Heteroatom Chemistry
Volume 13, Number 6, 2002

P–N Ligands in Lanthanide Chemistry

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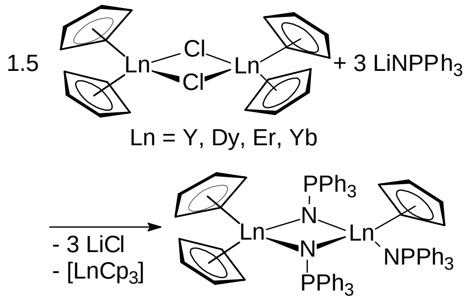
Received 25 March 2002

ABSTRACT: *The coordination chemistry of inorganic amides in Group 3 and lanthanide chemistry is discussed. Three different ligand systems (phosphinoamides, bis(phosphino)amides, and bis(phosphinimino)methanides) that consist of one or more P–N units were used. In this series the steric demand of the ligands is increased in a stepwise fashion and the negative charge is delocalized over more atoms. These properties were used in the design of new lanthanide complexes. For all three compounds the synthesis of the alkali metal derivatives is reported first, followed by the reaction of the alkali metal salts with various lanthanide trichlorides. Further reactions of the obtained lanthanide complexes as well as their application as catalysts are discussed. Most of the reported complexes show a dynamic behavior in solution. In phosphinoamide and bis(phosphino)amide complexes, in which the phosphorus atom is in oxidation state +3, there is always a weak coordination of the phosphorus atom to the lanthanide atom observed. In bis(phosphinimino)methanide complexes, in which the phosphorus atom is in oxidation state +5, no such interaction is noticeable. Instead a weak coordination of the methine atom to the center metal can be seen in the solid state.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:514–520, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10096

INTRODUCTION

Metallocenes of organolanthanides [1] have proven to be highly efficient catalysts [2] for a variety of olefin transformations including hydrogenation [3,4], polymerization [5], hydroamination [4,6], hydrosilylation [7], and hydroboration [8]. Recently, there has been a significant research effort by us and others to substitute the cyclopentadienyl ligand [9] by anionic nitrogen-based bidentate ligand systems [10] such as benzamidinates [11] or aminotroponiminates [12]. Another approach in this area is the use of inorganic amides. In particular P–N systems were used as ligands. For the phosphoraneiminato ligand NPPh$_3^-$ Dehnicke et al. have shown that that the ψ-isolobal relationship between NPPh$_3^-$ and η^5-C$_5$H$_5^-$ (Cp$^-$) is valid not only for d-transition metals but also for the lanthanides [13]. Thus, the reaction of LiNPPh$_3$ with the well known chloro-bridged bis(cyclopentadienyl)chlorides of the lanthanides [LnCp$_2$Cl]$_2$ (Ln = Y, Dy, Er, Yb) in equimolar amounts leads to the bimetallic complex [Ln$_2$Cp$_3$(NPPh$_3$)$_3$] (Eq. (1)) [14].



(1)

Phosphoraneiminato complexes with heterocubane structures are formed from reactions of the lithio derivate LiNPPh$_3$ with η^8-cyclooctatetraenide complexes [Ln(C$_8$H$_8$)Cl(THF)$_2$]$_2$ (Ln = Ce, Sm) in

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Contract grant sponsor: The Deutsche Forschungsgemeinschaft.
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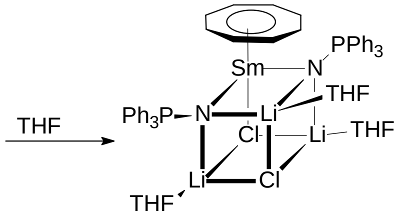
THF solutions [15]. As can be seen from Eq. (2), LiCl formed in the course of reaction is incorporated into the heterocubane framework.

$$0.5\,[\mathrm{Sm(C_8H_8)Cl(THF)_2}]_2 + 2\,\mathrm{LiNPPh_3} + \mathrm{LiCl}$$



(2)

