LiCH$_2$SiMe$_3$ (1.5 mmol, 3 eq.) solution in n-hexane (3 mL) via 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$_{\text{tBu}}$)Sc(CH$_2$SiMe$_3$)$_2$] (2)**

According to **A1**: from [Sc(CH$_2$SiMe$_3$)$_3$(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$_2$SiMe$_3$ (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 dried under high vacuum to give 2 as colourless, powdery solid. Yields: **A1** 219 mg (80%), **A2** 190 mg (70%).

**CHN**: (C$_{28}$H$_{50}$N$_2$PScSi$_2$, MW: 546.81): found (calcd.): C: 60.49% (61.50%), H: 9.01% (9.22%), N: 5.14% (5.12%).
1H NMR (300.1 MHz, C6D6): $\delta = 0.25$ (s, 4H, Sc-CH₂), 0.45 (s, 18H, SiMe₃), 1.11 (d, $^4J_{HP} = 1.2$ Hz, 18H, tBuH), 7.05–7.08 (m, 6H, m-/p-PhH), 7.84–7.91 (m, 4H, o-PhH) ppm.

13C NMR (75.5 MHz, C₆D₆): $\delta = 4.2$ (s, SiMe₃), 34.3 (d, $^3J_{CP} = 8.1$ Hz, tBuC₆Me), 39.7 (br s, SckC₂H₂), 54.3 (d, $^2J_{CP} = 1.6$ Hz, tBuC₄), 128.5 (d, overlapped with residual C₆D₆ signal, p-PhC), 131.9 (d, $^3J_{CP} = 2.9$ Hz, m-PhC), 133.1 (d, $^1J_{CP} = 90.1$ Hz, ipso-PhC), 133.3 (d, $^2J_{CP} = 10.5$ Hz, o-PhC) ppm.

31P NMR (121.5 MHz, C₆D₆): $\delta = 12.2$ (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), 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 [(NPN₄Bu)Y(CH₂SiMe₃)₂(THF)] (3)

According to A1: from [Y(CH₂SiMe₃)₃(THF)] (283 mg, 0.5 mmol, 1 eq.) with I (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: (C₃₂H₅₈N₂OPSi₂Y, MW: 662.87): found (calcd.): C: 53.68% (57.98%), H: 8.36% (8.82%), N: 4.34% (4.23%).

1H NMR (300.1 MHz, C₆D₆): $\delta = −0.26$ (d, $^2J_{HY} = 3.0$ Hz, 4H, Y-CH₂), 0.45 (s, 18H, SiMe₃), 1.12 (d, $^4J_{HP} = 0.9$ Hz, 18H, tBuH), 1.32–1.36 (br m, 4H, thfkC₂H₂), 3.90–3.95 (br m, 4H, thfkOCH₂), 7.10–7.23 (m, 6H, m-/p-PhH), 8.12–8.19 (m, 4H, o-PhH) ppm.

13C NMR (1k, 75.5 MHz, C₆D₆): $\delta = 5.1$ (s, SiMe₃), 25.2 (s, thfkCH₂), 32.4 (d, $^1J_{CY} = 38.7$ Hz, Y-CH₂), 34.9 (d, $^3J_{CP} = 8.9$ Hz, tBuC₆Me), 52.9 (d, $^2J_{CP} = 0.9$ Hz, tBuC₄), 70.2 (s, thfkOCH₂), 128.2 (d, $^4J_{CP} = 11.0$ Hz, p-PhC), 130.8 (d, $^3J_{CP} = 2.9$ Hz, m-PhC), 133.4 (d, $^2J_{CP} = 9.7$ Hz, o-PhC), 137.0 (d, $^1J_{CP} = 84.9$ Hz, ipso-PhC) ppm.

31P NMR (121.5 MHz, C₆D₆): $\delta = 18.1$ (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 $[\text{NPN}^\text{tBu}]_2\text{Y(CH}_2\text{SiMe}_3]\) (4)

According to A1: from $[\text{Y(CH}_2\text{SiMe}_3]_3(\text{THF})_3\] (283 mg, 0.5 mmol, 1 eq.) with 1 (328 mg, 1 mmol, 2 eq.).

