Tetrahydropentalenyl-phosphazene constrained geometry complexes of rare-earth metal alkyls†

Noa K. Hangaly, Alexander R. Petrov, Michael Elfferding, Klaus Harms and Jörg Sundermeyer*

Reactions of Cp^MHPPh₂ (1, diphenyl(4,4,6,6-tetramethyl-1,5,6-tetrahydrocyclopentalen-2-yl)phosphane) with the organic azides Ad₃ and Dip₃ (Ad = 1-adamantyl; Dip = 2,6-di-iso-propylphenyl) led to the formation of two novel CpPN ligands: P-aminocyclopentadienylidene-phosphorane (Cp^MHPPh₂NHAd; LAdH) and P-cyclopentadienyl-iminophosphorane (Cp^MHPPh₂NAd; LAdH). Both were characterized by NMR spectroscopy and X-ray structure analysis. For both compounds only one isomer was observed. Neither possesses any detectable prototropic or elementotropic isomers. Reactions of these ligands with [Lu(CH₂SiMe₃)₃(thf)₂] or with rare-earth metal halides and three equivalents of LiCH₂SiMe₃ produced the desired bis(alkyl) Cp^MPN complexes: [(Cp^MPN)M(CH₂SiMe₃)₂] (M = Sc (3Ad, 4Ad, 5Ad, 6Ad), La (2Ad, 2Dip), Y (3Ad, 4Ad), Sm (4Ad), Nd (5Ad), Pr (6Ad), Yb (7Ad)). These complexes were characterized by extensive NMR studies for the diamagnetic and the paramagnetic complexes with full signal assignment. An almost mirror inverted order of the paramagnetic shifts has been observed for ytterbium complex 7Ad compared to 4Ad and 5Ad. For the assignment of the NMR signals ([4Ad : 1Ad : 2Ad : 5Dip : 3Dip] = 1 : 6 : 2 : 2 : 1) the ³¹P NMR signals were compared to other paramagnetic lanthanide complexes with the same ligand. 1Ad, 2Ad, 2Dip, 3Ad and 3Dip were characterized by X-ray structure analysis revealing a sterically congested constrained geometry structure.

Introduction

The organometallic chemistry of the rare-earth metals began in the middle of the last century with the synthesis of their tris-(cyclopentadienyl) derivatives by Wilkinson and Birmingham. Since then the cyclopentadienyl (Cp) ligand has remained one of the most ubiquitous ligands of this chemistry. For a long time, rare-earth organometallic chemistry has been dominated by metalocenes, especially when these complexes are used as precursors in various stoichiometric and catalytic processes. More recently, however, considerable attention has been directed towards rare-earth mono-cyclopentadienyl complexes. But the selective synthesis of monomeric rare-earth metal mono-Cp complexes is generally difficult. A great steric bulk of the Cp ligand is advantageous for a successful synthesis. In search of better ligand systems, wide variations of the aromatic cyclopentadienyl framework have been described in the literature. These variations include for example totally or partly substituted Cp rings and ancillary linked donor atoms like O, N, P or S. The latter are used to form constrained geometry complexes (CGCs).

In this work we describe the synthesis, NMR studies and molecular structures of two novel cyclopentadienyl-phosphazene (CpPN) ligands with a tetrahydropentalene unit: Cp^MHPPh₂NHAd (LAdH) and Cp^MHPPh₂NAd (LAdH). This tetrahydropentalene unit is very attractive as it is easily synthesized by condensation of NaCp with Ph₂PCH₂ and two equivalents of acetone. Compared to other sterically demanding cyclopentadienyls such as C₅Me₄R, it is cheap and can easily be synthesized on a large scale. The new ligands bear a sterically very demanding, well crystallizing, electron rich and rigid cyclopentadienyl ring. Therefore we are confident that these and related tetrahydropentalenyl ligands are good alternatives for the commonly used but expensive C₅Me₄R building blocks in organometallic chemistry.

Constrained geometry complexes with the cyclopentadienyl-silylamido (CpSiN) type ligands, initially developed by Bercaw and Okuda became one of the best developed classes of CGCs (Scheme 1; A). In contrast, however, constrained geometry rare-earth metal(m) complexes with different single-atom bridging units in the ligand system have received...
much less attention and have remained almost unexplored to date. Some examples are CpSiSIP complexes (B)\(^{14}\) and CpSiSC complexes (C)\(^{12}\) which have dianionic ligands. There are also some complexes bearing monoanionic ligands which are iso-electronically related to the classical dianionic CpSiN ligand system such as CpSiNP (D)\(^{13}\), CpSiSIPm (E)\(^{14}\) and the cyclopentadienyl-phosphorane (CpPN) (F) that is the focus of our current investigation.\(^{15-19}\)

Previously we reported a general and convenient synthetic protocol for a large variety of CpPN type ligands,\(^{20}\) and their use in the stabilization of highly reactive alkyls of rare-earth and group 4 metals has been claimed.\(^{21}\) Independently, related fluorenyl- and indenyl-phosphazene ligands (FluPN and IndPN) and their rhodium\(^{22}\) and zirconium\(^{23}\) complexes were presented by Bourissou and co-workers. The synthesis and characterization of a series of rare-earth metal constrained geometry CpPN complexes \([(\eta^1-\eta^1-C_5Me_4Me_2NAd)\{-M(\text{CH}_3\text{SiMe}_3)\}_2]\) (M = Sc, Y, La, Ln (Ce-Lu)) and their high catalytic activities in the intramolecular hydroamination/cyclization have been reported by us.\(^{15,17}\) Recently, the organo-metallic chemistry and catalysis in ethylene polymerization of rare-earth metal CpPN, IndPN and FluPN complexes was studied. CpPN ligands, with less steric bulkiness of the Cp-ring, lead to the coordination of THF, while IndPN adopt a \(\eta^1\)-bonding fashion and the more bulky FluPN-type ligands display a \(\eta^1\)-bonding mode.\(^{18}\) Moreover, the reactivity toward various substrates was recently studied and, among others, CpPN amide, hydride and terminal imido complexes were synthesized, characterized and their reactivity was probed.\(^{19}\)

These current developments reveal that CpPN type complexes appear to be a promising class of catalysts. Therefore it is of general and fundamental interest to develop novel, sterically most demanding and rigid CpPN type ligands as useful building blocks and to study their stabilizing properties for dialkyls of the smallest and larger rare-earth metal cations (Sc, Lu, Y, Yb, Sm, Nd and Pr). Besides synthetic and XRD structural aspects, the focus of this study will be on the beautiful \(^1\)H and \(^{13}\)C NMR spectra obtained from paramagnetic organometallic compounds carrying the chelating rigid Cp\(^{74}\)PPh\(_2\)NHAd (L\(_{\text{Ad}}\)H) and Cp\(^{74}\)HPPh\(_2\)NDip (L\(_{\text{Dip}}\)H) ligands with the tetrahydropentalenol unit. Assignment of ligand group shifts of paramagnetic organometallic lanthanide complexes is not routinely reported in literature, but it might become a very valuable tool for following catalytic steps.

