

# Bis(phosphinimino)methanides as ligands in divalent lanthanide and alkaline earth chemistry – synthesis, structure, and catalysis

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Dedicated to Professor Herbert Schumann on the occasion of his 70th birthday

## Abstract

Divalent bis(phosphinimino)methanide lanthanide complexes of composition  $[(\text{Me}_3\text{SiNPPh}_2)_2\text{CH}]\text{Eu}(\text{THF})_2$  and  $[(\text{Me}_3\text{SiNPPh}_2)_2\text{CH}]\text{Yb}(\text{THF})_2$  have been prepared by a salt metathesis reactions of  $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$  and  $\text{LnI}_2$ . Further reactions of these complexes with  $[\text{K}(\text{THF})_n\text{N}(\text{PPh}_2)_2]$  led selectively to the heteroleptic amido complexes  $[(\text{Me}_3\text{SiNPPh}_2)_2\text{CH}]\text{Ln}\{(\text{Ph}_2\text{P})_2\text{N}\}(\text{THF})$  ( $\text{Ln} = \text{Eu}, \text{Yb}$ ). The ytterbium complex can also be obtained by reduction of  $[(\text{Me}_3\text{SiNPPh}_2)_2\text{CH}]\text{Yb}\{(\text{Ph}_2\text{P})_2\text{N}\}\text{Cl}$  with elemental potassium. The single crystals of  $[(\text{Me}_3\text{SiNPPh}_2)_2\text{CH}]\text{Ln}\{(\text{Ph}_2\text{P})_2\text{N}\}(\text{THF})$  contain enantiomerically pure complexes. As a result of the similar ionic radii of the divalent lanthanides and the heavier alkaline earth metals some similarities in coordination chemistry of the bis(phosphinimino)methanide ligand were anticipated. Therefore,  $\text{MI}_2$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ) was reacted with  $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$  to give  $[(\text{Me}_3\text{SiNPPh}_2)_2\text{CH}]\text{Ca}(\text{THF})_2$ ,  $[(\text{Me}_3\text{SiNPPh}_2)_2\text{CH}]\text{Sr}(\text{THF})_2$ , and  $[(\text{Me}_3\text{SiNPPh}_2)_2\text{CH}]\text{Ba}(\text{THF})_2$ , respectively. As expected the Sr and Eu complexes and the Ca and Yb complexes are very similar, whereas for the Ba compound, as a result of the large ion radius, a different coordination sphere is observed. For all new complexes the solid-state structures were established by single crystal X-ray diffraction. In the solid-state the  $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$  ligand acts as tridentate donor forming a long methanide carbon metal bond. Thus, all complexes presented can be considered as organometallic compounds.  $[(\text{Me}_3\text{SiNPPh}_2)_2\text{CH}]\text{Yb}(\text{THF})_2$  was also used as precatalyst for the intramolecular hydroamination/cyclization reaction of different aminoalkynes and aminoolefines. Good yields but moderate activities were observed.

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## 1. Introduction

In the last 15 years, enormous progress has been observed in the design and application of amido-metal chemistry of the early transition metals. In the early stages of this area cyclopentadienyl-analogous amido ligands were studied for comparison with and for further investigations of the well-known cyclopentadienyl moiety. Today, the stable amido-metal bond is utilized in

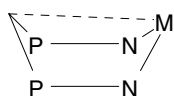
amido-metal chemistry to produce well-defined reaction centers in transition metal complexes. In this way, the reactivity of the resulting early transition metal compounds can be specifically tailored to allow applications in areas such as the activation of small poorly reactive molecules, homogeneous catalysis, or organic synthesis [1,2]. One synthetic approach among others is the use of P–N ligands such as phosphoraneiminate, phosphinimines, and phosphinimides in main group and transition metal chemistry [3–8]. Recently, the deprotonated derivatives of the well-known bis(phosphinimine),  $\text{CH}_2(\text{PPh}_2\text{N-SiMe}_3)_2$  [9] have drawn the attention of a number of research groups. It was shown that a monoanionic

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[10–13], and a dianionic species [14,15] ( $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$  and  $\{\text{C}(\text{PPh}_2\text{NSiMe}_3)_2\}^{2-}$ , respectively) can be generated by deprotonation of the precursor  $\text{CH}_2(\text{PPh}_2\text{NSiMe}_3)_2$ . The monoanionic species was used as a ligand in main group and transition metal chemistry, [16–19], whereas the dianionic ligand was reported by Cavell and co-workers [17,20] to form carbene like complexes with a series of transition metals and samarium. Recently, we introduced the monoanionic phosphinimine  $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$ , into yttrium and lanthanide chemistry. We have previously reported the synthesis of a series of lanthanide bis(phosphinimino)methanide dichloride complexes including yttrium,  $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}_2\text{LnCl}_2]_2$  ( $\text{Ln} = \text{Y}, \text{Sm}, \text{Dy}, \text{Er}, \text{Yb}, \text{Lu}$ ) [21]. These compounds were obtained by the reaction of  $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$  [12], with the corresponding yttrium or lanthanide trichlorides. Furthermore, reactions with the  $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}_2\text{LnCl}_2]_2$  compounds have led to the corresponding amido complexes,  $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}_2\text{Ln}(\text{NPh}_2)_2]$  ( $\text{Ln} = \text{Y}, \text{Sm}$ ) [21], diphosphinoamido complexes,  $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}_2\text{Ln}\{(\text{Ph}_2\text{P})_2\text{N}\}\text{Cl}]$  ( $\text{Ln} = \text{Y}, \text{La}, \text{Nd}, \text{Yb}$ ) [22], cyclopentadienyl complexes,  $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}_2\text{Ln}(\eta^5\text{-C}_5\text{H}_5)_2]$  ( $\text{Ln} = \text{Y}, \text{Sm}, \text{Er}$ ) [23], and cyclooctatetraene bis(phosphinimino) methanide complexes,  $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}_2\text{Ln}(\eta^8\text{-C}_8\text{H}_8)]$  ( $\text{Ln} = \text{Y}, \text{Sm}, \text{Er}, \text{Yb}, \text{Lu}$ ) [24], which have been reported by us. These derivatives were used as homogenous catalysts for a number of different catalytic applications. Thus,  $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}_2\text{Ln}\{(\text{Ph}_2\text{P})_2\text{N}\}\text{Cl}]$  are active catalysts for the ring-opening polymerization of  $\epsilon$ -caprolactone and the polymerization of methyl methacrylate, whereas  $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}_2\text{Ln}(\eta^8\text{-C}_8\text{H}_8)]$  was used as catalysts for the hydroamination/cyclization reaction.

In all lanthanide compounds we reported so far with,  $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$  tends to show an uncommon coordination mode. In the solid-state structures the methine carbon atom coordinates via a long interaction on to the metal atom. Thus, the six membered metallacycle ( $\text{N1-P1-C1-P2-N2-Ln}$ ), which is formed by chelation of the two trimethylsilylimine groups to the metal center, adopts a pseudo-boat conformation (Scheme 1). In one case the interaction between the methine carbon atom and the metal atom was also observed in solution. By using yttrium as metal center,  $^1J(\text{C}, \text{Y})$  and a  $^2J(\text{H}, \text{Y})$  coupling was reported. These observations were also supported by DFT calculations [21]. Thus, this class of compounds can be considered as organometallic compounds. Motivated by these results we were interested to extend our studies on to the



Scheme 1.

divalent lanthanides and to the heavier alkaline earth metals. It is well known that the divalent lanthanides and the heavier alkaline earth metals exhibit similar ion radii, thus comparable coordination chemistry can be applied. Currently in this field, there are limited related complexes containing the mesityl substituted bis(phosphinimino)methanide,  $\{\text{CH}(\text{PPh}_2\text{N-Mes})_2\}^-$  ligand in the coordination sphere, which have been reported by Hill et al. [25]. Best to our knowledge in this area one Sm(II) complex,  $[\text{Sm}\{\text{CH}(\text{PPh}_2\text{N-Mes})_2\}_2]$ , the related Ba compound  $[\text{Ba}\{\text{CH}(\text{PPh}_2\text{N-Mes})_2\}_2]$ , and the amido compounds  $[\{\text{CH}(\text{PPh}_2\text{N-Mes})_2\}_2\text{MN}(\text{SiMe}_3)_2]$  ( $\text{M} = \text{Ca}, \text{Sr}$ ) are the only known compounds.

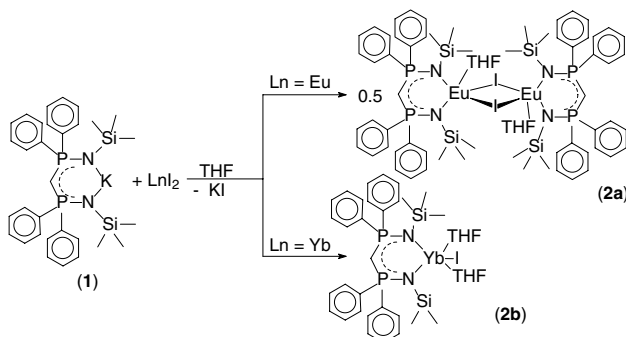
In this contribution, we present a full account of the reaction of  $\text{LnI}_2$  ( $\text{Ln} = \text{Eu}, \text{Yb}$ ) and  $\text{MI}_2$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ) with  $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$  as well as some further reactions of the obtained mono iodine compounds. Additionally the application of the ytterbium iodine complex as a catalyst in the hydroamination/cyclization is reported.