According to A2: from $[\text{YCl}_3(\text{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$_4$P$_2$SiY, MW: 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$_6$D$_6$): $\delta = 0.19$ (d, $^2$J$_{HY} = 3.0$ Hz, 2H, Y-CH$_2$), 0.58 (s, 9H, SiMe$_3$), 1.30 (s, 36H, tBuH), 7.14–7.24 (m, 12H, m-/p-PhH), 8.21–8.28 (m, 8H, o-PhH) ppm.

$^{13}$C NMR (75.5 MHz, C$_6$D$_6$): $\delta = 5.7$ (s, SiMe$_3$), 29.6 (d, $^1$J$_{CV} = 40.4$ Hz, Y-CH$_2$), 35.6 (d, $^3$J$_{CP} = 9.0$ Hz, tBuC$_{Me}$), 53.2 (s, tBuC$_0$), 128.3 (d, overlapped with residual C$_6$D$_6$ signal, p-PhC), 130.8 (d, $^3$J$_{CP} = 2.7$ Hz, m-PhC), 133.8 (d, $^2$J$_{CP} = 9.6$ Hz, o-PhC), 137.4 (d, $^1$J$_{CP} = 83.5$ Hz, ipso-PhC) ppm.

$^{31}$P NMR (121.5 MHz, C$_6$D$_6$): $\delta = 19.5$ (s) ppm.

**IR:** $\tilde{v} = 467$ (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 $[\text{NPN}^\text{tBu}]_2\text{Sc(CH}_3\text{)(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 syringe. After stirring for 1 h at 0 °C the mixture was filtered through Celite®. Upon solvent removal the residue was dried in vacuum, washed with n-pentane (3 mL) to give 5 as a colourless solid. Yield: 233 mg (59%).

**CHN:** (C$_{45}$H$_{67}$N$_4$O$_2$Sc, MW: 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$_6$D$_6$): $\delta = 0.61$ (s, 3H, Sc-CH$_3$), 1.37 (s, 40H, tBuH + thf-CH$_2$), 3.54–3.59 (s, 4H, thf-OCH$_2$), 7.15–7.19 (m, 12H, m-p-PhH), 8.26–8.34 (m, 8H, o-PhH) ppm.

$^{13}$C NMR (4k, 62.9 MHz, C$_6$D$_6$): $\delta = 22.8$ (s, ScC$_3$H$_3$), 25.7 (s, thfC$_2$H$_2$), 35.2 (d, $^3$J$_{CP}$ = 8.7 Hz, tBuC$_3$Me), 53.8 (d, $^2$J$_{CP}$ = 0.9 Hz, tBuC$_3$q), 68.0 (s, thf-OCH$_2$), 127.9 (d, overlapped with residual C$_6$D$_6$ signal, m/kPhC), 130.8 (d, $^3$J$_{CP}$ = 2.9 Hz, m-PhC), 134.2 (d, $^2$J$_{CP}$ = 9.7 Hz, o-PhC), 137.1 (d, $^1$J$_{CP}$ = 83.4 Hz, ipso-PhC) ppm.

$^{31}$P NMR (121.5 MHz, C$_6$D$_6$): $\delta = 19.6$ (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 low stability of 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$_4$NdP$_2$Si, MW: 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$_6$D$_6$): $\delta = -7.19$ (br s, 36H, tBuH), -4.34 (s, 9H, SiMe$_3$), 9.84 (t, $^3$J$_{HH}$ = 6.7 Hz, 4H, p-PhH), 10.59 (m, 8H, m-PhH), 19.66 (d, $^3$J$_{HH}$ = 3.8 Hz, 8H, o-PhH) ppm. The signal of Nd-CH$_2$ hydrogen atoms could not be clearly identified.

$^{31}$P NMR (121.5 MHz, C$_6$D$_6$): $\delta = -133.8$ (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 low stability of 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%).
\[22\]

CHN: \((C_{44}H_{67}N_{4}P_{2}SiSm, MW: 892.42):\) found (calcd.): C: 58.73% (59.22%), H: 7.67% (7.57%), N: 6.02% (6.28%).