### Results and discussion

#### Synthesis and characterization of the Cp\(^{74}\)PN-ligands

The ligands were prepared by a Staudinger reaction (Scheme 2) of the novel phosphane Cp\(^{74}\)HPPh\(_2\) (\(1\), diphenyl(4,4,6,6-tetramethyl-1,4,5,6-tetrahydropentalen-2-y1)phosphane)\(^{24}\) with organic azides (Ad\(_3\) and Dip\(_3\); Dip = 2,6-di-isopropylphenyl). It should be mentioned that compared to our previously published synthesis of \(1\) we could exchange the highly toxic TlCp by NaCp, which can easily be synthesized on a large scale out of Na and (CpH)\(_2\).\(^{25}\) The improved ligand synthesis is following the condensation of NaCp with one Ph\(_2\)PCl and two acetone molecules, which are cheap starting materials making the final Cp\(^{74}\)PN ligand very attractive as an alternative for commonly used but expensive ligands with a C\(_6\)Me\(_4\)R moiety.

The Staudinger reaction of the highly crowded Cp\(^{74}\)HPPh\(_2\) with Ad\(_3\) proceeds very slowly. Therefore, under classical Staudinger conditions a reaction time of 10 d is needed in refluxing THF, yielding L\(_{\text{Ad}}\)H (Cp\(^{74}\)PPH\(_2\)NHAd) in only 46% yield. Higher reaction temperatures accelerate the reaction and it was completed after only 2 d in refluxing toluene. The yellow crystalline compound L\(_{\text{Ad}}\)H was isolated from \(n\)-hexane in 75% yield. In contrast, the oxidation with the more electron-poor Dip\(_3\) was completed within 14 h in THF at room temperature. The desired, sterically demanding ligand L\(_{\text{Dip}}\)H (Cp\(^{74}\)HPPH\(_2\)NDip) was obtained in 78% yield after crystallization from cold acetonitrile.

Compared to L\(_{\text{Dip}}\)H, which is a highly air-sensitive substance with a melting point of 142.4–143.0 °C and a high solubility in \(n\)-hexane, compound L\(_{\text{Ad}}\)H is only moderately air-sensitive, has a higher melting point (176.5–177.0 °C) and is only marginally soluble in \(n\)-hexane. Further investigations by means of NMR spectroscopy and X-ray structure analysis show significant dissimilarities in their molecular compositions: compound L\(_{\text{Ad}}\)H occurs in the form of P-amino-cyclopentadienyl-phosphorane, whereas L\(_{\text{Dip}}\)H exists in the tautomeric form of a P-cyclopentadienyl-imino-phosphorane.

![Scheme 2](image-url)
NMR spectroscopy

The $^{31}$P NMR signal of L$_{Ad}$H (15.6 ppm) is essentially identical to those of compound C$_2$Me$_5$PR$_2$NH$_{Ad}$ (17.6 for R = Me$^{15}$ and 12.3 ppm for the main isomer in R = Ph$^{16}$ resp.). In contrast, compound L$_{Dip}$H shows a $^{31}$P NMR resonance at ~15.8 ppm. This chemical shift is in good agreement with the iminophosphorane tautomer IndP$_2$H$_2$NR (Ind = indenyl-1; $\delta_{P} = -8.3$ and ~16.5 ppm for R = Ph and Dip resp.). However, in contrast to C$_2$Me$_5$PPh$_2$NH$_{Ad}$, C$_2$Me$_5$HPMe$_2$NR ($R$ = SiMe$_3$, Dip)$^{20}$ and IndP$_2$H$_2$NR (R = Ph and Dip)$^{23}$ L$_{Ad}$H and L$_{Dip}$H show only one sharp resonance in the $^{31}$P NMR spectra, indicating the absence of isomers. Recently, we also observed only one tautomer in C$_2$Me$_5$HPR$_2$NC$_6$H$_3$R$^2$ ($R$ = Me, R$^2$ = iPr; R = Ph, R$^2$ = Me, iPr) at thermodynamic equilibrium.$^{18}$

The resonance of the NH-proton in L$_{Ad}$H at $\delta_{H}$ = 2.05 ppm appears as a doublet ($^2J_{HP}$ = 5.0 Hz). It does not correlate with any carbon atom in the molecule according to the HMQC correlation spectrum. This confirms the presence of an aminophosphorane. Unlike L$_{Ad}$H, compound L$_{Dip}$H shows four resonances in the aliphatic region (besides resonances of iminophosphorane tautomer IndP$_2$H$_2$NR ($\delta_{P} = -8.3$ and ~16.5 ppm for R = Ph and Dip resp.)). L$_{Ad}$H and L$_{Dip}$H show only one sharp resonance in the $^{31}$P NMR spectra, indicating the absence of isomers. Recently, we also observed only one tautomer in C$_2$Me$_5$HPR$_2$NC$_6$H$_3$R$^2$ ($R$ = Me, R$^2$ = iPr; R = Ph, R$^2$ = Me, iPr) at thermodynamic equilibrium.$^{18}$

Table 1 Selected bond lengths (Å) and angles (°) for L$_{Ad}$H and L$_{Dip}$H

|       | L$_{Ad}$H | L$_{Dip}$H |
|-------|-----------|------------|
| P1–N1 | 1.652(2)  | 1.556(2)   |
| P1–C1 | 1.704(2)  | 1.788(2)   |
| P1–C13 | 1.799(2)  | 1.819(2)   |
| P1–C19 | 1.801(2)  | 1.806(2)   |
| N1–C25 | 1.494(3)  | 1.408(2)   |
| C1–P1–N1 | 115.6(1) | 115.2(1)   |
| C13–P1–N1 | 102.6(1) | 113.2(1)   |
| C19–P1–N1 | 110.0(1) | 110.1(1)   |
| C1–P1–C13 | 112.5(1) | 106.6(1)   |
| C13–P1–C19 | 106.4(1) | 103.0(1)   |
| C19–P1–C1 | 109.3(1)  | 108.0(1)   |
| C1–P1–N1–C25 | 37.5(2) | 17.5(2)    |

The cyclopentadienyl rings of both ligands are essentially planar; the largest deviations from the ideal C$_5$ plane are $\Delta_{max} = 0.004(2)$ Å for L$_{Ad}$H and 0.006(2) Å for L$_{Dip}$H resp.

As anticipated the P–C$_{Cp}$ bond length in P$_2$ylide L$_{Ad}$H is quite short, P1–C1 1.704(2) Å, and can be compared with d(P–C$_{Cp}$) 1.718(2) Å in Ph$_3$P=CH$_2$H$_2$P$_2$NR (R = Ph, P$_2$ = C$_6$H$_5$)$^{26}$ while the P–N bond length 1.652(2) Å is rather long. This can be better compared with the values found in phosphonium salts [Ph$_3$P–NH(iso-Pr)]-Br (P–N = 1.621(3) Å)$^{27}$ The C–C bonds of the Cp ring of L$_{Ad}$H are conjugated (average bond length d(C–C) = 1.41 Å, maximum C–C bond difference d = 0.07 Å). The parameters resemble the expected values for a cyclopentadienylidene-aminophosphorane structure.

The structure of L$_{Dip}$H is unexceptional with a short P–N bond length of 1.552(2) Å, typical for imino-phosphoranes (compare: Ph$_3$P=N(2,6-C$_6$H$_3$) (1.553(2) Å)$^{28}$ and Ph$_3$P=N tert-Bu) (1.543(2) Å)$^{26}$.