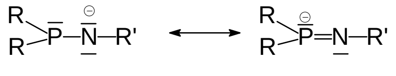
More recently dimeric homoleptic phosphoraneiminato complexes of the lanthanides $[\{\mathrm{Ln(NPPh_3)_3}\}_2]$ (Ln = La, Yb) were reported. These compounds were obtained by the reaction of $\mathrm{LnCl_3}$ and sodium phosphoraneiminate $\mathrm{NaNPPh_3}$ (Eq. (3)) [16]. Because of the larger ion radius only the lanthanum compound crystallized as THF solvate $[\mathrm{La_2(NPPh_3)_6(THF)_2}]$. Both the lanthanum and the ytterbium compound catalyzed the polymerization of ε-caprolactone. The polymer was obtained in high yields in a fast reaction.

$$2\,\mathrm{LnCl_3} + 6\,\mathrm{NaNPPh_3} \xrightarrow[-6\,\mathrm{NaCl}]{} [\{\mathrm{Ln(NPPh_3)}\}_2] \quad (3)$$

Beside the well established phosphoraneiminato ligand other P—N ligands have recently been used in d- and 4f-transition metal chemistry. Herein the coordination chemistry of three of those ligands in group 3 and lanthanide chemistry (**A–C**) (Scheme 1) is reviewed.

PHOSPHANOAMIDES

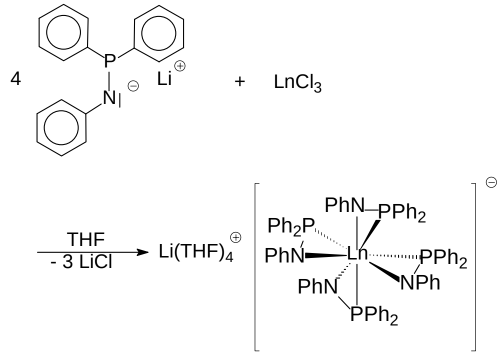
Phosphinoamines (phosphazanes), phosphanimides (phosphazenes), and their cyclic analogues have long been known and attracted the attention of experimentalists and theorists alike because both exhibit comparatively short P—N bond lengths [17]. If a phosphinoamine of the general formula $\mathrm{R_2PN(H)R'}$ or a phosphanimide of the general formula $\mathrm{R_2(H)P{=}NR'}$ is deprotonated, the resulting anion could be in principle described as phosphanoamide (**A**) or iminophosphide (**B**) (Eq. (4)) [18]. Theoretical studies have shown that the anion has a shortened P—N bond but basically it does correspond to **A** with the negative charge mainly located on nitrogen [17]. The phosphanoamides are known to act as both bridging and terminal ligands for the d-transition metals [19].



A **B**

(4)

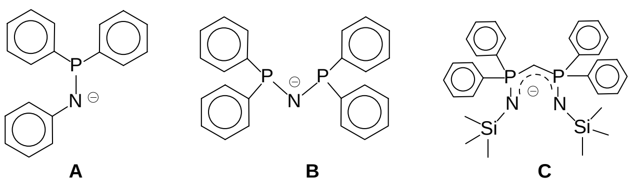
Transmetallation of lithium diphenylphosphinophenylamide ($\mathrm{LiPh_2PNPh}$) with anhydrous yttrium, ytterbium, and lutetium trichloride in THF led to products of composition $[\mathrm{Li(THF)_4}][(\mathrm{Ph_2PNPh})_4\mathrm{Ln}]$ (Ln = Y (**1a**), Yb (**1b**), and Lu (**1c**)) (Eq. (5)) [20]. Even with an excess of $\mathrm{LnCl_3}$, **1** was the only product which could be isolated. The single crystal X-ray structure shows that **1b** and **1c** consist of an ion pair composed of a $[\mathrm{Li(THF)_4}]^+$ cation and a $[(\mathrm{Ph_2PNPh})_4\mathrm{Ln}]^-$ anion (Fig. 1). The ligands of the anions have η^2-coordination, thus forming 4 three-membered rings (azaphosphametallacyclopropanes). Although a large number of homoleptic coordinated compounds with four-, five-, and six-membered ring systems are known, **1a–1c** were the first homoleptic complexes of the lanthanides, consisting only of three-membered ring systems.