\(^1\)H NMR (300.1 MHz, \(C_6D_6\)): \(\delta = -2.68 (s, 36H, tBuH), 1.53 (s, 9H, SiMe_3), 8.02 (br t, \(^3J_{HH} = 7.3\) Hz, 4H, \(p\)-PhH), 8.27 (br t, \(\delta = 72.4 (br s) ppm.\)

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 \([\text{NPN}^{tBu}]_2\text{Y-C≡CPh}\) (8)

To [\(\text{Ln(CH}_2\text{SiMe}_3)_3(\text{THF})_2\)] (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 drop-wise at 0 °C and stirred for 2.5 h. [\(\text{Y(CH}_2\text{SiMe}_3)_3(\text{THF})_3\)] (283 mg, 0.5 mmol, 1 eq.) was suspended in n-pentane (10 mL) at 0 °C followed by 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 syringed 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 washed with pre-cooled n-pentane (2 x 4 mL). Drying in a high vacuum, gave 8 as a colourless powder solid. Yield: 330 mg (78%).

CHN: \((C_{48}H_{61}N_{4}P_{2}Y, MW: 844.34):\) found (calcd.): C: 68.24% (67.57%), H: 7.28% (7.53%), N: 6.63% (5.78%).

\(^1\)H NMR (300.1 MHz, \(C_6D_6\)): \(\delta = 1.40 (s, 36H, tBuCMe), 7.00−7.13 (m, 12H, \(m-/p\)-PhH and \(m-/p\)-PhH-Alkynyl), 7.77 (dd, \(\delta = 8.3\) Hz, \(\delta = 1.3\) Hz, 2H, \(o\)-PhH-Alkynyl), 8.26−8.33 (m, 8H, \(o\)-PhH) ppm.

\(^{13}\)C NMR (4k, 62.9 MHz, \(C_6D_6\)): \(\delta = 35.2 (d, \delta = 8.8\) Hz, \(tBuCMe), 53.4 (d, \delta = 1.2\) Hz, \(tBuCq), 108.2 (s, \(ipso\)-PhC-Alkynyl), 125.8 (s, \(p\)-PhC-Alkynyl), 127.9 (s, \(m\)-PhC-Alkynyl), 128.4 (d, \(\delta = 16.6\) Hz, \(p\)-PhC), 130.0 (d, \(\delta = 36.2\) Hz, PhC≡CPh), 130.8 (d, \(\delta = 2.8\) Hz, \(m\)-PhC), 132.6 (s, \(o\)-PhC-Alkynyl), 133.8 (d, \(\delta = 9.9\) Hz, \(o\)-PhC), 136.9 (d, \(\delta = 84.0\) Hz, \(ipso\)-PhC) ppm. No signal of the PhC≡CPh can be observed.

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

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 to reactions of alkyl complexes with $[\text{PhNHMe}_2]^+\text{[B(C}_6\text{F}_5)_4]^{-}$

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

Synthesis of $[(\text{NPN}_{\text{Bu}})\text{Sc(CH}_2\text{SiMe}_3)(\text{THF})_n]^+[\text{B(C}_6\text{F}_5)_4]^{-}$ (9)

According to A3: from 2 (30.73 mg 56.2 μmol, 1.00 eq) with $[\text{PhNHMe}_2]^+[\text{B(C}_6\text{F}_5)_4]^{-}$ (44.06 mg, 55.0 μmol, 0.98 eq.).

$^1\text{H NMR}$ (400.0 MHz, $\text{C}_6\text{D}_6$/THF-d$_8$, 6:1): $\delta$ = 0.00 (s, $\text{SiMe}_4$), 0.17 (s, 9H, $\text{SiMe}_3$), 0.23 (s, 2H, Sc-CH$_2$), 0.89 (s, 18H, tBuH), 2.63 (s, 6H, aniline-Me$_2$), 6.64 (d, $^3J_{\text{HH}}$ = 8.2 Hz, 2H, aniline-m-PhH), 6.72 (t, $^3J_{\text{HH}}$ = 7.1 Hz, 1H, aniline-p-PhH), 7.18 (d, overlapping with residual $\text{C}_6\text{D}_6$ signal, 2H, aniline-o-PhH), 7.32−7.37 (m, 6H, o-/p-PhH), 7.86−7.91 (m, 4H, m-PhH) ppm.