Preparation and characterization of Cp$_{Th}$PN rare-earth metal alkyls

For the syntheses of the lutetium complexes, [Lu(CH$_2$SiMe$_3$)$_2$]$_2$(thf)$_3$ was used and the complexes were isolated in high yields as microcrystalline, colourless solids [[L$_{Ad}$]Lu(CH$_2$SiMe$_3$)$_2$] (2$_{Ad}$) and [[L$_{Dip}$]Lu(CH$_2$SiMe$_3$)$_2$] (2$_{Dip}$) (Scheme 3). For the...
other rare-earth metals (Sc, Y, Sm, Nd, Pr and Yb), the complexes were synthesized under essentially the same reaction conditions reported for \([\{\text{C}_5\text{Me}_4\text{PMe}_2\text{NAd}\}\text{M(CH}_2\text{SiMe}_3)_2\}\] complexes.\(^{15,17}\) Following this in situ protocol three equivalents of Li\(\text{CH}_3\text{SiMe}_3\) were added to a stirred suspension of an equimolar mixture of the respective \(\text{Cp}^n\text{PN}\)|H ligand (1\text{Ad}-H, 1\text{Dip}-H) and a rare-earth metal halide source in ether–toluene or ether–\(\eta^6\)-hexane at 0 °C. Filtration, solvent removal, extraction with \(n\)-hexane and crystallization afforded the \(\text{Cp}^n\text{PN}\) complexes \([\{\text{C}_5\text{Ad}\}\text{M(CH}_2\text{SiMe}_3)_2\}\] (M = Sc, Lu, Y, Sm, Nd) and \([\{\text{Dip}\}\text{M(CH}_2\text{SiMe}_3)_2\}\] (M = Sc (1\text{Py}), Y (3\text{Ad}), Sm (4\text{Ad}), Nd (5\text{Ad}), Pr (6\text{Ad}), Yb (7\text{Ad})). Complexes \([\{\text{Dip}\}\text{M(CH}_2\text{SiMe}_3)_2\}\] (M = Sc (1\text{Py}), Y (3\text{Ad})) (Scheme 3).

The complexes 1\text{Ad}-7\text{Ad} and 1\text{Dip}-3\text{Dip} are fairly air- and moisture-sensitive solids and show good solubility in saturated hydrocarbons and high solubility in ethers and aromatic solvents. All complexes were fully characterized by NMR spectroscopy and elemental analysis, and complexes 1\text{Ad}, 2\text{Ad}, 3\text{Ad}, 2\text{Dip} and 3\text{Dip} were also characterized by X-ray structure analysis.

The complexes with ligand 1\text{Dip} reveal a different thermostability in comparison with those bearing ligand 1\text{Ad}. Compounds 1\text{Dip}-3\text{Dip} appear to be less stable than the analogue complexes 1\text{Ad}-3\text{Ad}. Complexes 1\text{Dip} and 2\text{Dip} are still stable at room temperature in solution but decompose fast at elevated temperatures. Yttrium complex 3\text{Dip} is not stable at room temperature both in solution and in the solid state. Thus, for larger metals such as samarium, no stable complex could be isolated with this ligand.

Multinuclear NMR spectroscopy of \(\text{CpPN}\) complexes

All complexes were established by NMR spectroscopy. The \(^{31}\text{P}\) NMR spectra of diamagnetic 1\text{Ad}-3\text{Ad} and 1\text{Dip}-3\text{Dip} complexes appear in the region 6.4–7.3 and 8.9–9.3 ppm, respectively. The \(^{31}\text{P}\) resonances of the paramagnetic complexes 4\text{Ad}-7\text{Ad} are broadened signals at \(\delta = 24.4\) (4\text{Ad}, M = Sm), –92.00 (5\text{Ad}, M = Nd), –66.0 (6\text{Ad}, M = Pr) and –117.2 (7\text{Ad}, M = Yb).

According to the \(^{1}\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy, 1\text{Ad}-7\text{Ad} and 1\text{Dip}-3\text{Dip} crystallize without coordinated solvent molecules, whereas complexes with less steric bulkiness of the \(\text{Cp}\) ring in \([\{\text{C}_5\text{H}_4\text{PPh}_2\text{NDip}\}\text{M(CH}_2\text{SiMe}_3)_2\}\] (M = Lu, Y, Sm, Nd) are isolated with a coordinated THF molecule.\(^{18}\) \(^{1}\text{H}\) NMR spectra of the diamagnetic 1\text{Ad}-3\text{Ad} and 1\text{Dip}-3\text{Dip} complexes are very similar (for spectra see ESI†); therefore only some main aspects should be discussed here. Because of the \(\eta^6\)-coordination of the \(\text{Cp}\) ring, \(\text{Cp}\) protons appear as one doublet at about 6.2 ppm with a \(J_{\text{HP}}\) of about 3 Hz. The signals of the methyl and methylene group in the annulated five membered ring are, because of their fixed \(\text{exo}\) and \(\text{endo}\)-positions, chemically inequivalent. Consequently, the methyl group resonances appear as two singlets and the resonances of the methylene group appear as two doublets (\(J_{\text{HH}}\) about 12 Hz). Silylmethylene protons are, like in \([\{\text{C}_5\text{Me}_4\text{PMe}_2\text{NAd}\}\text{M(CH}_2\text{SiMe}_3)_2\}\], diastereotopic and for that magnetically non-equivalent. They appear as two doublets in all spectra. For yttrium complexes the protons appear as two doublet of doublets due to \(\text{Y}-\text{H}\) coupling (\(J_{\text{HH}} = 11.2\) Hz, \(J_{\text{YH}} = 2.7\) Hz). Furthermore, in this case the methylene carbons show a doublet with a \(J_{\text{HC}}\) coupling of 40.9 Hz in the \(^{13}\text{C}\) NMR spectrum. Both are in the same range as shown in the literature, for example for complexes \([\{\text{C}_5\text{Me}_4\text{PMe}_2\text{NAd}\}\text{Y(CH}_2\text{SiMe}_3)_2\}\] CCG.\(^{30}\)