## 2. Results and discussion

### 2.1. Lanthanide iodine complexes

Reaction of  $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$  (**1**) with ytterbium and europium diiodide in a 1:1 molar ratio in THF afforded the corresponding divalent lanthanide complexes  $[\{\text{Me}_3\text{SiNPPPh}_2\}_2\text{CH}\}\text{EuI}(\text{THF})_2$  (**2a**) and  $[\{\text{Me}_3\text{SiNPPPh}_2\}_2\text{CH}\}\text{YbI}(\text{THF})_2$  (**2b**) as crystals in good yields (Scheme 2) [26]. The potassium reagent **1**, which was described earlier [12] was used as starting material to avoid coordination of lighter alkali halides such as lithium chloride. The new complexes have been characterized by standard analytical/spectroscopic techniques, and the solid-state structures of both compounds were established by single crystal X-ray diffraction.

The signal of the methine proton ( $\delta$  1.91) in  $^1\text{H}$  NMR spectrum of the diamagnetic ytterbium compound (**2b**) is in the range of comparable trivalent lanthanide complexes ( $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{YCl}_2]_2$  ( $\delta$  1.93)) but shows



Scheme 2.

a slight downfield shift compared to **1** ( $\delta$  1.58). The signals of the phenyl protons are broadened in the  $^1\text{H}$  NMR spectrum. Complex **2b** shows a sharp signal in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\delta$  14.2) shifted downfield by about 10 ppm relative to the trivalent yttrium complex  $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{YCl}_2]_2$  ( $\delta$  20.4), showing that the phosphorus atoms in each case are chemically equivalent in solution. Beside the sharp signal small satellite signals are observed, which are caused by coupling of  $^{171}\text{Yb}$  with the phosphorus atoms.

The structures of **2a,b** were confirmed by single crystal X-ray diffraction in the solid-state. As a result of the different ionic radii **2a** forms a dimer in the solid-state whereas **2b** is monomeric. In **2a**, which crystallizes in the monoclinic space group  $P2_1/c$  the metal centers of the dimeric complexes are asymmetrically bridged by two  $\mu$ -iodine atoms (Eu–I 330.93(5) pm, Eu–I' 335.24(6) pm) (Fig. 1). Rectangular through the center of the Eu–I–Eu'–I' plane, a crystallographic  $C2$  axis is observed. The bis(phosphinimino)methanide ligand forms a six membered metallacycle (N1–P1–C1–P2–N2–Eu) by chelation of the two trimethylsilylimine groups to the lanthanide metal. The Eu–N distances are Eu–N1 259.6(2) pm and Eu–N2 256.3(2) pm showing an almost symmetric attachment of the ligand onto the metal center. The metallacycle adopts a twist boat conformation, in which the central carbon atom and the europium atom are displaced from the  $\text{N}_2\text{P}_2$  least-square-plane. The displacement depends on the metal center and also on the packing in the solid-state [22]. The Eu atom is displaced by 158 pm and the methine carbon atom (C1) about 67 pm out of plane. The interaction between the methine carbon atom and the europium atom results in a tridentate coordination of the

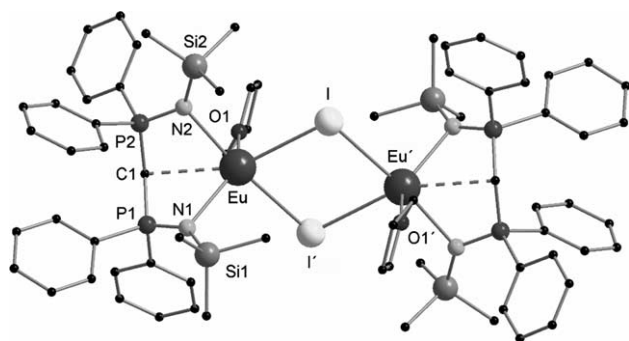


Fig. 1. Solid-state structure of **2a** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths (pm) or angles ( $^\circ$ ): Eu–I 330.93(5), Eu–I' 335.24(6), Eu–N1 259.6(2), Eu–N2 256.3(2), Eu–C1 294.5(2), Eu–O1 247.9(2), P1–N1 158.2(2), P2–N2 158.6(2); Eu–I–Eu' 99.213(7), I–Eu–I' 80.787(7), I–Eu–N1 132.23(5), I–Eu–N2 98.49(5), I–Eu–C1 157.99(4), I–Eu–O1 96.19(6), I'–Eu–N2 168.00(5), I'–Eu–N1 98.21(5), I'–Eu–C1 119.08(4), I'–Eu–O1 81.25(7), N1–Eu–N2 91.14(7), N1–Eu–C1 58.53(6), N1–Eu–O1 131.14(8), N2–Eu–C1 60.04(6), N2–Eu–O1 86.94(8), C1–Eu–O1 78.98(8), P1–C1–P2 126.88(15).

bis(phosphinimino)methanide ligand, which was observed earlier (see above). Best to our knowledge only five structural characterized Eu(II)–C  $\sigma$ -carbon bonds were reported so far [27,28] of which only one is a Eu(II)–CH bond (Eu–C 265(1) pm) [28]. The distance of the latter is significantly shorter than the distance between the central carbon atom (C1) and the europium atom (Eu–C1 294.5(2) pm) in **2a**. The geometry of the  $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$  ligand is as expected.

Compound **2b** crystallizes in the triclinic space group  $P\bar{1}$  with two molecules in the unit cell (Fig. 2). In contrast to **2a**, compound **2b** is monomeric in the solid-state. If the bis(phosphinimino)methanide ligand is considered as a tridentate donor the ytterbium center is six-coordinated. As observed for **2a** a six membered metallacycle (N1–P1–C1–P2–N2–Yb), which adopts a twist boat conformation is formed by the  $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$  ligand and the yttrium atom. The Yb atom is displaced by 159 pm and the methine carbon atoms (C1) about 72 pm out of plane. The distance of the central carbon atom C1 and the ytterbium atom (Yb–C1 270.0(4) pm) is significantly longer than usual Yb(II)–C distances [29] (e.g., 256(1) pm in  $[(\text{C}_5\text{Me}_5)_2\text{Yb}\{\text{CH}(\text{SiMe}_3)_2\}(\text{C}_5\text{Me}_5)\text{K}]_n$ ) [28]) however the folding of the six membered ring towards the ytterbium atom is caused by a weak

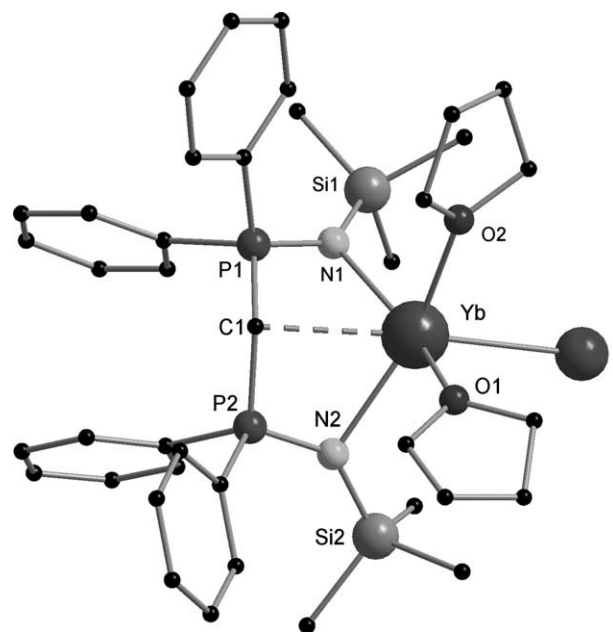


Fig. 2. Solid-state structure of **2b** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths (pm) or angles ( $^\circ$ ): Yb–I 305.86(6), Yb–N1 249.1(4), Yb–N2 247.5(3), Yb–C1 270.0(4), Yb–O1 246.6(4), Yb–O2 249.1(4), P1–N1 158.7(3), P2–N2 158.3(3), C1–P1 172.7(4), C1–P2 173.9(4); I–Yb–N1 108.37(7), I–Yb–N2 107.98(7), I–Yb–C1 165.91(8), I–Yb–O1 94.21(9), I–Yb–O2 92.94(9), N1–Yb–N2 92.36(11), N1–Yb–C1 62.84(11), N1–Yb–O1 154.85(13), N1–Yb–O2 91.17(14), N2–Yb–C1 63.29(10), N2–Yb–O1 90.99(13), N2–Yb–O2 76.38(15), C1–Yb–O1 96.90(12), C1–Yb–O2 98.06(12), O1–Yb–O2 76.38(15), P(1)–C(1)–P(2) 124.9(2).