$^{13}\text{C NMR}$ (100.6 MHz, $\text{C}_6\text{D}_6$/THF-d$_8$, 6:1): $\delta$ = −0.1 (s, $\text{SiMe}_4$), 3.7 (s, $\text{SiMe}_3$), 33.8 (d, $^3J_{\text{CP}}$ = 7.9 Hz, tBuC$_{\text{Me}}$), 40.2 (s, aniline-Me$_2$), 47.5 (br s, Sc-CH$_2$), 55.0 (d, $^2J_{\text{CP}}$ = 1.10 Hz, tBuC$_q$), 113.0 (s, aniline-m-PhC), 116.9 (s, aniline-p-PhC), 125.2 (br m, ipso-$\text{C}_6\text{F}_5$), 128.9 (d, $^4J_{\text{CP}}$ = 11.7 Hz, p-PhC), 129.3 (s, aniline-o-PhC), 132.2 (d, $^1J_{\text{CP}}$ = 89.5 Hz, ipso-PhC), 132.8 (d, $^3J_{\text{CP}}$ = 2.8 Hz, m-PhC), 133.5 (d, $^2J_{\text{CP}}$ = 10.3 Hz, o-PhC), 137.1 (dm, $^1J_{\text{CP}}$ = 247.8 Hz, m-$\text{C}_6\text{F}_5$), 139.0 (dm, $^1J_{\text{CP}}$ = 244.7 Hz, p-$\text{C}_6\text{F}_5$), 149.15 (dm, $^1J_{\text{CP}}$ = 241.1 Hz, o-$\text{C}_6\text{F}_5$), 151.1 (s, aniline-ipso-PhC) ppm.

$^{31}\text{P NMR}$ (161.9 MHz, $\text{C}_6\text{D}_6$/THF-d$_8$, 6:1): $\delta$ = 22.3 (s) ppm.

$^{19}\text{F NMR}$ (376.3 MHz, $\text{C}_6\text{D}_6$/THF-d$_8$, 6:1): $\delta$ = −166.7 (br s, 8F, m-PhF), −163.0 (t, $^3J_{\text{FF}}$ = 20.5 Hz, 4F, p-PhF), −131.8 (br s, 8F, o-PhF) ppm.

$^{11}\text{B NMR}$ (128.3 MHz, $\text{C}_6\text{D}_6$/THF-d$_8$, 6:1): $\delta$ = −16.3 (s) ppm.

Synthesis of $[(\text{NPN}_{\text{Bu}})\text{Y(CH}_2\text{SiMe}_3)(\text{THF})_n]^+[\text{B(C}_6\text{F}_5)_4]^{-}$ (10)

According to A3: from 3 (36.37 mg, 54.9 μmol, 1.00 eq) with $[\text{PhNHMe}_2]^+[\text{B(C}_6\text{F}_5)_4]^{-}$ (43.949 mg 54.9 μmol, 1.00 eq).