Lanthanides have a short relaxation time for the unpaired electron so that little line broadening occurs. The mechanism of action within the lanthanides is principally the pseudocontact mechanism, which falls off in a predictable manner with distance (1/\(R^6\)).\(^{31}\) The direction of shift depends on the anisotropy in the susceptibility, but it also depends on the angle between the principal axis of susceptibility and the vector \(R\) to the nucleus. Despite this principal insight, systematic NMR studies on paramagnetic organolanthanide compounds are not a routine characterization method.\(^{32}\) NMR studies are typically restricted to the diamagnetic derivatives (Lu(III), Sc, Y, and La(III))),\(^{3,4}\) whereas some of the best catalysts are obtained with the paramagnetic metal cations like neodymium or samarium.\(^{3,4}\) Here we report \(^{1}\text{H}\) NMR spectra recorded in \(\text{C}_6\text{D}_6\) at 27 °C of paramagnetic complexes 4\text{Ad}-7\text{Ad} that show defined, relatively sharp signals with distinctive paramagnetic shifts, indicating a rigid constrained-geometry structure in solution. The assignment of the NMR signals for complexes 4\text{Ad}-6\text{Ad} requires 2D NMR experiments due to the paramagnetic shift. The signals are summarized in Table 2. The width

| Table 2 \(^1\text{H}\) NMR resonances (\(\delta/\text{ppm}\)) and coupling constants (\(J/\text{Hz}\)) of the paramagnetic complexes 4\text{Ad}–7\text{Ad} in \(\text{C}_6\text{D}_6\) at 27 °C |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| \(4\text{Ad}\) (\(f^3\text{Sm}^{13}\)) | \(5\text{Ad}\) (\(f^2\text{Nd}^{13}\)) | \(6\text{Ad}\) (\(f^3\text{Pr}^{13}\)) | \(7\text{Ad}\) (\(f^{13}\text{Yb}^{13}\)) |
| 12.65, 12.52 | 33.48, 30.19 | 99.51, 93.03 | –239.26, –225.45 |
| 10.87 | 12.03 | 30.03 | –117.29 |
| 10.34 | 15.40 | 20.73 | –28.92 |
| 7.94 (7.5) | 9.92 | 12.08 (6.8) | –7.77 |
| 7.74 (7.4) | 9.13 | 10.63 (6.8) | –3.77 |
| 1.70 | 4.30 | 6.08 | –29.57 |
| –0.56 | –4.93 (10.2) | –10.72 (10.5) | 38.85 |
| –0.73 | –6.47 | –14.21 | 51.24 |
| –1.12 (11.6) | –7.52 (11.9) | –14.90 (10.5) | 49.65 |
| –1.29 | –5.48 | –11.93 | 41.74 |
| –1.58 | –13.41 | –21.50 | 65.27 |
| –2.15 (12.7) | –12.29 (8.5) | –23.81 (10.0) | 81.49 |
| –4.80 (12.7) | –24.05 (10.2) | –45.27 (10.0) | 148.51 |
| β–AdH | –27.26 | –52.96 | 162.74 |
of the resonances at half-height ($\nu_{1/2}$) is shown in the Experimental section.

In Fig. 2, the NMR spectrum of f$^3$Pr$^{3+}$ complex 6$_{\text{Ad}}$ which ranges from +100 to −53 ppm is shown as a representative example (for other spectra see ESI†).

All resonances of the adamantyl and annulated five-ring moiety protons are shifted upfield while the CH$_2$SiMe$_3$ alkyl groups, the phenyl substituents on the phosphorus and the cyclopentadienyl protons are shifted downfield.

Because of the paramagnetic shifting, the signals of the phenyl protons are distributed over a wide range. The o-PhH resonances are further downfield shifted due to the relatively small distance to the paramagnetic metal centre. The m-PhH and p-PhH signals are less shifted than they are located further away from the metal centre. Using the dependence of the paramagnetic shift on the distance to the paramagnetic metal centre, one can specify the methylene and methyl group resonances of the annulated five ring moiety. The methylene and methyl group resonances that are more upfield shifted are the ones closer to the paramagnetic centre (exo-proton/group) leaving the other to be the endo-proton/group.

For the Sm(II) complex the $^{13}$C NMR spectrum was showing similar but only slightly paramagnetically shifted signals compared to those of the diamagnetic homologues.

CpPN complexes of ytterbium(II) have never been described before. The $^1$H NMR spectrum of f$^3$Yb$^{3+}$ complex 7$_{\text{Ad}}$ reaches from −240 to +163 ppm but still shows all the expected defined signals. For unambiguous assignment of all the NMR signals we also synthesized the new complex [C$_5$Me$_4$PMe$_2$NAd]Yb(CH$_2$SiMe$_3$)$_2$] (7). Similar to 7$_{\text{Ad}}$ the related complex 7 reveals a $^{31}$P NMR signal at $\delta = −133.1$ ppm. Integration of corresponding $^1$H NMR signals of 7$_{\text{Ad}}$ and 7 of the same paramagnetic shift region allowed the assignment of all signals. Both spectra show an almost mirror inverted order of shifts compared to all other paramagnetic complexes [(C$_5$PN)M(CH$_2$SiMe$_3$)$_2$] (M = Sm (4$_{\text{Ad}}$), Nd (5$_{\text{Ad}}$), Pr (6$_{\text{Ad}}$)) or with [(C$_5$Me$_3$PMe$_2$NAd)M(CH$_2$SiMe$_3$)$_2$]$_7$. In Fig. 3, the NMR spectrum of 7$_{\text{Ad}}$ is shown as an example (for 7 see ESI†). The analogue praseodymium complex (6$_{\text{Ad}}$) displays a downfield shift of the diastereotopic protons Pr−CH$_2$−SiMe$_3$ from 93.03 and 99.51 ppm and an upfield shift of the adamantyl and annulated five-ring moiety protons to the range between −10 and −53 ppm (Fig. 2), whereas for 7$_{\text{Ad}}$ both are shifted to the contrary way: the diastereotopic proton signals are shifted strongly upfield to −225.45 and −239.26 ppm and the adamantyl and annulated five-ring moiety protons are shifted strongly downfield to the range between 38 and 163 ppm. This trend can also be assigned for the other proton signals. It is a consequence of the sign variation of spin densities and therefore of the chemical shift within the lanthanide series.‡

**Molecular structures of Cp$^3$PN complexes**

The molecular structures of 1$_{\text{Ad}}$•3$_{\text{Ad}}$, 2$_{\text{Dip}}$ and 3$_{\text{Dip}}$ were established by X-ray structure analyses. Single crystals were obtained by cooling saturated n-hexane (2$_{\text{Dip}}$ and 3$_{\text{Dip}}$) or n-pentane (1$_{\text{Ad}}$) solution to −30 °C. One pentane molecule is incorporated in the unit cell of structure 1$_{\text{Ad}}$. Single crystals of 2$_{\text{Ad}}$ were obtained from benzene at room temperature with one solvent molecule per unit cell. Single crystals of 3$_{\text{Ad}}$ were obtained by slowly evaporating a toluene solution, while one toluene molecule is incorporated in the unit cell. Complexes 1$_{\text{Ad}}$•3$_{\text{Ad}}$ crystallize in the triclinic space group P1 with the two formal units in the related complex 7. Similar to 7$_{\text{Ad}}$ the related complex 7 reveals a $^{31}$P NMR signal at $\delta = −133.1$ ppm. Integration of the resonances at half-height ($\nu_{1/2}$) is shown in the Experimental section.