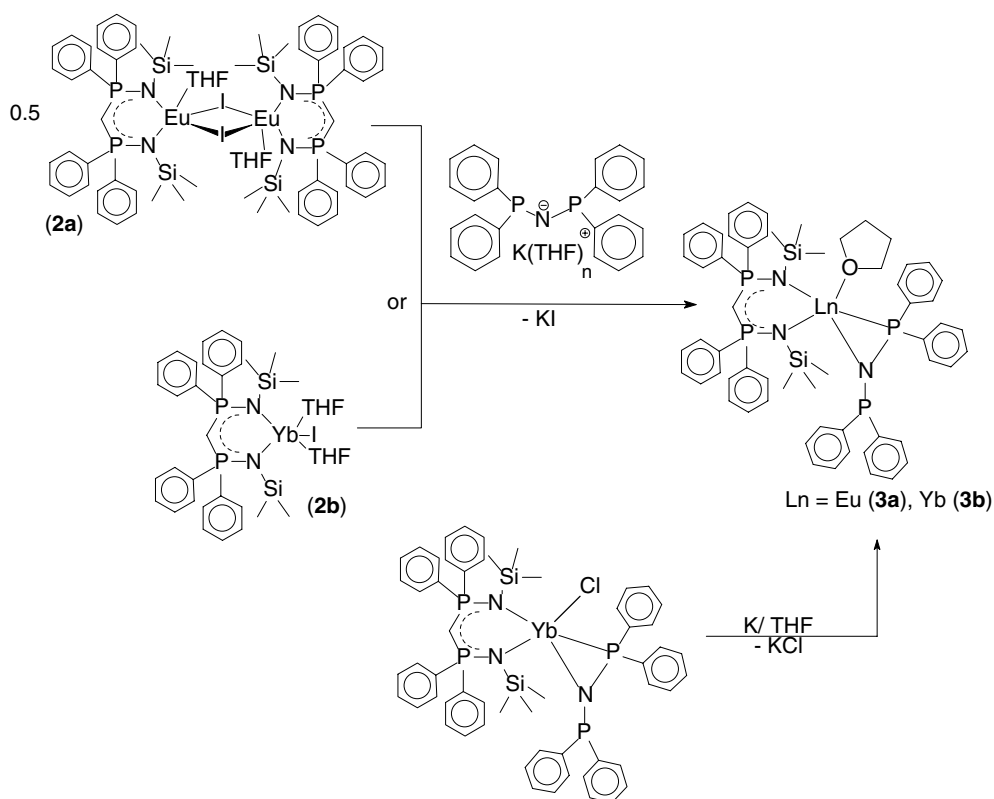
interaction. The geometry of the coordination polyhedron can be considered as strongly distorted octahedron having bond angles of I–Yb–O1 94.21(9)°, I–Yb–O2 92.94(9)°, N1–Yb–N2 92.36(11)°, N1–Yb–O2 91.17(14)°, N2–Yb–O1 90.99(13)°, and O1–Yb–O2 76.38(15)°.

## 2.2. Lanthanide amido complexes

When Hill et al. reported the synthesis of the homoleptic complex  $[\text{Sm}\{\text{CH}(\text{PPh}_2\text{N-Mes})_2\}_2]$ , which was obtained by a transamination of the neutral ligand ( $\{\text{CH}_2(\text{PPh}_2\text{N-Mes})_2\}$ ) with  $[\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2]$ , they were unable to isolate any heteroleptic compound such as  $[\text{Sm}\{\text{CH}(\text{PPh}_2\text{N-Mes})_2\}\{\text{N}(\text{SiMe}_3)_2\}]$ . To obtain bis(phosphinimino)methanide amido complexes of the divalent lanthanides we used compounds **2a,b** as starting material. As amido ligand we employed the flexible  $\{\text{Ph}_2\text{P}_2\text{N}\}^-$  ligand, which recently was introduced by us into lanthanide chemistry [30–32].

Reaction of  $[\text{K}(\text{THF})_n\text{N}(\text{PPh}_2)_2]$  with **2a,b** in THF in a 1:1 molar ratio led selectively to the amido complexes of composition  $[\{\text{Me}_3\text{SiNPPH}_2\}_2\text{CH}\}\text{Ln}\{\text{Ph}_2\text{P}_2\text{N}\}(\text{THF})]$  (Ln = Eu (**3a**), Yb (**3b**)) (Scheme 2) [26]. In a different approach compound **3b** was also obtained by reduction of the recently reported trivalent complex  $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{Yb}\{\text{Ph}_2\text{P}_2\text{N}\}\text{Cl}]$  [22] with elemental potassium in refluxing THF (Scheme 3) [26].

By recrystallizing from THF/*n*-pentane (1:2) single crystals of **3a,b** can be obtained. The solid-state structures of both **3a** and **3b** were established by single crystal X-ray diffraction (Fig. 3). Compounds **3a,b** crystallize in the orthorhombic space group  $P2_12_12_1$  with four molecules in the unit cell. Since **3a,b** are chiral molecules, which crystallize in a chiral space group, the single crystals of **3a,b** contain enantiomerically pure complexes. For both enantiomers the solid-state structure was determined by single crystal X-ray diffraction (Fig. 3). The chirality in **3a,b** is not caused by the arrangement of the ligands around the metal center but by the folding of the THF molecule and the  $\{\text{Ph}_2\text{P}_2\text{N}\}^-$  ligand relative to the C1–Ln axis (Fig. 3). Obviously the observed chirality is thus a solid-state effect only. The coordination polyhedra of **3a,b** are formed by the  $\{\text{CH}(\text{PPh}_2\text{N-SiMe}_3)_2\}^-$  ligand, the  $\eta^2\text{-}\{\text{Ph}_2\text{P}_2\text{N}\}^-$  ligand and one THF molecule. Thus, the lanthanide atom is six-coordinated if the  $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$  ligand is considered as tridentate donor. As observed for **2a,b** a six membered ring (N1–P1–C1–P2–N2–Ln), adopts a twist boat conformation, which is formed by the  $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$  ligand and the lanthanide atom. The displacement of the Ln and C1 atoms out of the  $\text{N}_2\text{P}_2$  least-square-plane are Eu 126 pm, Yb 116 pm and C1 63 pm (**3a**) and 65 pm (**3b**). The distance of the central carbon atom C1 and the lanthanide atom (287.8(4) pm (**3a**), 278.6(4) pm (**3b**)) is in the range observed for **2a,b** (Ln–C1



Scheme 3.



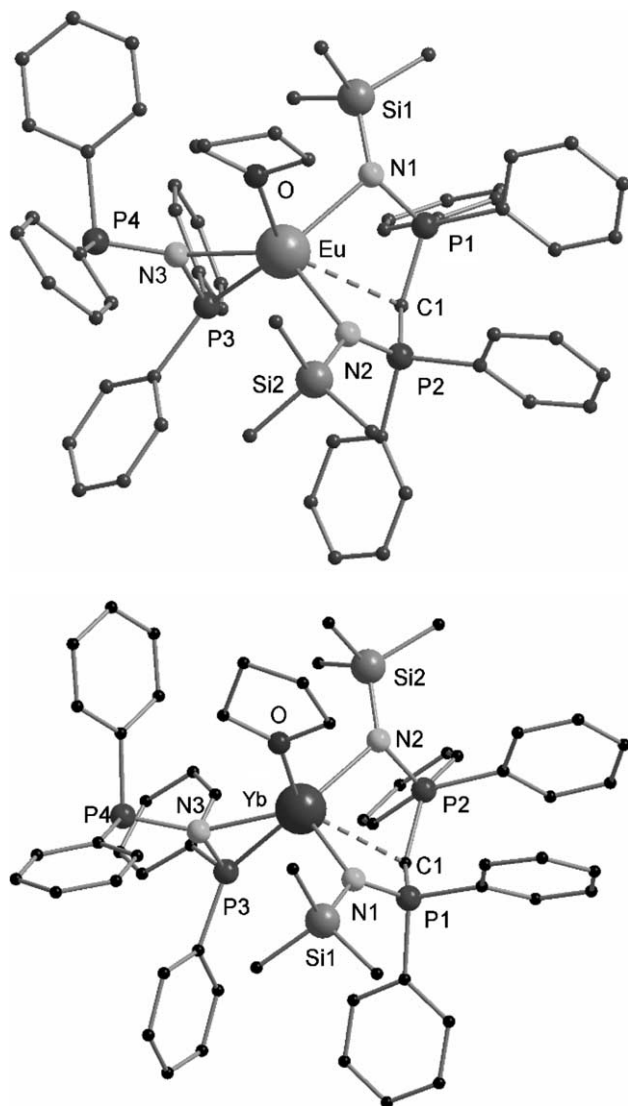


Fig. 3. Solid-state structure of **3a** (top) and **3b** (bottom) showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths (pm) or angles ( $^{\circ}$ ): **3a**: Eu–N1 253.9(4), Eu–N2 257.9(4), Eu–N3 252.7(4), Eu–C1 287.8(4), Eu–P1 322.90(12), Eu–P2 325.06(12), Eu–P3 306.54(13), Eu–O 253.8(3), P1–N1 159.8(4), P1–C1 173.4(5), P2–N2 160.5(4), P2–C1 172.9(5); N1–Eu–N2 102.56(12), N1–Eu–N3 118.31(12), N2–Eu–N3 134.71(12), N3–Eu–C1 122.41(12), N1–Eu–P3 110.07(9), N2–Eu–P3 116.76(9), N3–Eu–P1 126.01(9), N3–Eu–P2 132.24(9), N3–Eu–P3 32.77(9), N1–Eu–O 90.70(11), N2–Eu–O 95.98(13), N3–Eu–O 101.85(12), C1–Eu–O 134.69(12), O–Eu–P3 134.62(9), P1–N1–Eu 100.1(2), P2–N2–Eu 99.3(2), P1–C1–P2 132.7(3), P3–N3–P4 121.2(2). **3b**: Yb–N1 242.9(3), Yb–N2 246.0(3), Yb–N3 241.2(3), Yb–C1 278.6(4), Yb–P1 312.15(11), Yb–P2 314.39(11), Yb–P3 294.96(11), Yb–O 242.9(2), P1–N1 160.2(3), P1–C1 173.7(4), P2–N2 160.4(3), P2–C1 173.2(4); N1–Yb–N2 106.60(10), N1–Yb–N3 119.99(10), N2–Yb–N3 130.93(10), N3–Yb–C1 124.06(12), N1–Yb–P3 112.41(8), N2–Yb–P3 114.62(8), N3–Yb–P1 128.88(8), N3–Yb–P2 132.35(8), N3–Yb–P3 34.43(8), N1–Yb–O 90.41(9), N2–Yb–O 93.45(12), N3–Yb–O 100.41(11).