(5)

Ln = Y (**1a**), Yb (**1b**), Lu (**1c**)

At a first glance the $\mathrm{N_4P_4}$ coordination polyhedron of the anions looks highly symmetric and a D_2 symmetry is expected. A closer look shows that the polyhedron has no symmetry at all and may be best described in terms of an extremely distorted cube. In fact none of the classical polyhedra known for coordination number eight gives a correct description [21]. Keeping in mind that the central metal is coordinated by four identical ligands, the C_1 symmetry of the polyhedron seems to be surprising. Nevertheless, the anions are chiral with both enantiomers cocrystallizing in the unit cell. Not only the positions of the phenyl ring, disturbing the nearly realized C_2 symmetry, but also the strong difference of



SCHEME 1 The ligand systems discussed in the text.

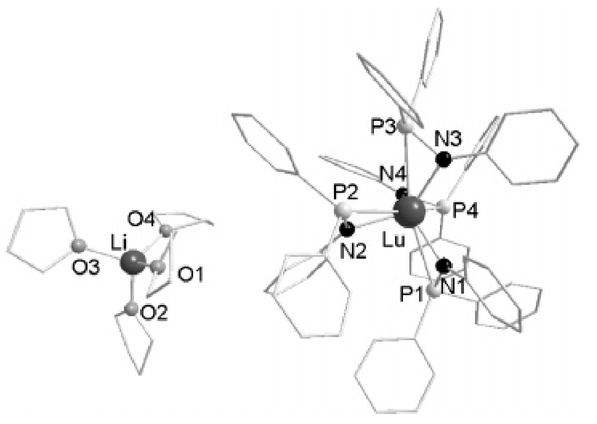


FIGURE 1 Crystal structure of **1c**. Hydrogen atoms are omitted for clarity.

the Ln—P distances are the reasons for the unsymmetry. Although the Ln—N bond lengths are equal within the error the, Ln—P distances differ by about 15 pm. The geometry of the LnN_4 subunit is a distorted tetrahedron. The two P_2N_2 planes of the coordination polyhedron are distorted to give elongated parallelograms.

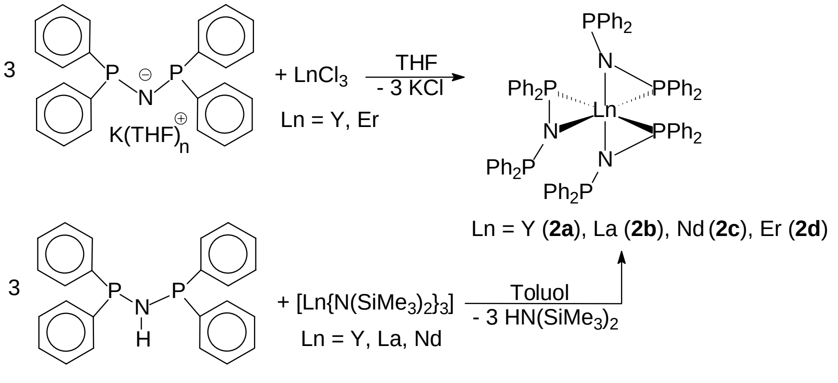
The ^{31}P NMR spectra of **1a** and **1c** show only one signal. For **1c** a ^2J(P,Y) coupling could be observed whereas the ^1J(P,Y) and ^2J(P,P) couplings were not detectable even at low temperature (203 K). Therefore, the Ln—P interaction can only be weak. To better understand the nature of the distorted structure, theoretical investigations on DFT (density functional theory) [22] and MP2 (Møller–Plesset second-order perturbation theory) [23] level were carried out. From the results of the calculations it can be emphasized that the unsymmetric coordination pattern of the phosphorus atoms is best explained by steric effects. The following effects of the large Ph substituents must be considered. On one hand, the steric demand of the Ph groups in η^1-coordinated (N-bound) R_2PNR^- ligands forces the phosphorus atoms to approach the metal center, tending towards η^2-coordination. On the other hand, the formation of four equally spaced chelating rings is hindered by the newly arising steric interactions of the "near-η^2" coordination. Nevertheless, based on the very weak calculated Ln—P binding interactions, packing constraints were suggested to have a further influence on the geometry.