$^1\text{H NMR}$ (300.1 MHz, $\text{C}_6\text{D}_6$/THF-d$_8$, 6:1): $\delta$ = −0.49 (d, $^2J_{\text{HY}}$ = 3.3 Hz, 2H, Y-CH$_2$), 0.00 (s, 12H, $\text{SiMe}_4$), 0.19 (s, 9H, $\text{SiMe}_3$), 0.96 (d, $^4J_{\text{HP}}$ = 0.7 Hz, 18H, tBuH), 2.66 (s, 6H, aniline-
General synthetic protocol to rare-earth metal bis-NPN-chlorido complexes
A4: For [ScCl$_3$(THF)$_3$], [YCl$_3$(THF)$_3$], [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 thus obtained [LnCl$_3$(THF)$_n$] suspensions kept at 0 °C a solution of LiCH$_2$SiMe$_3$ (141 mg, 1.5 mmol, 3 eq.) in n-hexane (10 mL) was added drop-wise via syringe. After 3 hours (Sc, Y, Gd, Lu) or 1 h (Nd, Sm, Tb, Yb) stirring at 0 °C, assuming approx. 80% yield of triskalkyl species, a solution of 1 (262 mg, 0.8 mmol, 2 eq.) in diethyl ether (10 mL) was syringed. After stirring for 2.5 h the reaction mixture was concentrated to one-half of its initial volume, treated with n-pentane (10 mL), filtered through Celite® and washed with n-pentane (10 mL). The solvent was removed in vacuum and the residue was extracted with n-pentane (20 mL) and treated with freshly dried over basic Al$_2$O$_3$ chloroform (0.5 mL) and allowed to stir overnight. Fine microcrystalline solids formed. The solvent was decanted and the solid 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, soluble in benzene, toluene and ethers. Yields are calculated assuming the fact that only 80% (i.e. 0.4 mmol) of triskalkyl species took part in the reaction with 1.

Synthesis of [(NPN$^{t}$Bu)$_2$Sc-Cl] (12)

According to A4: from 184 mg of [ScCl$_3$(THF)$_3$] as a light-brown solid.
Yield: 97 mg (33%).

**CHNCI:** (C$_{40}$H$_{56}$ClN$_4$P$_2$Sc, MW: 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$_6$D$_6$): $\delta = 1.41$ (s, 36H, $t$BuH), 7.14–7.19 (m, 12H, $m$-/$p$-PhH), 8.30–8.36 (m, 8H, o-PhH) ppm.

$^{13}$C NMR (75.5 MHz, C$_6$D$_6$): $\delta = 34.9$ (d, $^3$J$_{CP}$ = 8.4 Hz, $t$BuC$_{Me}$), 54.5 (d, $^2$J$_{CP}$ = 1.2 Hz, $t$BuC$_q$), 128.0 (d, overlapped with residual C$_6$D$_6$ signal, p-PhC), 131.1 (d, $^3$J$_{CP}$ = 2.8 Hz, m-PhC), 134.4 (d, $^2$J$_{CP}$ = 10.0 Hz, o-PhC), 135.8 (d, $^1$J$_{CP}$ = 85.0 Hz, ipso-PhC) ppm.

$^{31}$P NMR (121.5 MHz, C$_6$D$_6$): $\delta = 19.6$ (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 \([\text{NPN}^{t\text{Bu}}_2\text{Y-Cl}]\) (13)

According to A4: from 224 mg of \([\text{YCl}_3(\text{thf})_3]\) as a light-brown solid. Yield: 150 mg (48%).

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

\(^1\text{H} \text{ NMR} \) (300.1 MHz, C\(_6\)D\(_6\)): \(\delta = 1.34 \) (s, 36H, \(t\text{BuH}\)), 7.14–7.20 (m, 12H, \(m-/p\text{-PhH}\)), 8.22–8.29 (m, 8H, \(o\text{-PhH}\)) ppm.

\(^{13}\text{C} \text{ NMR} \) (75.5 MHz, C\(_6\)D\(_6\)): \(\delta = 35.1 \) (d, \(^3J_{\text{CP}} = 8.7 \) Hz, \(t\text{BuC}_6\)), 53.4 (s, \(t\text{BuC}_4\)), 128.3 (d, overlapped with residual C\(_6\)D\(_6\) signal, \(p\text{-PhC}\)), 130.9 (d, \(^3J_{\text{CP}} = 2.7 \) Hz, \(m\text{-PhC}\)), 133.7 (d, \(^2J_{\text{CP}} = 9.8 \) Hz, \(o\text{-PhC}\)), 136.6 (d, \(^1J_{\text{CP}} = 84.8 \) Hz, ipso-\(\text{PhC}\)) ppm.

\(^{31}\text{P} \text{ NMR} \) (121.5 MHz, C\(_6\)D\(_6\)): \(\delta = 18.5 \) ppm.

\text{IR-Spektroskopie} \: \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\(^{-1}\).

