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Bis(phosphinimino)methanide borohydride complexes of neodymium and scandium

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Dedicated to the memory of Professor Herbert Schumann († 2010), a pioneer of organolanthanide chemistry.

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ABSTRACT

Bis(phosphinimino)methanide rare earth metal bis(borohydrides) [{$(Me_3SiNPPh_2)_2CH$}$Nd(BH_4)_2(THF)$] (**1**) and [{$(Me_3SiNPPh_2)_2CH$}$Sc(BH_4)_2$] (**2**) were prepared by reaction of [$Ln(BH_4)_3(THF)_n$] and K{$CH(PPh_2NSiMe_3)_2$}. All new compounds have been characterized by standard analytical/spectroscopic techniques, and the solid state structures were established by single crystal X-ray diffraction. In compound **1** both BH_4^- groups are η^3-coordinated, whereas an η^3- and an η^2-coordination mode is observed for compound **2** at 200 K. Interestingly, a second conformational polymorph of **2** exists, in which both BH_4^- groups show an η^3-coordination mode.

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1. Introduction

Recently, borohydride compounds of various metals have been discussed as potential hydrogen storage materials [1]. However, in lanthanide borohydride chemistry the focus has been more on the synthetic and catalytic application. Although tris(borohydrides) of the lanthanides are known since the early 1960s [2], the use of [$Ln(BH_4)_3(THF)_n$] in synthetic and catalytic chemistry started in the 1980s, in which Mirsaidov et al. developed a convenient approach to these compounds by the reaction of $LnCl_3$ (Ln = La, Ce, Pr, Nd, Sm) with $NaBH_4$ [3–5]. Today, lanthanide tris(borohydrides) [$Ln(BH_4)_3(THF)_n$] [6] are known to be efficient catalysts for the (co) polymerization of ethylene [7–9], isoprene [9–13], butadiene [14], styrene [12,15], and some polar monomers such as lactide [16–21], ϵ-caprolactone [16–18,22–31], trimethylene carbonate [31] and methyl methacrylate [20,23,32,33].

In synthetic chemistry [$Ln(BH_4)_3(THF)_n$] turned out to be valuable starting materials for the salt metathesis reactions with alkali metal reagents. The thus formed byproduct, MBH_4, is easily removable. In most of these metathetical reactions the BH_4^- groups reacted like a pseudohalide [9,11,13,15,16,19,20,22,33–38]. By using this approach, borohydride derivatives of the rare earth elements, such as mono cyclopentadienyl complexes, [11,13,15,16,34,35] metallocenes, [9,22] alkoxides, [16,19,36] guanidinates [20,33,37] and cyclooctatetraene complexes [34,38] have been prepared. Although BH_4^- is isosteric with Cl^-, it is a much more electron-donating ligand [39], therefore allowing the isolation of otherwise unsaturated and inaccessible metallic species.

Recently we reported on amido metal borohydride complexes of the rare earth metals. Thus, 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl ($(DIP_2\text{-pyr})^-$) borohydride and chloride complexes were synthesized [40,41]. The neodymium complexes were used as Ziegler-Natta catalysts for the polymerization of 1,3-butadiene to poly-*cis*-1,4-butadiene [14].

In addition, we have introduced the bis(phosphinimino)methanide $\{CH(PPh_2NSiMe_3)_2\}^-$, which was previously used as a ligand in main group and transition metal chemistry by a number of research groups [42–45], into the borohydride chemistry of the

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rare earth elements [46]. In this context the bis(borohydrides) [{($Me_3SiNPPh_2$)$_2$CH}La(BH_4)$_2$(THF)] and [{($Me_3SiNPPh_2$)$_2$CH}Ln(BH_4)$_2$] (Ln = Y, Lu) were synthesized by two different synthetic routes. The new compounds were used as initiators for the ring-opening polymerization (ROP) of ϵ-caprolactone. At 0 °C, the molar mass distribution values reached the narrowest values ever obtained for the ROP of ϵ-caprolactone initiated from a rare earth metal borohydride species. DFT investigations of the reaction mechanism indicated that this type of complex is reacting in an unprecedented manner, in which for the first time the B–H activation proceeds within two steps.

To get a better understanding of the bis(phosphinimino)methanide borohydride complexes of the rare earth elements, we herein report on the synthesis of the neodymium and the scandium derivative. By using two metals with significantly different ion radii, our intention was to get a deeper insight into the coordination behavior of such complexes.