BIS(PHOSPHINO)AMIDES

The neutral diphosphine ligand $(Ph_2P)_2NH$ [24] is well known in late transition-metal chemistry for assembling metal centers in bi- and polynuclear metal complexes [25]. In early transition-metal chemistry only the titanium complex $[TiCl_2\{N(PPh_2)_2\}_2]$ was reported [19c].

Reaction of $[K(THF)_n][N(PPh_2)_2]$ ($n = 1.25, 1.5$), which was obtained from $(Ph_2P)_2NH$ and KH, with anhydrous yttrium or lanthanide trichlorides in a 3:1 molar ratio in THF afforded homoleptic diphosphinoamide complexes $[Ln\{N(PPh_2)_2\}_3]$ (**2**) (Ln = Y, Er) as large sized crystals in good yields (Scheme 2) [26]. Complex **2** can also be obtained by the reaction of the homoleptic bis(trimethylsilyl)amides of Group 3 metals and lanthanides ($[Ln\{N(SiMe_3)_2\}_3]$) [27] (Ln = Y, La, Nd) with three equivalents of $(Ph_2P)_2NH$ in boiling toluene (Scheme 2). The compounds are here after referred to as $[Ln\{N(PPh_2)_2\}_3]$ (Ln = Y (**2a**), La (**2b**), Nd (**2c**) Er (**2d**)).

Because of the similar ion radii of the lanthanides, the single crystal X-ray structures of **2a–d** are isostructural. Three symmetrically chelating (η^2) $(Ph_2P)_2N^-$ ligands are coordinated to the lanthanide atom with the six coordinate LnN_3P_3 geometry closely trigonal prismatic (Fig. 2). In this arrangement the three phosphorus atoms, which are bound to the lanthanide atom, are located on one triangular plane of the trigonal prism, whereas the nitrogen atoms are located on the opposite plane.



SCHEME 2 Reaction pathways that lead to **2a–d**.

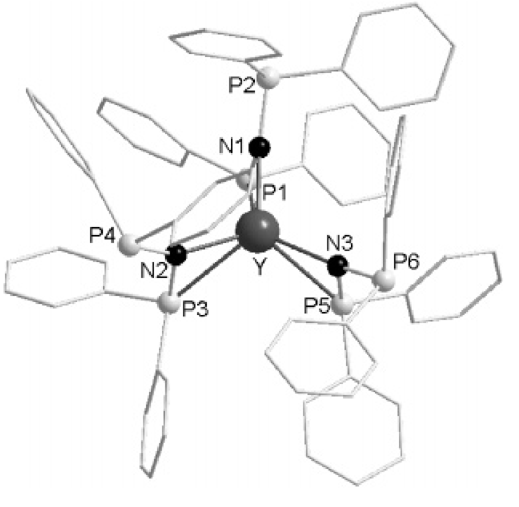


FIGURE 2 Crystal structure of **2a**. Hydrogen atoms are omitted for clarity.

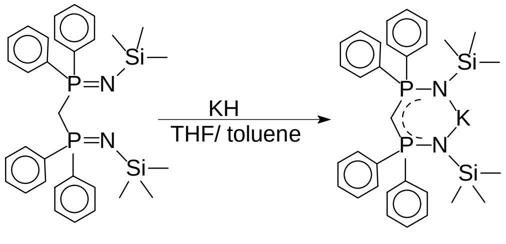
While one of the phosphorus atoms of each ligand binds to the lanthanide center, the other phosphorus atom bents away. Within the ligand the P—N bond distance varies significantly. The phosphorus atom, which binds to the lanthanide atom, is always located closely to the nitrogen atom. The arrangement of the $(Ph_2P)_2N^-$ ligand around the lanthanide atoms is in contrast to the isoelectronic diphosphinomethanide ligand $(R_2P)_2CH^-$, which was pioneered by Karsch et al. [28]. The phosphinomethanide ligand always has η^3-coordination in a heteroallylic fashion.