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Synthesis of \([\text{NPN}^{t\text{Bu}}_2\text{Nd-Cl}]\) (14)

According to A4: from 197 mg of \([\text{NdCl}_3(\text{thf})_2]\) as a light-blue solid. Yield: 134 mg (40%).

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

\(^1\text{H} \text{ NMR} \) (300.1 MHz, C\(_6\)D\(_6\)): \(\delta = 6.40 \) (s br s, 36H, \(t\text{BuH}\)), 10.21 (br s, 4H, \(p\text{-PhH}\)), 10.91 (br s, 8H, \(m\text{-PhH}\)), 22.92 (s br s, 8H, \(o\text{-PhH}\)) ppm.

\(^{31}\text{P} \text{ NMR} \) (121.5 MHz, C\(_6\)D\(_6\)): \(\delta = 113.9 \) (br s) ppm.

\text{IR} \: \nu = 466 (s), 529 (s), 557 (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), 2950 (m), 3052 (w) cm\(^{-1}\).

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Synthesis of \([\text{NPN}^{t\text{Bu}}_2\text{Sm-Cl}]\) (15)

According to A4: from 200 mg of \([\text{SmCl}_3(\text{thf})_2]\) as a yellow solid. Yield: 188 mg (56%).

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

\(^1\text{H} \text{ NMR} \) (300.1 MHz, C\(_6\)D\(_6\)): \(\delta = 2.28 \) (s, 36H, \(t\text{BuH}\)), 7.93–7.98 (m, 4H, \(p\text{-PhH}\)), 8.11–8.13 (m, 8H, \(m\text{-PhH}\)), 11.69 (s, 8H, \(o\text{-PhH}\)) ppm.

\(^{31}\text{P} \text{ NMR} \) (121.5 MHz, C\(_6\)D\(_6\)): \(\delta = 81.8 \) (br s) ppm.
IR-Spektroskopie: $\tilde{v} = 464$ (s), 529 (s), 556 (m), 593 (s), 670 (s), 697 (s), 740 (s), 831 (s), 998 (w), 1027 (m), 1079 (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 $[(\text{NPN}^{\text{tBu}})_2\text{Gd-Cl}]$ (16)**

According to A4: from 132 mg of [GdCl$_3$] as a colourless solid. Yield: 236 mg (69%).

CHNCIGd: (C$_{40}$H$_{56}$ClN$_4$P$_2$Gd, MW: 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 $[(\text{NPN}^{\text{tBu}})_2\text{Tb-Cl}]$ (17)**

According to A4: from 133 mg of [TbCl$_3$] as a colourless solid. Yield: 272 mg (80%).

CHNCITb: (C$_{40}$H$_{56}$ClN$_4$P$_2$Tb, MW: 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%)

**Synthesis of $[(\text{NPN}^{\text{tBu}})_2\text{Yb-Cl}]$ (18)**

According to A4: from 140 mg of [YbCl$_3$] as a yellow solid. Yield: 121 mg (35%).

CHNCICyb (C$_{40}$H$_{56}$ClN$_4$P$_2$Yb, MW: 863.36): found (calcd.): C: 55.04% (55.65%), H: 6.99% (6.54%), N: 6.51% (6.60%), Cl: 4.31% (4.11%). Yb: 19.60% (20.04%)

$^1$H NMR (300.1 MHz, C$_6$D$_6$): $\delta = -18$ (br s, 36H, tBuH), 6.5 (br m, 20H, PhH) ppm.

$^{31}$P NMR (121.5 MHz, C$_6$D$_6$): $\delta = -142.5$ (br s) ppm.

**Synthesis of $[(\text{NPN}^{\text{tBu}})_2\text{Lu-Cl}]$ (19)**

According to A4: from 224 mg of [LuCl$_3$] as a colourless solid. Yield: 294 mg (85%).

CHNCILu: (C$_{40}$H$_{56}$ClN$_4$P$_2$Lu, MW: 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$_6$D$_6$): $\delta = 1.30$ (s, 36H, tBuH), 7.12−7.16 (m, 12H, m-/pPhH), 8.22−8.23 (m, 8H, oPhH) ppm.