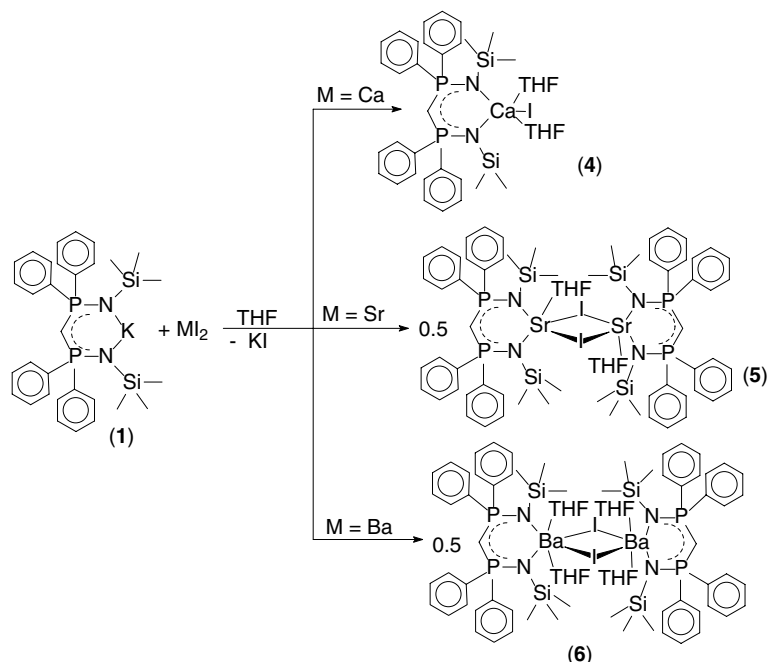
294.5(2) pm (**2a**), 270.0(4) pm (**2b**). As seen in other diphosphanylamide complexes of the lanthanides, e.g., in  $\{[(\text{Ph}_2\text{P})_2\text{N}]\text{LnCl}_2(\text{THF})_3\}$  [31] the diphosphanyla-

midate ligand in **3a,b** is  $\eta^2$ -coordinated via the nitrogen and one phosphorus atom. Thus, one of the phosphorus atoms of the ligand binds to the lanthanide center, whereas the other phosphorus atom is bent away. The Ln–N3 and Ln–P3 bond lengths are 252.7(4) and 306.54(13) pm (**3a**) and 241.2(3) and 294.96(11) pm (**3b**). The free electron pair of the non-bonded phosphorus atom points away from the lanthanide center. Within the ligand the P–N bond distance varies slightly.

The multinuclear NMR data of the diamagnetic compound **3b** is consistent with the solid-state structure. The  $^1\text{H}$  NMR spectrum of compound **3b** shows a characteristic sharp singlets of the  $\text{Me}_3\text{Si}$  groups. The signal of the methine protons in **3b** is overlapped when deuterated THF is used as the solvent. Whereas using  $\text{C}_6\text{D}_6$  as a solvent, only a broad peak is observed ( $\delta$  1.91 ppm). The phenyl region in the  $^1\text{H}$  NMR spectrum is as expected. More characteristic is the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. Complex **3b** shows two sharp signals in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\delta$  19.8, 49.2 ppm), indicating that the phosphorus atoms of each ligand are chemically equivalent in solution at room temperature. The dynamic behavior of the  $\{(\text{Ph}_2\text{P})_2\text{N}\}^-$  ligand was also observed in all other lanthanide complexes reported so far [22,31–33]. Furthermore small satellite signals caused by  $^2J(\text{Yb}, \text{P})$  coupling are observed.

### 2.3. Alkaline earth iodine complexes

It is well established that the reactivity and coordination behavior of the divalent lanthanide metals and the heavier alkaline earth metals is somewhat similar [34]. This similarity in coordination chemistry originates from the similar ion radii (for CN 6 (pm):  $\text{Ca}^{2+}$  100,  $\text{Yb}^{2+}$  102,  $\text{Sr}^{2+}$  118,  $\text{Eu}^{2+}$  117,  $\text{Ba}^{2+}$  135) [35]. Therefore, we expected a certain relationship between **2a** and an analogous strontium(II) compound and between **2b** and a related calcium(II) compound, whereas barium(II) is too large to be part of this analogy. To prove our expectations **1** was reacted with  $\text{MI}_2$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ) in THF at room temperature to give the corresponding bis(phosphinimino)methanide complexes  $\{[(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}]\text{CaI}(\text{THF})_2\}$  (**4**),  $\{[(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}]\text{SrI}(\text{THF})_2\}$  (**5**), and  $\{[(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}]\text{BaI}(\text{THF})_2\}$  (**6**), as crystalline solids in good yields (Scheme 4) [26]. The new complexes have been characterized by standard analytical/spectroscopic techniques, and the solid-state structures of all compounds were established by single crystal X-ray diffraction (Figs. 4–6). As observed for the divalent lanthanide compounds a six membered ring (N1–P1–C1–P2–N2–M), which adopts a twist boat conformation is formed by the  $\{[\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2]^-$  ligand and the alkaline earth metal atom. The expected similarities between **2b** and **4** as well as **2a** and **5** are observed in the solid-state. Thus, both pairs of compounds have the same monomeric  $\{[(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}]\text{MI}$



Scheme 4.

(THF)<sub>2</sub>] (**2b** and **4**) and dimeric composition [ $\{(\text{Me}_3\text{SiN}-\text{PPh}_2)_2\text{CH}\}\text{MI}(\text{THF})_2$ ] (**2a** and **5**), respectively. On the other hand **2b** and **4** crystallize in different Laue groups.

Compound **2b** crystallizes in the triclinic space group  $P\bar{1}$  with two molecules in the unit cell (Fig. 2), whereas compound **4** crystallizes in the monoclinic space group  $P2_1/n$  with four molecules of **4** and four molecules of non-coordinated THF in the unit cell.

Even Yb(II) and Ca(II) have almost the same ionic radii, the bond distances and angles within **2b** and **4** are different. Thus the N1–M–N2 bite angle in **4** (88.8(2)°) is smaller than the corresponding angle in **2a** (92.36(11)°) and the M–N bond distances in **4** (Ca–N1 250.2(5) pm and Ca–N2 241.1(5) pm) differ from those in **2b** (Yb–N1 249.1(4) pm, Yb–N2 247.5(3) pm), respectively. It is observed in compound **4** that the  $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$

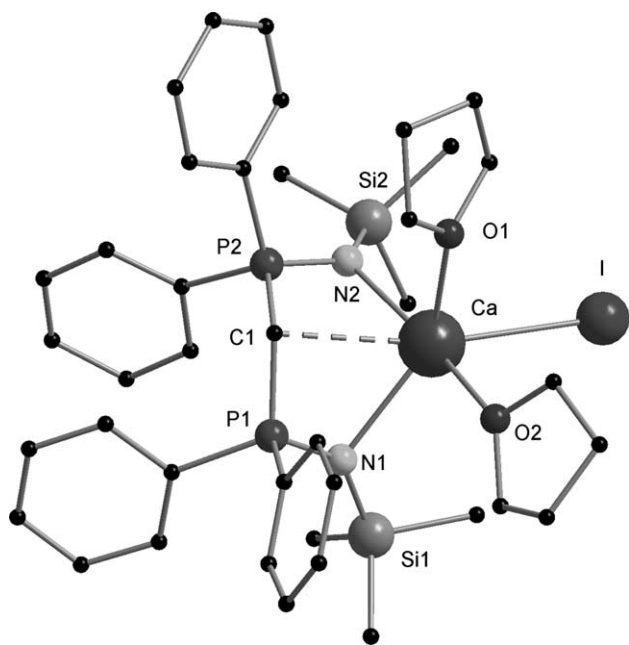


Fig. 4. Solid-state structure of **4** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths (pm) or angles (°): Ca–I 313.53(13), Ca–N1 250.2(5), Ca–N2 241.1(5), Ca–C1 273.5(6), Ca–O1 241.3(5), Ca–O2 239.3(5), P1–N1 159.0(5), P2–N2 159.0(5), C1–P1 173.1(6), C1–P2 174.4(6); I–Ca–N1 124.93(11), I–Ca–N2 103.28(12), I–Ca–C1 166.80(13), I–Ca–O1 92.25(12), I–Ca–O2 87.04(13), N1–Ca–N2 88.8(2), N1–Ca–C1 61.9(2), N1–Ca–O1 141.9(2), N1–Ca–O2 90.2(2), N2–Ca–C1 64.3(2), N2–Ca–O1 90.3(2), N2–Ca–O2 168.0(2), C1–Ca–O1 83.7(2), C1–Ca–O2 104.9(2), O1–Ca–O2 83.1(2), P1–C1–P2 122.8(3).