Compounds **2** show a dynamic behavior in solution. Although at room temperature complexes **2a–c** each show one sharp signal in the $^{31}P\{^1H\}$ NMR spectra in accordance with the solid-state structure, at low temperature (173 K) two signals are observed. From the coalescence temperature ($T_c = 200$ K) and the separation of the two coalescing signals, the free energy ΔG_{T_c} for the exchange of the two phosphorus atoms was calculated to be 34.04 kJ/mol [26]. The efficacy of the homoleptic complexes **2** as precatalysts for polymerization reaction was assayed using ε-caprolactone. The polymer was obtained in high yield in very high reaction rates.

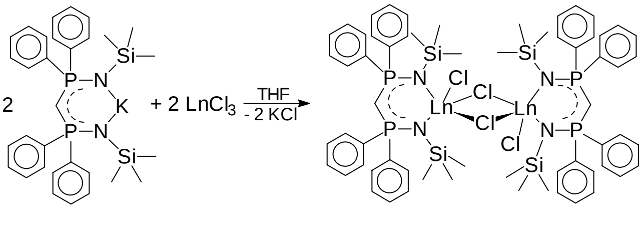
BIS(PHOSPHINIMINO)METHANIDES

Another approach to the area of P—N ligands is the bis(phosphinimino)methanide ligand $CH(PPh_2NSiMe_3)_2^-$. Because of the higher steric demand and the different oxidation state of the phosphorus atom compared to the ligands previously discussed, it was anticipated that $CH(PPh_2NSiMe_3)_2^-$ may combine the advantages of phosphinimines and amidinates. It was shown that a monoanionic [29,30] and a dianionic species [31,32] ($CH(PPh_2NSiMe_3)_2^-$, and $C(PPh_2NSiMe_3)_2^{2-}$, respectively) can be generated by deprotonation of the precursor $CH_2(PPh_2NSiMe_3)_2$. The monoanionic species was fairly used as ligands in main group and transition-metal chemistry [33–36], whereas the dianionic ligand was reported by Cavell and coworkers to form carbene-like complexes with a series of transition metals and samarium [36,37].

Reaction of the potassium methanide complex $K\{CH(PPh_2NSiMe_3)_2\}$, which was obtained from $CH_2(PPh_2NSiMe_3)_2\}$ and KH (Eq. (6)) [29,38], with anhydrous yttrium or lanthanide trichlorides in a 1:1.1 molar ratio afforded the corresponding yttrium and lanthanide complexes $[\{CH(PPh_2NSiMe_3)_2\}LnCl_2]_2$ (Ln = Y (**3a**), Sm (**3b**), Er (**3c**), Dy (**3d**), Yb (**3e**), Lu (**3f**)) (Eq. (7)) [38,39].



(6)



Ln = Y (**3a**), Sm (**3b**), Dy (**3c**), Er (**3d**), Yb (**3e**), Lu (**3f**)

(7)

The structures of **3a–f** were confirmed by single crystal X-ray diffraction in the solid-state. Because of the similar ion radii of the lanthanides, the single crystal X-ray structures of **3a–f** are isostructural (structure of **3a** is shown in Fig. 3). Complexes **3a–f** are dimeric complexes in which the metal centers are bridged asymmetrically by two μ-chlorine atoms. In the center of the Ln—Cl2—Ln—Cl2 plane, a crystallographic inversion center is observed. A six-membered metallacycle (N1—P1—C1—P2—N2—Ln) is formed by chelation of the two trimethlysilylimine groups to the lanthanide atom. The ring adopts a twist boat conformation in which the central carbon atom and the lanthanide atom are displaced from the N_2P_2 least-square-plane. The distance between the central carbon atom (C1) and the lanthanide atom is longer than usual Ln–C distances [1]; however, the folding of the six-membered ring towards