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CpPN complexes of ytterbium(II) have never been described before. The $^1$H NMR spectrum of f$^3$Yb$^{3+}$ complex 7$_{\text{Ad}}$ reaches from −240 to +163 ppm but still shows all the expected defined signals. For unambiguous assignment of all the NMR signals we also synthesized the new complex [C$_5$Me$_4$PMe$_2$NAd]Yb(CH$_2$SiMe$_3$)$_2$] (7). Similar to 7$_{\text{Ad}}$ the related complex 7 reveals a $^{31}$P NMR signal at $\delta = −133.1$ ppm. Integration of corresponding $^1$H NMR signals of 7$_{\text{Ad}}$ and 7 of the same paramagnetic shift region allowed the assignment of all signals. Both spectra show an almost mirror inverted order of shifts compared to all other paramagnetic complexes [(C$_5$PN)M(CH$_2$SiMe$_3$)$_2$] (M = Sm (4$_{\text{Ad}}$), Nd (5$_{\text{Ad}}$), Pr (6$_{\text{Ad}}$)) or with [(C$_5$Me$_3$PMe$_2$NAd)M(CH$_2$SiMe$_3$)$_2$]$_7$. In Fig. 3, the NMR spectrum of 7$_{\text{Ad}}$ is shown as an example (for 7 see ESI†). The analogue praseodymium complex (6$_{\text{Ad}}$) displays a downfield shift of the diastereotopic protons Pr−CH$_2$−SiMe$_3$ from 93.03 and 99.51 ppm and an upfield shift of the adamantyl and annulated five-ring moiety protons to the range between −10 and −53 ppm (Fig. 2), whereas for 7$_{\text{Ad}}$ both are shifted to the contrary way: the diastereotopic proton signals are shifted strongly upfield to −225.45 and −239.26 ppm and the adamantyl and annulated five-ring moiety protons are shifted strongly downfield to the range between 38 and 163 ppm. This trend can also be assigned for the other proton signals. It is a consequence of the sign variation of spin densities and therefore of the chemical shift within the lanthanide series.‡

**Molecular structures of Cp$^3$PN complexes**

The molecular structures of 1$_{\text{Ad}}$•3$_{\text{Ad}}$, 2$_{\text{Dip}}$ and 3$_{\text{Dip}}$ were established by X-ray structure analyses. Single crystals were obtained by cooling saturated n-hexane (2$_{\text{Dip}}$ and 3$_{\text{Dip}}$) or n-pentane (1$_{\text{Ad}}$) solution to −30 °C. One pentane molecule is incorporated in the unit cell of structure 1$_{\text{Ad}}$. Single crystals of 2$_{\text{Ad}}$ were obtained from benzene at room temperature with one solvent molecule per unit cell. Single crystals of 3$_{\text{Ad}}$ were obtained by slowly evaporating a toluene solution, while one toluene molecule is incorporated in the unit cell. Complexes 1$_{\text{Ad}}$•3$_{\text{Ad}}$ crystallize in the triclinic space group P1 with the two formal units in
the unit cell (Fig. 4). In contrast to $1_{Ad}$ the different incorporated solvent molecules in structures $2_{Ad}$ and $3_{Ad}$ have little effect on the unit cell and for that they are isostructural. Structures $2_{Dip}$ and $3_{Dip}$ are also isostructural and crystallize in the orthorhombic space group $Pbca$ with 8 formal units in the unit cell. Selected bond lengths ($\text{Å}$) and angles (°) for $1_{Ad}$–$3_{Ad}$, $2_{Dip}$ and $3_{Dip}$ are presented in Table 3. In the structure of the complexes $2_{Dip}$ and $3_{Dip}$ one of the CH$_2$SiMe$_3$ groups is disordered and treated with an occupancy factor of 56 : 44 and 62 : 38, respectively (Fig. 5).

Despite the sterically demanding Cp-moiety $1_{Ad}$–$3_{Ad}$, $2_{Dip}$ and $3_{Dip}$ reveal that the Cp ring coordinates to the metal centre in a typical $\eta^5$ mode, while 1dPN adopt an $\eta^1$-bonding fashion and the more bulky FluPN-type ligands have a rare $\eta^1$-bonding mode.$^{18}$ In the solid state, all complexes adopt mononuclear structures, in which the metal atoms reveal a pseudo-tetrahedral coordination by the $\eta^5$-bonded C5-ring and the nitrogen atom of the CpPN-ligand together with two $\sigma$-bonded alkyl groups. The pseudo-tetrahedral environment around the metal centre can be shown by comparison of the CH$_2$SiMe$_3$–M–N, C(CH$_2$SiMe$_3$)$_2$–M–N, C(CH$_2$SiMe$_3$)$_2$–M–C(CH$_2$SiMe$_3$)$_2$ bond angles, which are all very close to 109°.

The average M–CH$_3$ bond lengths are comparable to those reported for [M(CH$_2$SiMe$_3$)$_2$L] complexes (for M = Sc;$^{33}$ Lu;$^{34}$ Y).$^{35}$ The P–C1 bond lengths in $1_{Ad}$–$3_{Ad}$ (1.775(2), 1.775(2) and 1.776(2) Å) are longer than in the free ligand (1.703(2) Å), while the P–N bonds are essentially shorter (1.603(2), 1.596(2) and 1.605(2) Å versus 1.653(2) Å for $1_{Ad}$). However, for $2_{Dip}$ and $3_{Dip}$ P–C1 bonds (1.767(4) and 1.758(4) Å) are shorter (1.788(2) Å) and P–N bonds (1.626(4) and 1.609(3) Å) longer (1.556(2) Å). The reason for this different behaviour is the different tautomeric forms of the free ligand.

The $C_{pcentr.}$–M–N-angles ($M = 1_{Ad}$: 97.5; $2_{Ad}$: 93.9; $3_{Ad}$: 92.4; $2_{Dip}$: 92.2; $3_{Dip}$: 90.2°) are similar to those of [C$_2$Me$_4$PMe$_2$-
Table 3  Selected bond lengths (Å) and angles (°) for 1Ad, 2Ad, 3Ad, 2Dip and 3Dip

|      | 1Ad   | 2Ad   | 3Ad   | 2Dip  | 3Dip  |
|------|-------|-------|-------|-------|-------|
| P1–N1| 1.603(2)| 1.596(2)| 1.605(2)| 1.623(3)| 1.610(3)|
| P1–C1| 1.775(2)| 1.775(2)| 1.776(2)| 1.767(4)| 1.758(3)|
| M–N  | 2.210(2)| 2.288(2)| 2.339(2)| 2.293(3)| 2.342(3)|
| M–C(CH2SiMe3)1 | 2.236(2) | 2.348(3) | 2.407(2) | 2.347(4) | 2.40(2) |
| M–C(CH2SiMe3)2 | 2.215(2) | 2.349(2) | 2.409(2) | 2.317(4) | 2.400(3) |
| M–Z  | 2.388  | 2.371  | 2.419  | 2.409  | 2.455  |
| C1–P1–N1 | 101.0(1) | 102.4(1) | 102.6(1) | 100.7(2) | 101.3(1) |
| Z–M–N1 | 97.5  | 93.9  | 92.4  | 92.2  | 90.2  |
| C(CH2SiMe3)1–M–N1 | 115.7(1) | 103.4(1) | 103.4(1) | 101.7(2) | 100.2(6) |
| C(CH2SiMe3)1–M–N1 | 102.6(1) | 112.8(1) | 115.2(1) | 115.4(1) | 117.3(1) |
| C(CH2SiMe3)2–M–C(CH2SiMe3)1 | 104.1(1) | 107.7(1) | 108.6(1) | 100.5(1) | 100.5(6) |
| C1–P1–N1–C25 | -172.2(2) | 174.5(2) | -173.3(2) | 155.3(3) | 156.0(3) |