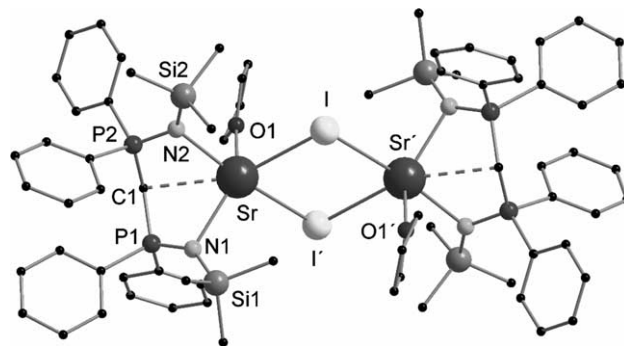


Fig. 5. Solid-state structure of **5** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths (pm) or angles (°): I–Sr 331.02(6), I'–Sr 334.34(7), Sr–N1 260.1(2), Sr–N2 256.6(2), Sr–C1 295.8(3), Sr–O1 247.4(2), P1–N1 157.8(2), P2–N2 158.7(2); Sr–Sr' 98.493(9), I–Sr–I' 81.507(9), I–Sr–N1 132.08(5), I–Sr–N2 98.58(5), I–Sr–C1 157.93(5), I–Sr–O1 94.73(7), I'–Sr–N1 97.17(5), I'–Sr–N2 169.27(6), I'–Sr–C1 118.81(5), I'–Sr–O1 81.73(7), N1–Sr–N2 90.74(8), N1–Sr–C1 58.24(7), N1–Sr–O1 132.75(8), N2–Sr–C1 59.80(7), N2–Sr–O1 87.58(9), C1–Sr–O1 80.85(9), P1–C1–P2 126.7(2).

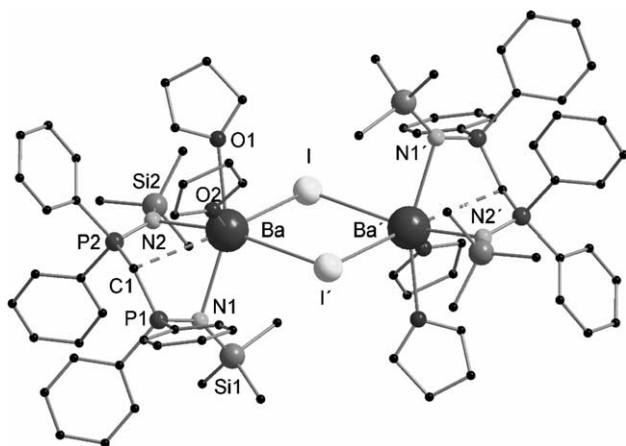


Fig. 6. Solid-state structure of **6** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths (pm) or angles ( $^{\circ}$ ): Ba–I 351.77(6), Ba–I' 361.26(6), Ba–N1 286.6(3), Ba–N2 278.4(2), Ba–C1 312.7(3), Ba–O1 280.6(3), Ba–O2 275.7(3), P1–N1 157.6(3), P2–N2 158.4(3); I–Ba–I' 78.064(10), Ba–I–Ba' 101.936(10), I–Ba–N1 117.58(5), I–Ba–N2 98.76(5), I–Ba–C1 152.87(5), I–Ba–O1 79.88(6), I–Ba–O2 130.22(6), I'–Ba–N1 89.29(5), I'–Ba–N2 165.18(5), I'–Ba–C1 123.87(5), I'–Ba–O1 109.38(6), I'–Ba–O2 77.81(7), N1–Ba–N2 79.30(7), N1–Ba–C1 53.86(7), N1–Ba–O1 157.36(7), N1–Ba–O2 104.94(8), N2–Ba–C1 55.75(7), N2–Ba–O1 84.00(8), N2–Ba–O2 114.12(8), C1–Ba–O1 103.90(8), C1–Ba–O2 74.28(8), P1–C1–P2 124.8(2).

ligand is slightly asymmetrically attached to the metal center. Thus, the deviations in bond distances and angles between **2b** and **4** seem to be result of the crystal packing in the different space groups. The distance of the central carbon atom C1 and the calcium atom in **4** (Ca–C1 273.5(6) pm) is in the range of the corresponding Ca–C bond observed in  $[\{\text{CH}(\text{PPh}_2\text{N-Mes})_2\}_2\text{CaN}(\text{SiMe}_3)_2]$  (271.3(7) pm) [25]. The displacement of the Ca and C1 atom out of the  $\text{N}_2\text{P}_2$  least-square-plane are 166 pm and 71 pm. Bond distances and angles within the  $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$  ligand are as expected.

In contrast to the pair **2b** and **4** compounds **2a** and **5** are isostructural to each other. Both crystallize as dimeric compounds in the monoclinic space group  $P2_1/c$ . Thus the metal centers of the dimeric complexes are asymmetrically bridged by two  $\mu$ -iodine atoms (Sr–I 331.02(6) pm, Sr–I' 334.34(7) pm) (Fig. 5). Rectangular through the center of the Sr–I–Sr'–I' plane, a crystallographic  $C_2$  axis is observed. The interaction between the methine carbon atom (C1) and the strontium atom (295.8(3) pm), which is longer than usual Sr–C distances is in the range of the related bond in  $[\{\text{CH}(\text{PPh}_2\text{N-Mes})_2\}\text{CaN}(\text{SiMe}_3)_2]$  (286.1(2) pm) [25]. As observed for **2a** the metal atom is displaced by 158 pm and the methine carbon atom (C1) about 67 pm out of the  $\text{N}_2\text{P}_2$  least-square-plane.

As expected the barium compound **6** (Fig. 6) has no structural analogues in divalent lanthanide chemistry. Compound **6** crystallizes in the monoclinic space group  $P2_1/n$  having two molecules in the unit cell. As observed for **2a** and **5** compound **6** is a dimeric complex in which the center metals are asymmetrically bridged by two

$\mu$ -iodine atoms (Ba–I 351.77(6), Ba–I' 361.26(6)). Rectangular through the center of the Ba–I–Ba'–I' plane, a crystallographic  $C_2$  axis is observed. In contrast to the isostructural compounds **2a** and **5** in **6** an additional molecule of THF is coordinated to the barium atom. By considering the  $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$  ligand as tridentate donor the barium atom is seven-coordinated. The increased coordination number of the barium atom is a result of the larger ion radius. As observed for the previous discussed complexes, the bis(phosphinimino)methanide ligand forms a six membered metallacycle (N1–P1–C1–P2–N2–Ba), which adopts a twist boat conformation having a Ba–C1 interaction of 312.7(3) pm. The Ba atom is displaced by 199 pm and the methine carbon atom (C1) about 68 pm out of the  $\text{N}_2\text{P}_2$  least-square-plane. Interestingly, in the related di(bis(phosphinimino)methanide) complex  $[\text{Ba}\{\text{CH}(\text{PPh}_2\text{N-Mes})_2\}_2]$ , no carbon barium bond is observed [25]. In the latter complex the ligand acts only as a bidentate donor. Surprisingly, no complex of composition  $[\{\text{CH}(\text{PPh}_2\text{N-Mes})_2\}\text{BaX}]$  could be isolated so far. The Ba–N and Ba–O distances in compound **6** are Ba–N1 286.6(3) pm, Ba–N2 278.4(2) pm, Ba–O1 280.6(3) pm, and Ba–O2 275.7(3) pm. As a result of the larger coordination number in compound **6** compared to **4** and **5**, the N–M–N bite angle is diminished (N1–M–N2: 88.8(2) $^{\circ}$  (**4**), 90.74(8) $^{\circ}$  (**5**), 79.30(7) $^{\circ}$  (**6**)). The bond distances and angles within the  $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$  ligand are as expected.

Beside the solid-state structures compounds **4**, **5**, and **6** were also investigated in solution by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR methods. The spectra are consistent with time averaged mirror symmetric structures in solution. No reorganization of the coordination sphere is necessary to explain the dynamic behavior. The signal of the methine proton ( $\delta$  1.88 (**4**), 1.95 (**5**), 1.34 (**6**)) in  $^1\text{H}$  NMR spectra of all alkaline earth metal compounds is in the range of  $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$  ( $\delta$  1.58) [12]. The phenyl region in the  $^1\text{H}$  NMR spectra is as expected. Complex **4**, **5**, and **6** each show a sharp signal in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\delta$  18.7 (**4**), 17.9 (**5**), 16.1 (**6**)), which are in the range of the alkali metal salts  $\text{Li}(\text{THF})\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$  ( $\delta$  17.6) and  $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$  ( $\delta$  13.0) [12]. These observations show that the phosphorus atoms in each case are chemically equivalent in solution.