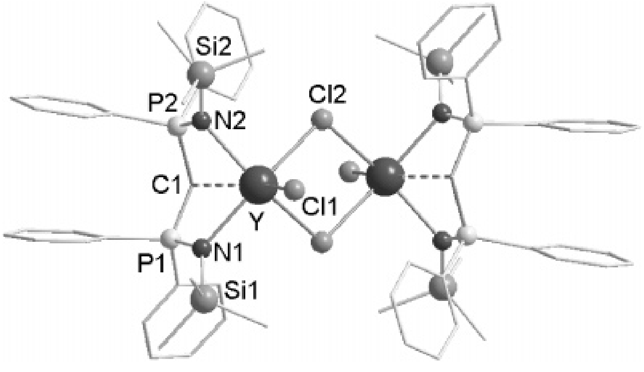


FIGURE 3 Crystal structure of **3a**. Hydrogen atoms are omitted for clarity.

the lanthanide atom is caused by a weak interaction. This is supported by DFT calculations, which show a similar interaction [22]. The Ln—C1 bond lengths increase with increasing ion radius of the center metal in a linear fashion. The resultant tridentate coordination of the ligand was observed earlier, e.g. in $[Al(CH_3)_2\{CH(PPh_2NSiMe_3)_2\}]$ [35] and $[Ir\{CH(PPh_2N(p\text{tolyl}))_2\}(COD)]$ [33].

Transmetallation of the yttrium and the samarium chloro complex **3a** and **3b**, respectively, with an excess of $KNPh_2$ in toluene, afforded the corresponding bisamido complexes $[\{CH(PPh_2NSiMe_3)_2\}Ln(NPh_2)_2]$ (Ln = Y (**4a**), Sm (**4b**)) as crystalline solids (Eq. (8)) [38,39]. The crystal structure of **4a** reveals a distorted tetrahedral arrangement of the nitrogen atoms around the yttrium atom (Fig. 4). As observed for **3a–f** a six-membered ring (N1—P1—C1—P2—N2—Y), which adopts a twist boat conformation, is formed by the $CH(PPh_2NSiMe_3)_2^-$ ligand and the yttrium atom. The methine carbon atom is bound to the lanthanide atom. The multinuclear NMR data of **4** are consistent with the solid-state structure.

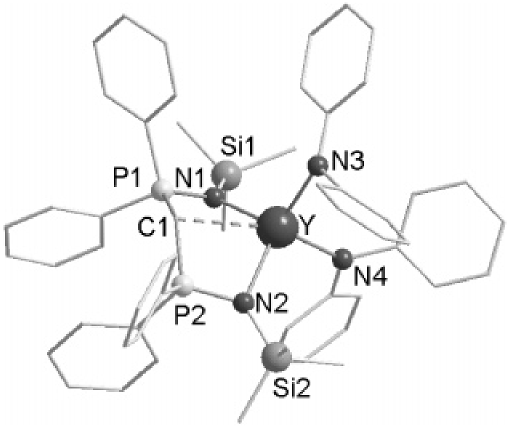
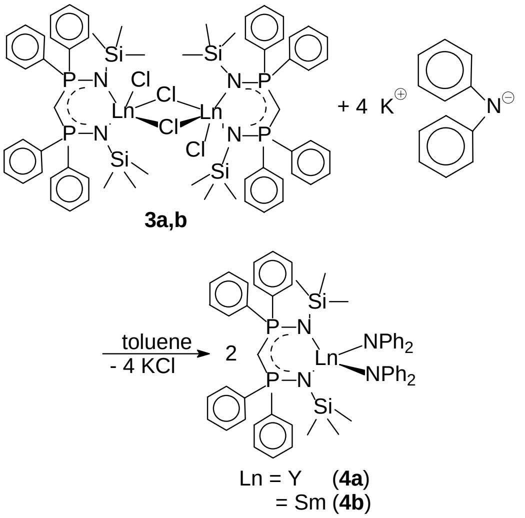
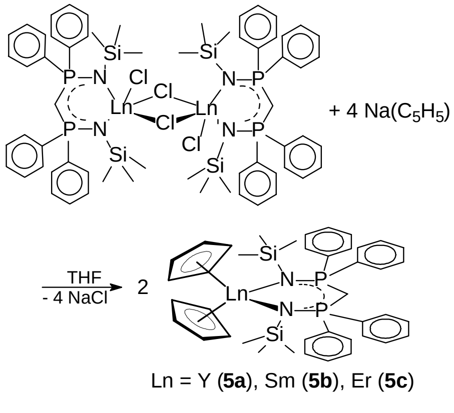


FIGURE 4 Crystal structure of **4a**. Hydrogen atoms are omitted for clarity.