Conclusions

A new sterically most demanding CpPN chelate ligand system, cheaper than all tetramethyl-based building blocks and therefore more privileged to provide constrained-geometry complexes and catalysts of many more metals, has been developed. By condensation of NaCp with Ph2PCl and with two molecules of acetone, followed by carbolithiation and Staudinger reaction of the phosphane Cp™HPPPh2 (1, diphenyl(4,4,6,6-tetramethyl-1,4,5,6-tetrahydropentalen-2-yl)phosphane) with organic azides (AdN3 and DipN3; Ad = 1-adamantyl; Dip = 2,6-di-isopropylphenyl), the two novel chelate ligands Cp™HPPPh2NHAd (1AdH) and Cp™HPPPh2NDip (1DipH) were obtained in high selectivity and yields. Depending on the substituent at the nitrogen atom, they occur either in the P-amino-cyclopentadienylidene-phosphorane (R = Ad) or in the P-cyclopentadienyliminophosphorane (R = Dip) tautomeric form. Neither possesses any NMR detectable prototropic or elementotropic isomers. The rare-earth metal complexes were synthesized following a one-pot protocol, which combines deprotonation and salt elimination methods by addition of 3 equivalents of LiCH2SiMe3 as a base/ligand to a stirred mixture of the corresponding THF or DME solvated rare-earth metal trihalide and the appropriate {Cp™PN}H ligand. The very short synthetic protocol allows the successful isolation of the highly reactive and labile alkyl complexes of early lanthanides, which are usually prone to decompose in solution at ambient temperature. All complexes [{Cp™PN}M(CH2SiMe3)2] (M = Sc (1Ad), 1Dip), Lu (2Ad, 2Dip), Y (3Ad, 3Dip), Sm (4Ad), Nd (5Dip), Pr (6Ad), Yb (7Ad)) were isolated as microcrystalline solids and were completely characterized by microanalysis and partially by X-ray crystal structure determination. As a non-routine characterization method for organolanthanide complexes an extensive NMR study of a series of paramagnetic complexes with assignment of all signals is presented. Paramagnetic complexes Sm (4Ad), Nd (5Dip), Pr (6Ad) reveal an almost mirror inverted signal order compared to previously unknown ytterbium(III) CpPN complexes 7Ad or its counterpart [{η3-η5-CpMe4PMe2NAd}Yb(CH2SiMe3)2] 7.

Experimental section

General procedures

All manipulations were performed under purified argon or nitrogen using standard high vacuum or Schlenk- or Glovebox-techniques. Solvents were dried and distilled under argon employing standard drying agents. All organic reagents were purified by conventional methods. NMR spectra were recorded.
Suitable crystals were obtained from a concentrated benzene solution at room temperature (LAdH, 2Ad), by cooling concentrated n-hexane (2Dip and 3Dip) or n-pentane (1Ad) solution to −30 °C and by slow evaporation of toluene solution (3Ad). Crystal data were collected with a Stoe-IPDS area-detector diffractometer using graphite-monochromatised Mo-Kα-radiation (λ = 0.71073 pm) at 193 K (LAdH, 3Ad, 2Dip) or with a Stoe IPDS2 diffractometer at 100 K. Data reduction was carried out using the IPDSI software or X-Area (Stoe). The data were empirically corrected for absorption and other effects by using multiscans, except for compound LAdH, where no improvement in the refinement was achieved through its application. The structures were solved by direct methods (Sir-92, Sir-2004, and SHELEXS-97) and refined by full-matrix least-squares techniques against F2 (SHELXL-97). C Bonded hydrogen atoms were included in idealized positions and refined with fixed isotropic displacement factors. The N-bound hydrogen atom of LAdH was located and refined isotropically. The program PLATON was used to check the results of the X-ray analyses. Diamond was used for 30% thermal ellipsoid representations.

Synthesis of Cp^3HPPH3 (1). To 9.43 g Na(C2H5)2 (108 mmol, 1.03 eq.) in 200 mL of n-pentane at 0 °C, 23.16 mL of PPH3Cl (105 mmol, 1.00 eq.) was added. The mixture was stirred for 16 h at ambient temperature, and then 10 mL of ethanol-1,2-diol was added under vigorous stirring. The solution was decanted from the precipitate, the precipitate was washed twice with 20 mL of n-pentane, and the solvent of the transferred solution was evaporated in a vacuum. The following steps were carried out according to the literature, while spectroscopic features match perfectly with the reported ones.

Synthesis of ligand LAdH. To a solution of phosphine 1 Cp^3HPPH3 (2.40 g, 6.93 mmol, 1.00 eq.) in 30 mL of toluene, AdN3 (1.35 g, 7.62 mmol, 1.10 eq.) was added and stirred at 120 °C for 17 h. The colour of the reaction mixture progressively turns brown. The reaction proceeding was monitored by 31P NMR spectroscopy. The solvent was completely removed in a vacuum and the oily residue was dissolved in 10 mL of n-hexane yielding a clear dark brown solution. Upon sonification of the n-hexane solution a yellow powder precipitated. It was filtered off, washed with 3 mL of n-hexane and dried in a vacuum. Yield: 2.33 g (470 mmol, 68%). M.p. = 176.5–177.0 °C. 1H NMR (300.1 MHz, CD2Cl2): δ = 1.44 (s, 6H, δ-AdH), 1.53 (s, 6H, β-AdH), 1.68 (s, 12H, CMe2), 1.80 (br s, 3H, γ-AdH), 2.05 (d, 3JCP = 5.0 Hz, 1H, NH), 2.46 (s, 2H, CH2(CMe2)), 6.17 (d, 3JCP = 3.1 Hz, 2H, CPhH), 7.00–7.03 (m, 6H, m-p-PhH) ppm. 13C{1H} NMR (75.5 MHz, CD2Cl2): δ = 30.4 (s, γ-AdC), 33.4 (s, CMe2), 36.2 (s, δ-AdC), 39.3 (d, 3JCP = 1.3 Hz, CMe2), 44.5 (d, 3JCP = 4.0 Hz, β-AdC), 54.0 (d, 3JCP = 2.0 Hz, α-AdC), 65.0 (s, CH2(CMe2)), 80.8 (d, 3JCP = 116.1 Hz, α-CPhC), 106.6 (d, 3JCP = 16.0 Hz, β-CPhC), 128.5 (d, 3JCP = 12.3 Hz, m-PhC), 131.7 (d, 3JCP = 2.7 Hz, p-PhC), 131.9 (d, 3JCP = 105.3 Hz, ipso-PhC), 132.9 (d, 3JCP = 10.5 Hz, o-PhC), 146.8 (d, 3JCP = 18.5 Hz, γ-CPhC) ppm. 31P{1H} NMR (121.5 MHz, CD2Cl2): δ = 15.6 (s) ppm. EI-MS: m/z (%) = 495 (70.1) [M⁺], 480 (100) [M⁺ – Me⁺], 466 (52) [M⁺ – 2 Me⁺], 135 (22.1) [Ad⁺]. Anal. calc. for C45H34P3N: C 82.38, H 8.54, N 2.83; found C 81.40, H 8.45, N 2.59.