#### 2.4. Hydroamination/cyclization catalysis

The mechanism of the lanthanide metallocene catalyzed hydroamination/cyclization reaction was some years ago established by Marks et al. [36]. In the initial step of this mechanism a leaving group (R) on the metallocene precatalyst,  $[(\text{C}_5\text{Me}_5)_2\text{Ln-R}]$ , is replaced by the substrate. Alternatively, it was shown that the divalent samarocens  $[(\text{C}_5\text{Me}_5)_2\text{Sm}]$  and  $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2]$  catalyze the hydroamination/cyclization of a variety of

aminoolefins [37]. Mechanistic studies showed that the active catalysts are trivalent complexes, which were generated by an in situ oxidation reaction of the samarocen precatalyst. Based on these results we were interested in studying the catalytic activity of the divalent ytterbium complex **2b** as precatalyst for the hydroamination/cyclization reaction. The scope and the limitation by using **2b** as catalyst in the intramolecular hydroamination/cyclization reaction were tested with different aminoalkynes and aminoolefins. The results are summarized in Table 1. The reaction scope is limited so far on five membered rings formation. The rigorously anaerobic reactions of the catalysts with dry, degassed aminoolefins and aminoalkynes proceeds regioselectively (>95%) in benzene. The two aminoalkynes, which were tested by us were converted to the cyclic product at elevated temperature in quantitative yields (entries 1–6). At room temperature a sluggish activity is observed only (entry 7). In contrast aminoolefins could be reacted only if they have geminal rigid substituents in  $\beta$ -position to the amino group (Thorpe–Ingold-effect) [38] (entries 8 and 9). Kinetic studies were undertaken by in situ  $^1\text{H}$  NMR spectroscopy. The reaction of a 20-fold molar excess of the substrates were monitored with constant catalyst concentration until complete substrate consumption. The decrease of the substrate peak was integrated versus the product signals. Kinetics data of the cyclization of 5-phenyl-4-pentyn-1-amine indicates a zero order kinetic in substrate concentration, in an analogy to the results

of the metallocene catalysts. During the initiation of the catalysis a color change from red to yellow is observed, indicating an in situ oxidation reaction of **2b**.

### 3. Summary

Divalent bis(phosphinimino)methanide lanthanide complexes of composition  $[\{(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}\}\text{Eu}(\text{THF})_2]$  (**2a**) and  $[\{(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}\}\text{Yb}(\text{THF})_2]$  (**2b**) have been prepared by a salt metathesis reaction of  $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$  and  $\text{LnI}_2$ . The structures of both compounds were confirmed by single crystal X-ray diffraction in the solid-state. As a result of the different ion radii  $[\{(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}\}\text{Eu}(\text{THF})_2]$  forms a dimer in the solid-state whereas  $[\{(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}\}\text{Yb}(\text{THF})_2]$  is monomeric. Reaction of  $[\text{K}(\text{THF})_n\text{N}(\text{PPh}_2)_2]$  with **2a,b** in THF in a 1:1 molar ratio led selectively to the amido complexes of composition  $[\{(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}\}\text{Ln}\{(\text{Ph}_2\text{P})_2\text{N}\}(\text{THF})]$  ( $\text{Ln} = \text{Eu}$  (**3a**),  $\text{Yb}$  (**3b**)). In an alternative approach, compound **3b** was also obtained by reduction of the recently reported trivalent complex  $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{Yb}\{(\text{Ph}_2\text{P})_2\text{N}\}\text{Cl}]$  with elemental potassium in refluxing THF. The single crystals of **3a,b** contain enantiomerically pure complexes.

To probe the well established similarity in reactivity and coordination chemistry between the divalent lanthanide metals and the heavier alkaline earth metals for the bis(phosphinimino)methanide ligand,  $\text{MI}_2$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ) was reacted with  $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$  to give  $[\{(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}\}\text{Ca}(\text{THF})_2]$ ,  $[\{(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}\}\text{Sr}(\text{THF})_2]$ , and  $[\{(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}\}\text{Ba}(\text{THF})_2]$ . As expected the Sr and Eu complexes as well as the Ca and Yb complexes are very similar whereas for the Ba compound as a result of the large ion radius a different coordination sphere, in which the barium atom is seven-coordinated, is observed.

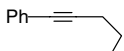





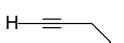







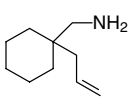
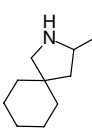
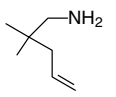

For all new complexes the solid-state structures were established by single crystal X-ray diffraction. The crystal structures of these complexes show that the methine carbon atom is bound to the lanthanide atom. Thus, all complexes presented in this paper can be considered as organometallic compounds. Finally,  $[\{(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}\}\text{Yb}(\text{THF})_2]$  was also used as precatalyst for the intramolecular hydroamination/cyclization reaction of different aminoalkynes and aminoolefins. Good yields but moderate activities were observed.

### 4. Experimental

#### 4.1. General

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and

Table 1  
Hydroamination/cyclization reaction of terminal aminoolefins and alkynes using **2b** as catalyst<sup>a</sup>

Entry	Substrate	Product	Cat. mol%	T °C	Yield % <sup>b</sup>	T h	TOF h <sup>-1</sup>
1			5.3	120	>95	6	3.15
2			5.3	90	>95	18	1.05
3			5.3	60	80	108	0.14
4			2.8	120	>95	3	11.9
5			2.8	60	>95	56	0.63
6			1.4	60	60	192 <sup>c</sup>	0.22
7			2.8	RT	17	96	0.06
8			5.1	120	92	96	0.19
9				120	–	120	

<sup>a</sup> Condition, cat 20 mg (0.028 mM), C6D6.

<sup>b</sup> Calculated by  $^1\text{H}$  NMR.

<sup>c</sup> Cat 10 mg (0.014 mM).



moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum ( $10^{-4}$  Torr) line, or in an argon-filled M. Braun glove box. Ether solvents (THF and ethyl ether) were predried over Na wire and distilled under nitrogen from K (THF) or Na wire (ethyl ether) as well as benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from  $\text{LiAlH}_4$ . All solvents for vacuum line manipulations were stored in vacuo over  $\text{LiAlH}_4$  in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all  $\geq 99$  atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on a Jeol JNM-LA 400 FT NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85% phosphoric acid ( $^{31}\text{P}$  NMR), respectively. IR spectra were obtained on a Shimadzu FTIR-8400s. Elemental analyses were carried out with an Elementar vario EL.  $\text{YbCl}_3$  [39],  $\text{EuI}_2$  [40],  $\text{YbI}_2$  [41],  $[\text{K}(\text{THF})_n\text{N}(\text{PPh}_2)_2]$  ( $n = 1.25, 1.5$ ) [30] and  $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$  [12] were prepared according to literature procedures.

#### 4.2. Synthesis of $[\{(Me_3SiNPPPh_2)_2CH\}EuI(\text{THF})]_2$ (**2a**)

300 mg (0.5 mmol) of **1** and 275 mg (0.5 mmol) of  $\text{EuI}_2(\text{THF})_2$  was taken together under an inert atmosphere. 15 ml of THF was condensed onto it at  $-196^\circ\text{C}$ . The solution mixture was allowed to warm to room temperature and kept under stirring for 16 h. During the reaction, the solution turned to deep yellow color with white precipitate formed. The reaction mixture was filtered and the filtrate was concentrated to 5 ml. Pentane (10 ml) was layered on the top of the THF solution. After one day yellow crystals were obtained.

Yield: 310 mg (65%). IR (KBr  $[\text{cm}^{-1}]$ ): 3055 (m,  $\nu(\text{C}=\text{C}-\text{H})$ ), 2947 (m,  $\nu(\text{C}-\text{H})$ ), 2891 (br), 1589 (s,  $\nu(\text{C}=\text{C})$ ), 1483 (m), 1435 (s), 1245 (m), 1113 (br), 1059 (s), 1027 (s), 950 (br), 832 (br), 742 (m), 709 (s), 693 (s), 661 (s), 554 (s), 515 (s).  $\text{C}_{70}\text{H}_{94}\text{Eu}_2\text{I}_2\text{N}_4\text{O}_2\text{P}_4\text{Si}_4$  (1881.55) Calc.: C 46.26, H 5.21, N 3.08. Found: C 45.96, H 5.40, N 2.94.

#### 4.3. $[\{(Me_3SiNPPPh_2)_2CH\}YbI(\text{THF})_2]$ (**2b**)

300 mg (0.5 mmol) of **1** and 286 mg (0.5 mmol) of  $\text{YbI}_2(\text{THF})_2$  was taken together under an inert atmosphere. 15 ml of THF was condensed onto it at  $-196^\circ\text{C}$ . The solution mixture was allowed to warm to room temperature and kept under stirring for 16 h. During the reaction, the solution turned to deep red color and a white precipitate formed. The reaction mixture

was filtered and the filtrate was concentrated to 5 ml. Pentane (10 ml) was layered on the top of the THF solution. After one day red crystals were obtained.