(8)

To compare the coordination behavior and the steric demands of $CH(PPh_2NSiMe_3)_2^-$ and cyclopentadienyl groups, mixed cyclopentadienyl-bis(phosphinimino)methanide complexes were synthesized by the reaction of **3a, 3b**, and **3d** with $Na(C_5H_5)$ in a 1:4 molar ratio. The corresponding metallocenes $[(\eta^5\text{-}C_5H_5)_2Ln\{CH(PPh_2NSiMe_3)_2\}]$, (Ln = Y (**5a**), Sm (**5b**), Er (**5c**)) were obtained as products (Eq. (9)) [38,40]. Complexes **5a–c** can also be obtained in a one-pot reaction starting from $LnCl_3$, $K\{CH(PPh_2NSiMe_3)_2\}$, and $Na(C_5H_5)$.



(9)

Because of the similar ion radii of the lanthanides, **5a–c** are isostructural (structure of **5b** is shown in Fig. 5). The structures show the expected η^5-coordination of the cyclopentadienyl ligands. As observed for **3a–f** and **4a,b**, a six-membered metallacycle (N1—P1—C1—P2—N2—Ln) is formed by chelation of the two trimethlysilylimine groups to the lanthanide atom. The ring adopts a twist boat conformation in which the central carbon atom and the

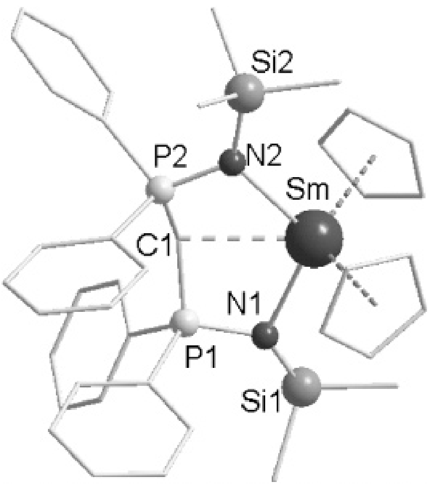


FIGURE 5 Crystal structure of **5b**. Hydrogen atoms are omitted for clarity.

lanthanide atom are displaced from the N_2P_2 least-square-plane. The crystal structures show that the methine carbon atom is bound to the lanthanide atom. In contrast, no interaction between the lanthanide atom and the methine group is observed in solution. This effect might be caused by a nonrigid structure of **5a–c** in solution. The data obtained from the crystal structures suggest that the steric demand of the $CH(PPh_2NSiMe_3)_2^-$ ligand is much higher than that of cyclopentadienyl groups. Therefore, by using the bulky $CH(PPh_2NSiMe_3)_2^-$ ligand in lanthanide chemistry the synthesis of new complexes, which are significantly different from well-known cyclopentadienyl compounds, should be possible.

CONCLUSIONS

It can be emphasized that a series of lanthanide complexes having different P—N ligands in the coordination sphere were reported. There is a strong dependence between the steric demand of the ligand and the observed coordination modes. By using these properties the reaction pathway and thus the substitution pattern on the lanthanide complexes can be controlled. Most of the reported complexes show a dynamic behavior in solution. In phosphinoamide and bis(phosphino)amide complexes, in which the phosphorus atom is in oxidation state +3, a weak coordination of the phosphorus atom to the lanthanide atom is observed exclusively. In bis(phosphinimino)methanide complexes, in which the phosphorus atoms are in oxidation state +5 no such interaction is noticeable. Instead a weak coordination of the methine atom to the center metal can be seen in the solid state.

ACKNOWLEDGMENT

I am deeply grateful to my coworkers M. Gamer and Dr. T. Wetzel who are named on our joint publications cited in this review.

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