Synthesis of ligand LAdH. To a solution of Cp^3HPPH3 (6.59 g, 19.0 mmol, 1.00 eq.) in 75 mL of THF, DipN3 (4.46 g, 21.9 mmol, 1.15 eq.) was added and stirred overnight at room temperature, whereupon N2-evolution occurs. Removal of the solvent in a vacuum yielded a foamy residue. The compound was crystallized from acetonitrile at ambient temperature. A pale rose, crystalline solid was obtained. Yield: 7.51 g (14.4 mmol, 76%). M.p. = 142.5–143.0 °C. 1H NMR (300.1 MHz, CD2Cl2): δ = 1.00 (s, 6H, CMe6), 1.03 (s, 6H, CMe6), 1.18 (d, 3JHH = 7.0 Hz, 12H, Me2CH), 1.91 (s, 2H, CH2(CMe2)), 3.08 (s, 2H, CPhCH2), 3.66 (sept, 3JCP = 6.8 Hz, 2H, Me2CH), 6.77 (d, 3JHP = 8.5 Hz, 1H, CPhH), 7.03–7.06 (m, 6H, m-/p-PhH), 7.07–7.12 (m, 1H, p-DipH), 7.25 (d, 3JHH = 7.4 Hz, 2H, m-DipH), 7.79–7.87 (m, 4H, o-PhP) ppm. 13C{1H} NMR (75.5 MHz, CD2Cl2): δ = 24.1 (s, Me6CH), 29.1 (s, Me6CH), 29.9 (s, CMe6), 30.3 (s, CMe6), 37.1 (d, 3JCP = 10.4 Hz, β-CPhC), 40.0 (s, CMe6), 41.8 (s, CMe6), 61.6 (s, CH2(CMe2)), 119.9 (d, 3JCP = 3.3 Hz, m-DipC), 123.2 (d, 3JCP = 2.2 Hz, m-DipC), 128.6 (d, superimpose with residual protons of C6D6, p-DipC), 131.1 (d, 3JCP = 2.5 Hz, m-PheC), 132.3 (d, 3JCP = 9.6 Hz, o-PheC), 134.6 (d, 3JCP = 106.4 Hz, ipso-PheC), 140.7 (d, 3JCP = 105.3 Hz, β-PheC), 142.6 (d, 3JCP = 100.0 Hz, α-PheC), 143.1 (d, 3JCP = 6.9 Hz, ipso-DipC), 145.5 (s, o-DipC), 155.3 (d, 3JCP = 14.5 Hz, γ-PheC), 163.2 (d, 3JCP = 6.2 Hz, γ-CPhC) ppm. 31P{1H} NMR (121.5 MHz, CD2Cl2): δ = −15.8 (s) ppm. EI-MS: m/z (%) = 521 (47.0) [M⁺], 506 (31.6) [M⁺ – Me⁺], 485 (95.2) [PhP⁺], Anal. calc. for C45H32P3N: C 72.13, H 8.52, N 2.88.
To a stirred suspension of [ScCl₃(thf)] or [MCl₃(dme)][{C₅Me₄PMe₂NAd}Yb(CH₂SiMe₃)₂] (0.50 mmol, 1.00 eq.) and the protonated ligand (0.50 mmol, 1.00 eq.) in 15 mL of ether, a solution of LiCH₂SiMe₃ (1.50 mmol, 3.00 eq.) in 10 mL of toluene was added dropwise at 0 °C. The reaction mixture was stirred at 0 °C for another 0.5 h and concentrated in a vacuum to half of the original volume. LiCl was filtered off over Celite®. The solvent was stripped off, whereupon a colourless foamy solid forms, which was crystallized from n-hexane. Storage at −30 °C followed by filtration and drying in a vacuum resulted in isolation of a microcrystalline solid.

**Analytical data for [(L₁₆)Sc(CH₂SiMe₃)₂] (1Ad).** Yield: 251 mg (0.35 mmol, 70%) of a colourless, microcrystalline solid. [H NMR (300.1 MHz, C₆D₆); δ = −0.39 (dd, ²J₉H = 11.2 Hz, ²J₇H = 2.7 Hz, 2H, Y-HCH), −0.04 (dd, ²J₉H = 11.2 Hz, ²J₇H = 2.7 Hz, 2H, Y-HCH), 0.47 (s, 18H, SiMe₃), 1.18 (s, 6H, MeC₆H₅), 1.45 (d, ²J₉H = 12.0 Hz, 3H, δ-AdH), 1.56 (d, ²J₉H = 12.0 Hz, 3H, δ-AdH), 1.68 (s, 6H, MeC₆H₅), 1.97–2.01 (m, 4H, γ-AdH superimpose with 1H, HCH(CMe₂)₃), 2.17 (d, ²J₉H = 2.0 Hz, 6H, β-AdH), 2.33 (d, ²J₉H = 13.0 Hz, 1H, HCH(CMe₂)₃), 5.94 (d, ²J₉H = 2.8 Hz, 2H, CPh₃), 7.00–7.07 (m, 6H, m-p-Ph₃Ph), 7.83–7.88 (m, 4H, o-Ph₃Ph) ppm. [³¹P{¹H}] NMR (75.5 MHz, C₆D₆); δ = 0.6 (s, 3P), 30.7 (s, γ-AdC), 32.3 (s, MeC₆H₅), 32.5 (s, MeC₆H₅), 36.4 (s, δ-AdC), 40.4 (s, MeC₆H₅), 40.4 (s, Sc-C₆H₅), 47.3 (d, ²J₉P = 8.3 Hz, β-AdC), 56.1 (d, ²J₉P = 7.1 Hz, α-AdC), 62.9 (s, CH₃(CMe₂)₃), 94.5 (d, ²J₉P = 114.4 Hz, α-CPc), 107.1 (d, ²J₉P = 12.9 Hz, β-CPc), 128.5 (d, ²J₉P = 11.9 Hz, p-Ph₃Ph), 130.9 (d, ²J₉P = 86.9 Hz, i-Ph₃Ph), 132.5 (d, ²J₉P = 2.8 Hz, m-Ph₃Ph), 133.5 (d, ²J₉P = 10.5 Hz, o-Ph₃Ph), 150.3 (d, ²J₉P = 13.7 Hz, γ-CPc) ppm. [³¹P{¹H}] NMR (121.5 MHz, C₆D₆); δ = 7.3 (s) ppm. Anal. calc'd: C₆H₁₃N₃PSi₂. C 10.68, H 7.35, N 1.66; found: C 10.65, H 7.34, N 1.61. General procedure for the preparation of complexes [[Cp³P₂Ph₃NR]M(CH₂SiMe₃)₂] (M = Sc (R = Ad: 1Ad), R = Dip: 1Dip, Y (R = Ad: 3Ad), R = Dip: 3Dip), Sm (R = Ad: 4Ad), Nd (R = Ad: 5Ad), Pr (R = Ad: 6Ad), Yb (R = Ad: 7Ad)) and [[C₆Me₅PMe₄NAd][Yb(CH₂SiMe₃)₂]] 7