Yield: 402 mg (80%). IR (KBr  $[\text{cm}^{-1}]$ ): 3055 (m,  $\nu(\text{C}=\text{C}-\text{H})$ ), 2948 (m,  $\nu(\text{C}-\text{H})$ ), 2889 (w), 1589 (s,  $\nu(\text{C}=\text{C})$ ), 1483 (m), 1436 (s), 1244 (m), 1159 (s), 1114 (br), 1068 (s), 832 (s), 782 (s), 745 (br), 692 (s), 648 (s), 552 (s), 506 (s).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz,  $25^\circ\text{C}$ ):  $\delta$  0.44 (s, 18H,  $\text{SiMe}_3$ ), 1.52 (br, 8H, THF), 1.91 (br, 1H, CH), 3.8 (br, 8H, THF), 6.96 (br, 12H, Ph), 7.74 (br, 8H, Ph).  $^{31}\text{P}\{\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 161.70 MHz,  $25^\circ\text{C}$ ):  $\delta$  14.2 ( $^2J(\text{P}, \text{Yb}) = 66.4$  Hz).  $\text{C}_{39}\text{H}_{55}\text{IP}_2\text{Si}_2\text{N}_2\text{O}_2\text{Yb}$  (1001.94) Calc.: C 46.75, H 5.53, N 2.80. Found: C 45.21, H 4.60, N 2.78.

#### 4.4. $[\{(Me_3SiNPPPh_2)_2CH\}Eu\{(Ph_2P)_2N\}(\text{THF})]$ (**3a**)

300 mg (0.5 mmol) of **1** and 275 mg (0.5 mmol) of  $\text{EuI}_2(\text{THF})_2$  was taken in a 25 ml flask inside the glove box. 15 ml of THF was condensed at  $-196^\circ\text{C}$  onto the mixture. The reaction mixture was stirred at room temperature for 16 h. The THF was evaporated under vacuo and 250 mg (0.5 mmol) of  $[\text{K}(\text{THF})_n\text{N}(\text{PPh}_2)_2]$  was added to the reaction vessel. To this mixture 15 ml of THF was condensed at  $-196^\circ\text{C}$ . The solution was stirred at room temperature for 18 h. The solution was filtered to remove the potassium iodide and the filtrate was concentrated to 5 ml. Pentane (10 ml) was layered on top of the THF solution. After one day orange crystals were obtained.

Yield: 330 mg (57%). IR (KBr  $[\text{cm}^{-1}]$ ): 3053 (m,  $\nu(\text{C}=\text{C}-\text{H})$ ), 2949 (m,  $\nu(\text{C}-\text{H})$ ), 2891 (w), 1577 (s,  $\nu(\text{C}=\text{C})$ ), 1482 (m), 1434 (s), 1242 (m), 1120 (br), 1027 (s), 954 (br), 829 (s), 739 (s), 594 (s), 5553 (m).  $\text{C}_{59}\text{H}_{67}\text{EuN}_3\text{OP}_4\text{Si}_2$  (1166.23) Calc.: C 60.76, H 5.79, N 3.60. Found: C 59.41, H 5.68, N 3.47.

#### 4.5. $[\{(Me_3SiNPPPh_2)_2CH\}Yb\{(Ph_2P)_2N\}(\text{THF})]$ (**3b**)

*Route A.* **3b** can be obtained in an analogous way to **3a** (Yield 325 mg (55%)).

*Route B.* A mixture of 300 mg (0.5 mmol)  $[\{(Me_3SiNPPPh_2)_2CH\}K]$ , 140 mg (0.5 mmol)  $\text{YbCl}_3$  and 250 mg (0.5 mmol)  $[\text{K}(\text{THF})_n\text{N}(\text{PPh}_2)_2]$  was taken under inert atmosphere. To this mixture 15 ml of THF was condensed at  $-196^\circ\text{C}$ . The solution was stirred at room temperature for 18 h. Then THF was evaporated under vacuo. 19.5 mg (0.5 mmol) of potassium was added to the reaction vessel. Further 15 ml of THF was introduced and refluxed for another 16 h. THF was removed under vacuo and 20 ml of toluene was added. The compound was extracted by filtration and then washed with pentane. The title compound was crystallized from THF/pentane (1:2).

Yield: 250 mg (42%) dark red crystals. IR (KBr [ $\text{cm}^{-1}$ ]): 3053 (m,  $\nu(\text{C}=\text{H})$ ), 2949 (m,  $\nu(\text{C}-\text{H})$ ), 2891 (w), 1577 (s,  $\nu(\text{C}=\text{C})$ ), 1476 (m), 1434 (s), 1242 (m), 1112 (br), 1027 (m,  $\nu(\text{PC})$ ), 937 (m), 831 (s), 739 (s), 715 (m), 694 (s).  $^1\text{H}$  NMR ( $d_8$ -THF, 400 MHz, 20 °C):  $\delta$  -0.23 (s, 18H,  $\text{SiMe}_3$ ), 1.75 (br, 5H, THF + CH), 3.61 (br, 4H, THF), 6.93–7.10 (m, 20H, Ph), 7.15–7.27 (m, 4H, Ph), 7.37–7.52 (m, 16H, Ph), 7.86 (br, 4H, Ph).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz, 20 °C):  $\delta$  0.13 (s, 18H,  $\text{SiMe}_3$ ), 1.39 (br, 4H, THF), 1.91 (br, 1H, CH), 3.70 (br, 4H, THF), 6.62–7.11 (m, 24H, Ph), 7.41–7.60 (m, 8H, Ph), 7.74–7.86 (m, 8H, Ph).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 161.7 MHz, 20 °C):  $\delta$  17.2 (PCP), 46.7 (PNP).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $d_8$ -THF, 100.4 MHz, 20 °C):  $\delta$  4.4 ( $\text{SiMe}_3$ ), 26.4 (b, THF + CH), 68.2 (s, THF), 127.5 (s, Ph), 128.0 (s, Ph), 128.4 (m, Ph), 130.5 (s, Ph), 132.3 (m, Ph), 133.2 (m, Ph), 138.1 (d, Ph), 147.9 (dd, Ph).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $d_8$ -THF, 161.7 MHz, 20 °C):  $\delta$  19.8 (PCP) ( $^2J(\text{P}, \text{Yb}) = 62$  Hz), 49.2 (PNP) ( $^2J(\text{P}, \text{Yb}) = 53$  Hz).  $\text{C}_{59}\text{H}_{67}\text{N}_3\text{OP}_4\text{Si}_2\text{Yb}$  (1187.30) Calc.: C 59.69, H 5.69, N 3.54. Found: C 59.75, H 5.63, N 3.42.

4.6. [ $\{(\text{Me}_3\text{SiNPPPh}_2)_2\text{CH}\}\text{CaI}(\text{THF})_2$ ] (**4**),  
 [ $\{(\text{Me}_3\text{SiNPPPh}_2)_2\text{CH}\}\text{SrI}(\text{THF})_2$ ] (**5**),  
 [ $\{(\text{Me}_3\text{SiNPPPh}_2)_2\text{CH}\}\text{BaI}(\text{THF})_2$ ] (**6**)

*General procedure.* 300 mg (0.5 mmol) of **1** and 0.5 mmol of  $\text{MI}_2$  was taken together under an inert atmosphere. 15 ml of THF was condensed onto it. The solution mixture was allowed to warm at room temperature and kept under stirring for 16 h. During the reaction a white precipitate formed. The reaction mixture was filtered to remove potassium iodide and the filtrate was concentrated to 5 ml. Pentane (10 ml) was layered on the top of the THF solution. After one day colorless crystals were obtained.

**4:** Yield: 350 mg (74%)  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz, 25 °C):  $\delta$  0.45 (s, 18H,  $\text{SiMe}_3$ ), 1.34 (t, 8H, THF), 1.88 (br, 1H, CH), 3.27 (t, 8H, THF), 6.94–7.15 (m, 12H, *o*-, *p*-Ph), 7.65–7.72 (m, 8H, *m*-Ph).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 161.70 MHz, 25 °C):  $\delta$  18.7.  $\text{C}_{35}\text{H}_{47}\text{CaIP}_2\text{Si}_2\text{N}_2\text{O}_2$  (812.87) (**4** – THF) Calc.: C 51.72, H 5.83, N 3.45. Found: C 51.51, H 6.28, N 3.02.

**5:** Yield: 320 mg (73%)  $^1\text{H}$  NMR ( $d_8$ -THF, 400 MHz, 25 °C):  $\delta$  0.14 (s, 18H,  $\text{SiMe}_3$ ), 1.59 (br, 1H, CH), 1.74–1.79 (m, 4H, THF), 3.58–3.62 (m, 4H, THF), 7.15–7.35 (m, 12H, *o*-, *p*-Ph), 7.58–7.70 (m, 8H, *m*-Ph).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $d_8$ -THF, 161.70 MHz, 25 °C):  $\delta$  17.9.  $\text{C}_{62}\text{H}_{78}\text{N}_4\text{I}_2\text{P}_4\text{Si}_4\text{Sr}_2$  (1546.60) (**5** – 2THF) Calc.: C 48.15, H 5.08, N 3.62. Found: C 47.42, H 5.54, N 2.99.

**6:** Yield: 420 mg (87%)  $^1\text{H}$  NMR ( $d_8$ -THF, 400 MHz, 25 °C):  $\delta$  0.06 (s, 18H,  $\text{SiMe}_3$ ), 1.34 (br, 1H, CH), 1.72–1.79 (m, 8H, THF), 3.56–3.62 (m, 8H, THF), 7.13–7.35 (m, 12H, *o*-, *p*-Ph), 7.52–7.70 (m, 8H, *m*-Ph).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $d_8$ -THF, 161.70 MHz, 25 °C):  $\delta$  16.1.