$^{13}$C NMR (75.5 MHz, C$_6$D$_6$): $\delta = 35.0$ (d, $^3$J$_{CP}$ = 8.6 Hz, tBuC$_{Me}$), 53.4 (s, tBuC$_q$), 128.1 (d, overlapped with residual C$_6$D$_6$ signal, $p$-PhC), 130.9 (d, $^4$J$_{CP}$ = 2.5 Hz, $m$-PhC), 133.7 (d, $^2$J$_{CP}$ = 10 Hz, o-PhC), 136.5 (d, $^1$J$_{CP}$ = 85 Hz, $ipso$-PhC) ppm.

$^{31}$P NMR (121.5 MHz, C$_6$D$_6$): $\delta = 20.0$ (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 100K, for 13 and 19 with IPDS-I at 200K and 180K correspondingly. Data reduction was carried out using the IPDSI software or X-Area (Stoe). 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, Sir-92, and Sir-2004 programs and refined against $F_o^2$ by full-matrix least squares using SHELXL-97. Details of the X-ray structure determinations are listed in Table 3. CCDC no. 1414805 (4), 1414808 (6), 1414807 (7), 901056 (13), 901055 (19) and 1414806 (20*3C6D6) contain the supplementary crystallographic data for this paper.
Table 3. Details of the X-ray structure determinations of complexes 4, 6, 7, 13, 19 and 20*3C_6D_6.

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<td>1.85 to 26.19</td>
<td>2.57 to 25.50</td>
<td></td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>-23&lt;=h&lt;=23, -13&lt;=k&lt;=12, -28&lt;=l&lt;=25</td>
<td>-21&lt;=h&lt;=21, -12&lt;=k&lt;=10, -27&lt;=l&lt;=22</td>
<td>-23&lt;=h&lt;=23, -13&lt;=k&lt;=13, -28&lt;=l&lt;=29</td>
<td>-13&lt;=h&lt;=13, -16&lt;=k&lt;=15, 0&lt;=l&lt;=18</td>
<td>-13&lt;=h&lt;=13, -15&lt;=k&lt;=15, -18&lt;=l&lt;=18</td>
<td></td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>24581</td>
<td>31218</td>
<td>16180</td>
<td>16199</td>
<td>59927</td>
<td></td>
</tr>
<tr>
<td><strong>Completeness to θ=25.00°</strong></td>
<td>98.7%</td>
<td>100.0%</td>
<td>93.7%</td>
<td>99.7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>9447 / 0 / 484</td>
<td>9656 / 0 / 484</td>
<td>7588 / 0 / 433</td>
<td>7154 / 0 / 433</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Final R indices{I &gt; 2σ(I)}</strong></td>
<td>0.0679</td>
<td>0.0702</td>
<td>0.0577</td>
<td>0.0549</td>
<td>0.0780</td>
<td></td>
</tr>
<tr>
<td><strong>Goodness of fit on F²</strong></td>
<td>0.936</td>
<td>0.761</td>
<td>0.852</td>
<td>1.038</td>
<td>0.808</td>
<td></td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>0.0483, wR₁ = 0.0882</td>
<td>0.0340, wR₁ = 0.0838</td>
<td>0.0362, wR₁ = 0.0685</td>
<td>0.0353, wR₁ = 0.0645</td>
<td>0.0398, wR₁ = 0.0757</td>
<td></td>
</tr>
<tr>
<td><strong>Goodness of fit on F²</strong></td>
<td>0.0394</td>
<td>0.0362</td>
<td>0.0353</td>
<td>0.0353</td>
<td>0.1070</td>
<td></td>
</tr>
<tr>
<td>**R₁ = \sum</td>
<td></td>
<td>F_o</td>
<td>-</td>
<td>F_c</td>
<td></td>
<td>/\sum</td>
</tr>
</tbody>
</table>

* R₁ = \sum ||F_o| - |F_c||/\sum |F_o|; wR₁ = (\sum w(|F_o|^2 - |F_c|^2)^2) / \sum w(|F_o|^2) |^{1/2}
Acknowledgements

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Literature


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