**Analytical data for [(L₁₆)Sm(CH₂SiMe₃)₂] (4Ad).** Yield: 170 mg (0.21 mmol, 41%) of a yellow, microcrystalline solid. [H NMR (300.1 MHz, C₆D₆); δ = −7.18 (s, 6H, ν₁₂ = 10 Hz, β-AdH), −4.80 (d, ²J₉H = 12.7 Hz, 1H, endo-HCH(CMe₂)₃), −2.15 (d, ²J₉H = 12.7 Hz, 1H, exo-HCH(CMe₂)₃), −4.58 (s, 6H, ν₃ = 4 Hz, endo- MeC₆H₅), −1.29 (s, 6H, ν₁₂ = 3 Hz, exo-MeC₆H₅), −1.12 (d, ²J₉H = 11.6 Hz, 3H, endo-δ-AdH), −0.73 (s, 3H, ν₁₂ = 10 Hz, γ-AdH), −0.56 (d, ²J₉H = 11.6 Hz, 3H, exo-δ-AdH), 1.70 (s, 18H, ν₁₂ = 2 Hz, SiMe₃), 7.74 (t, ²J₉H = 7.4 Hz, 2H, p-Ph₃Ph), 7.94 (t, ²J₉H = 7.5 Hz, 4H, m-Ph₃Ph), 10.34 (s, 4H, ν₁₂ = 17 Hz, Y-HCH(CMe₂)₃)} ppm. 0.5 h and concentrated in a vacuum to half of the original volume. LiCl was filtered off over Celite®. The solvent was stripped off, whereupon a colourless foamy solid forms, which was crystallized from n-hexane. Storage at −30 °C followed by filtration and drying in a vacuum resulted in isolation of a microcrystalline solid.
Analytical data for [(L Dip)Y(CH2SiMe3)2] (3a). Yield: 125 mg (0.16 mmol, 32%) of a colourless, microcrystalline solid. 1H NMR (300.1 MHz, Cd2): δ = −0.31 (br d, δ Y-HC = 8.9 Hz, 2H, Y-HC), −0.09 (br d, δ Y-HC = 9.0 Hz, 2H, Y-HC), 0.39 (s, 18H, SiMe3), 0.45 (s, 6H, Me3SiCMe), 1.35 (s, 6H, Me3SiCMe), 1.68 (s, 6H, Me3SiCMe), 2.03 (d, $J_{N\wedge Y} = 12.4$ Hz, 1H, H(H(C)C2Me3)), 2.36 (d, $J_{N\wedge Y} = 13.3$ Hz, 1H, H(H(C)C2Me3)), 3.47 (sept, $J_{N\wedge Y} = 6.8$ Hz, 2H, Me3SiCMe), 6.49 (d, $J_{N\wedge P} = 2.6$ Hz, 2H, Cp), 6.96–7.02 (br m, 9H, p-m-DipPh, p-m-DipPh), 7.50–7.57 (br m, 4H, o-PPh) ppm. 31P{1H} NMR (75.5 MHz, Cd2): δ = 4.4 (s, SiMe3), 22.7 (br s, Me3SiCMe), 26.9 (br s, Me3SiCMe), 29.0 (br s, Me3SiCMe), 31.9 (br s, Me3SiCMe), 32.2 (br s, Me3SiCMe), 37.1 (d, $J_{Y\wedge P} = 42.3$ Hz, Y-CH3), 40.1 (s, CMe3), 62.6 (s, CH2C2Me3), 94.2 (d, $J_{Y\wedge P} = 114.1$ Hz, α-CpC), 107.0 (d, $J_{Y\wedge P} = 12.9$ Hz, β-CpC), 124.7 (d, $J_{Y\wedge P} = 3.5$ Hz, m-DipC), 125.1 (d, $J_{Y\wedge P} = 3.9$ Hz, p-DipC), 128.7 (d, $J_{Y\wedge P} = 12.0$ Hz), 130.8 (d, $J_{Y\wedge P} = 97.5$ Hz, ipso-PPh), 132.6 (d, $J_{Y\wedge P} = 2.7$ Hz, m-PPh), 133.3 (d, $J_{Y\wedge P} = 9.8$ Hz, o-PPh), 140.4 (d, $J_{Y\wedge P} = 10.5$ Hz, ipso-DipPh), 145.4 (d, $J_{Y\wedge P} = 6.0$ Hz, o-DipP), 150.2 (d, $J_{Y\wedge P} = 13.8$ Hz, γ-CpC) ppm. 31P{1H} NMR (121.5 MHz, Cd2): δ = 9.1 (s) ppm.

Analytical data for [(C2Me5PMe2Nad)Y(CH2SiMe3)2] (3d). Yield: 126 mg (0.19 mmol, 37%) of a dark red, microcrystalline solid. 1H NMR (500.2 MHz, Cd2): δ = −234.89 (br s, 2H, $\nu_{1/2} = 240$ Hz, Yb-HC), −215.83 (br s, 2H, $\nu_{1/2} = 270$ Hz, Yb-HC), −117.29 (s, 2H, $\nu_{1/2} = 309$ Hz, Cp), −29.57 (s, 18H, $\nu_{1/2} = 40$ Hz, SiMe3), −28.92 (s, 4H, $\nu_{1/2} = 64$ Hz, α-PPh), −7.77 (s, 4H, $\nu_{1/2} = 22$ Hz, m-PPh), −3.77 (s, 2H, $\nu_{1/2} = 22$ Hz, p-PPh), 38.85 (s, 3H, $\nu_{1/2} = 34$ Hz, exo-δ-AdH), 41.74 (s, 6H, $\nu_{1/2} = 36$ Hz, exo-MeCMe), 49.65 (s, 3H, $\nu_{1/2} = 34$ Hz, endo-δ-AdH), 51.24 (s, 3H, $\nu_{1/2} = 48$ Hz, γ-Ad), 65.27 (s, 6H, $\nu_{1/2} = 146$ Hz, endo-MeCMe), 81.49 (s, 1H, $\nu_{1/2} = 49$ Hz, exo-H(CHC2Me3)), 148.51 (s, 1H, $\nu_{1/2} = 178$ Hz, endo-H(CHC2Me3)), 162.74 (s, 6H, $\nu_{1/2} = 240$ Hz, β-AdH) ppm. 31P{1H} NMR (202.5 MHz, Cd2): δ = −117.2 (br s) ppm. Analytical data for [(C2H5)3NPSi, 62.6 (s, CH2C2Me3), 94.2 (d, $J_{Y\wedge P} = 114.1$ Hz, α-CpC), 107.0 (d, $J_{Y\wedge P} = 12.9$ Hz, β-CpC), 124.7 (d, $J_{Y\wedge P} = 3.5$ Hz, m-DipC), 125.1 (d, $J_{Y\wedge P} = 3.9$ Hz, p-DipC), 128.7 (d, $J_{Y\wedge P} = 12.0$ Hz), 130.8 (d, $J_{Y\wedge P} = 97.5$ Hz, ipso-PPh), 132.6 (d, $J_{Y\wedge P} = 2.7$ Hz, m-PPh), 133.3 (d, $J_{Y\wedge P} = 9.8$ Hz, o-PPh), 140.4 (d, $J_{Y\wedge P} = 10.5$ Hz, ipso-DipPh), 145.4 (d, $J_{Y\wedge P} = 6.0$ Hz, o-DipP), 150.2 (d, $J_{Y\wedge P} = 13.8$ Hz, γ-CpC) ppm. 31P{1H} NMR (121.5 MHz, Cd2): δ = 9.1 (s) ppm.
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