$\text{C}_{39}\text{H}_{55}\text{BaIN}_2\text{P}_2\text{Si}_2$  (822.02) (**6** – 2THF) Calc.: C 45.30, H 4.78, N 3.41. Found: C 45.79, H 5.27, N 2.87.

4.7. *General procedure for the hydroamination reaction (NMR scale reaction)*

Compound **2b** was weighed under argon gas into an NMR tube.  $\text{C}_6\text{D}_6$  (~0.7 ml) was condensed into the NMR tube, and the mixture was frozen to  $-196$  °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before the insertion into the core of the NMR machine ( $t_0$ ). The ratio between the reactant and the product was exactly calculated by comparison of the integration of the corresponding signals.

4.8. *X-ray crystallographic studies of 2a,b, 3a,b, 4, 5 and 6*

Crystals of **2a,b**, **3a,b**, **4**, **5** and **6** were grown from a THF/pentane (1:2). Suitable crystals were coated in mineral oil (Aldrich) and mounted on glass fibers. The crystal was transferred directly to the  $-100$  °C cold stream of a Bruker SMART 1000 or a STOE IPDS 2T diffractometer with Mo  $\text{K}\alpha$  radiation. Structures were solved using SHELXS-97 [42] and refined against  $F^2$  using SHELXL-97 [43].

**2a:**  $\text{C}_{74}\text{H}_{102}\text{Eu}_2\text{I}_2\text{N}_4\text{O}_3\text{P}_4\text{Si}_4$  (**2a**·THF), monoclinic,  $P2_1/c$  (No. 14); lattice constants  $a = 1953.4(4)$  pm,  $b = 995.8(2)$  pm,  $c = 2329.9(4)$  pm,  $\beta = 112.649(4)^\circ$ ,  $V = 4182.7(13) \times 10^6$  pm $^3$ ,  $Z = 2$ ;  $\mu(\text{Mo K}\alpha) = 2.402$  mm $^{-1}$ ;  $\theta_{\text{max.}} = 30.58$ ; 12708 [ $R_{\text{int}} = 0.0221$ ] independent reflections measured, of which 10,384 were considered observed with  $I > 2\sigma(I)$ ; max. residual electron density 1.121 and  $-1.119$  e  $\text{Å}^{-3}$ ; 405 parameters,  $R_1(I > 2\sigma(I)) = 0.0268$ ;  $wR_2(\text{all data}) = 0.0793$ .

**2b:**  $\text{C}_{39}\text{H}_{55}\text{IN}_2\text{O}_2\text{P}_2\text{Si}_2\text{Yb}$ , triclinic,  $P\bar{1}$  (No. 2); lattice constants  $a = 1027.2(2)$  pm,  $b = 1197.8(2)$  pm,  $c = 1899.5(3)$  pm,  $\alpha = 98.833(4)^\circ$ ,  $\beta = 90.468(4)^\circ$ ,  $\gamma = 110.059(3)^\circ$ ,  $V = 2164.6(6) \times 10^6$  pm $^3$ ,  $Z = 2$ ;  $\mu(\text{Mo K}\alpha) = 3.036$  mm $^{-1}$ ;  $\theta_{\text{max.}} = 30.54$ ; 12985 [ $R_{\text{int}} = 0.1125$ ] independent reflections measured, of which 10,681 were considered observed with  $I > 2\sigma(I)$ ; max. residual electron density 3.328 and  $-3.015$  e  $\text{Å}^{-3}$ ; 428 parameters,  $R_1(I > 2\sigma(I)) = 0.0534$ ;  $wR_2(\text{all data}) = 0.1500$ .

**3a:**  $\text{C}_{59}\text{H}_{67}\text{EuN}_3\text{OP}_4\text{Si}_2$ , orthorhombic,  $P2_12_12_1$  (No. 19); lattice constants  $a = 1080.3(2)$  pm,  $b = 2177.7(4)$  pm,  $c = 2422.7(4)$  pm,  $V = 5699(2) \times 10^6$  pm $^3$ ,  $Z = 4$ ;  $\mu(\text{Mo K}\alpha) = 1.296$  mm $^{-1}$ ;  $\theta_{\text{max.}} = 30.57$ ; 17416 [ $R_{\text{int}} = 0.0784$ ] independent reflections measured, of which 12,788 were considered observed with  $I > 2\sigma(I)$ ; max. residual electron density 2.653 and  $-1.195$  e  $\text{Å}^{-3}$ ; 637 parameters, Flack parameter  $-0.045(10)$ ,  $R_1(I > 2\sigma(I)) = 0.0473$ ;  $wR_2(\text{all data}) = 0.1166$ .

**3b:**  $\text{C}_{59}\text{H}_{67}\text{N}_3\text{OP}_4\text{Si}_2\text{Yb}$ , orthorhombic,  $P2_12_12_1$  (No. 19); lattice constants  $a = 1076.6(2)$  pm,  $b =$

2158.1(5) pm,  $c = 2439.9(5)$  pm,  $V = 5669(2) \times 10^6$  pm<sup>3</sup>,  $Z = 4$ ;  $\mu(\text{Mo K}\alpha) = 1.847$  mm<sup>-1</sup>;  $\theta_{\text{max.}} = 30.61$ ; 17335 [ $R_{\text{int}} = 0.0718$ ] independent reflections measured, of which 13,513 were considered observed with  $I > 2\sigma(I)$ ; max. residual electron density 1.209 and  $-1.279$  e Å<sup>-3</sup>; 637 parameters, Flack parameter  $-0.052(5)$ ,  $R_1(I > 2\sigma(I)) = 0.0393$ ;  $wR_2(\text{all data}) = 0.0736$ .

**4:** C<sub>43</sub>H<sub>63</sub>CaIn<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Si<sub>2</sub> (**4** THF), monoclinic,  $P2_1/n$  (No. 14); lattice constants  $a = 1194.7(2)$  pm,  $b = 1516.9(3)$  pm,  $c = 2636.7(5)$  pm,  $\beta = 101.25(3)^\circ$ ,  $V = 4687(2) \times 10^6$  pm<sup>3</sup>,  $Z = 4$ ;  $\mu(\text{Mo K}\alpha) = 0.950$  mm<sup>-1</sup>;  $\theta_{\text{max.}} = 29.26$ ; 12,686 [ $R_{\text{int}} = 0.0588$ ] independent reflections measured, of which 6975 were considered observed with  $I > 2\sigma(I)$ ; max. residual electron density 1.548 and  $-0.880$  e Å<sup>-3</sup>; 472 parameters,  $R_1(I > 2\sigma(I)) = 0.0757$ ;  $wR_2(\text{all data}) = 0.2399$ .

**5:** C<sub>74</sub>H<sub>102</sub>I<sub>2</sub>N<sub>4</sub>O<sub>3</sub>P<sub>4</sub>Si<sub>4</sub>Sr<sub>2</sub> (**5** THF), monoclinic,  $P2_1/c$  (No. 14); lattice constants  $a = 1952.1(4)$  pm,  $b = 993.6(2)$  pm,  $c = 2336.2(5)$  pm,  $\beta = 112.784(4)^\circ$ ,  $V = 4177.7(14) \times 10^6$  pm<sup>3</sup>,  $Z = 2$ ;  $\mu(\text{Mo K}\alpha) = 2.194$  mm<sup>-1</sup>;  $\theta_{\text{max.}} = 30.10$ ; 12,177 [ $R_{\text{int}} = 0.0291$ ] independent reflections measured, of which 9379 were considered observed with  $I > 2\sigma(I)$ ; max. residual electron density 1.143 and  $-1.010$  e Å<sup>-3</sup>; 405 parameters,  $R_1(I > 2\sigma(I)) = 0.0392$ ;  $wR_2(\text{all data}) = 0.1065$ .

**6:** C<sub>78</sub>H<sub>110</sub>Ba<sub>2</sub>I<sub>2</sub>N<sub>4</sub>O<sub>4</sub>P<sub>4</sub>Si<sub>4</sub> monoclinic,  $P2_1/c$  (No. 14); lattice constants  $a = 1183.8(2)$  pm,  $b = 2019.1(4)$  pm,  $c = 1886.7(4)$  pm,  $\beta = 98.375(4)^\circ$ ,  $V = 4461.5(15) \times 10^6$  pm<sup>3</sup>,  $Z = 2$ ;  $\mu(\text{Mo K}\alpha) = 1.740$  mm<sup>-1</sup>;  $\theta_{\text{max.}} = 30.56$ ; 13,607 [ $R_{\text{int}} = 0.0291$ ] independent reflections measured, of which 10,057 were considered observed with  $I > 2\sigma(I)$ ; max. residual electron density 1.518 and  $-1.668$  e Å<sup>-3</sup>; 428 parameters,  $R_1(I > 2\sigma(I)) = 0.0376$ ;  $wR_2(\text{all data}) = 0.0859$ .

## 5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC, Nos. 259915–259921. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ [fax: +44(1223)336 033] or e-mail deposit@ccdc.cam.ac.uk or [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

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