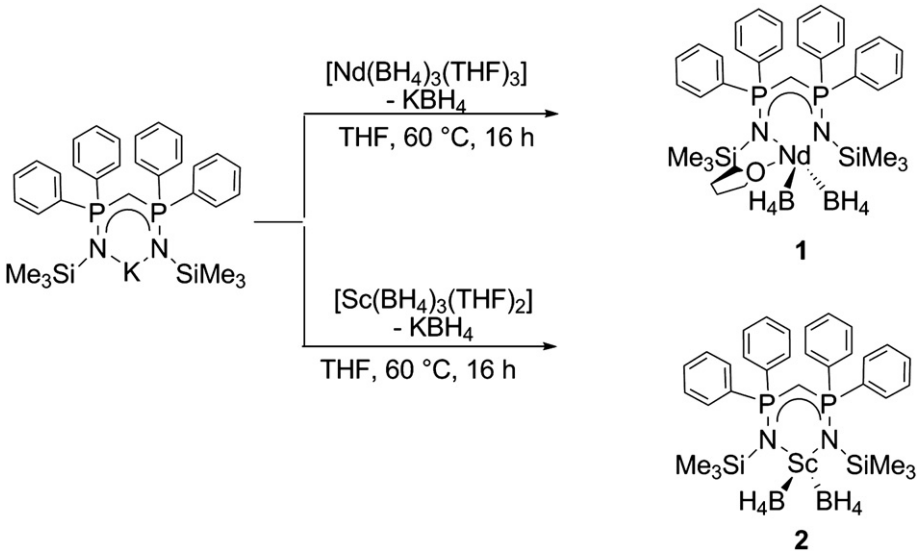
2. Results and discussion

The desired bis(phosphinimino)methanide rare earth metal bis(borohydrides) [{($Me_3SiNPPh_2$)$_2$CH}Nd(BH_4)$_2$(THF)] (**1**) and [{($Me_3SiNPPh_2$)$_2$CH}Sc(BH_4)$_2$] (**2**) were obtained by the reaction from [Ln(BH_4)$_3$(THF)$_n$] and K{CH(PPh_2NSiMe_3)$_2$} [47] in THF at elevated temperature (Scheme 1) [48]. Compound **1** was isolated as purple crystals, whereas compound **2** is as expected colorless. The new compounds have been characterized by standard analytical/spectroscopic techniques and the solid state structures were established by single crystal X-ray diffraction. As a result of the strong paramagnetic center metal, no NMR spectra of compound **1** were recorded.

The ^{1}H NMR spectrum of compound **2** shows the characteristic signals for the two different types of ligands. A sharp singlet for the $SiMe_3$ groups ($\delta = 1.09$ ppm) and a triplet for the PCHP group is observed ($\delta = 2.06$ ppm) for the {CH(PPh_2NSiMe_3)$_2$}$^-$ ligand. The signals of the phenyl region are not very characteristic. One broad peak is observed for the BH_4^- anion at $\delta = 0.99$–1.41 ppm. The ^{31}P{^{1}H} NMR spectrum shows the expected signal for the {CH(PPh_2NSiMe_3)$_2$}$^-$ ligand at δ 19.9 ppm. In the EI-MS spectrum, a molecular peak is observed as expected for **2**, while the mass spectra of compound **1** shows the loss of a THF molecule and one borohydride anion. In the IR spectra of compound **1** and **2** two characteristic peaks for each complex (2204 cm^{-1} and 2418 cm^{-1} (**1**), and 2291 cm^{-1} and 2495 cm^{-1} (**2**)) were observed. The signals of compound **1** can be assigned to terminal tridentate Ln (η^3–H_3B–H) units [6] and are in agreement with other bis(phosphinimino)methanide complexes such as [{($Me_3SiNPPh_2$)$_2$CH}La(BH_4)$_2$(THF)] and [{($Me_3SiNPPh_2$)$_2$CH}Ln(BH_4)$_2$] (Ln = Y, Lu) [46]. We could not doubtless assign the coordination mode of the BH_4^- groups of compound **2** based on the IR data.

Single crystals of compound **1** were obtained as pale purple plates from THF/*n*-pentane. The solid state structure of **1** was established by single crystal X-ray diffraction (Fig. 1). Compound **1** crystallizes in the triclinic space group *P*-1 having two molecules of **1** and two molecules of THF in the unit cell. If the BH_4^- groups are considered as monodentate and the {CH(PPh_2NSiMe_3)$_2$}$^-$ ligand as tridentate the structure of compound **1** reveals a six-fold coordination sphere of the ligands around the metal atom resulting in a distorted octahedral coordination polyhedron (e.g. B1–Nd–B2 100.15(11)° and B1–Nd–C1 152.47(9)°). A similar coordination sphere was observed earlier in [{($Me_3SiNPPh_2$)$_2$CH}La(BH_4)$_2$(THF)] [46]. The {CH(PPh_2NSiMe_3)$_2$}$^-$ ligand in compound **1** coordinates with the two nitrogen atoms and the central carbon atom (C1) to the metal center (Nd–N1 2.499(2) Å, Nd–N2 2.477(2) Å and Nd–C1 2.711(2) Å) forming a six membered metallacycle (N1–P1–C1–P2–N2–Nd) which adopt a twist boat conformation. In contrast to the dimeric monoborohydride complex [(C_8H_8)Nd(BH_4)(THF)]$_2$, in which the BH_4^- groups act as bridging ligands, compound **1** forms a monomer in the solid state [38]. The hydrogen atoms of the BH_4^- groups in **1** were freely refined. An η^3-coordination of the BH_4^- groups is thus clearly seen. This is consistent with the observed η^3-coordination mode of the BH_4^- anions in the bis(borohydride) compound [{C_5(*i*Pr)$_5$}Nd(BH_4)$_2$(THF)] which is also monomeric in the solid state [35].

Single crystals of compound **2** were obtained as colorless plates from hot toluene. The solid state structure of compound **2** was determined at 200 K by single crystal X-ray diffraction (Fig. 2). Compound **2** crystallizes enantiomerically pure in the chiral monoclinic space group $P2_1$ with two molecules of **2** and two molecules of toluene in the unit cell. As a result of the smaller ion radius of the center metal, there is no solvent molecule in the coordination sphere. The coordination polyhedron of complex **2** is therefore formed by two BH_4^- anions and the {CH(PPh_2NSiMe_3)$_2$}$^-$ ligand only. Considering the BH_4^- groups as monodentate and the



Scheme 1.

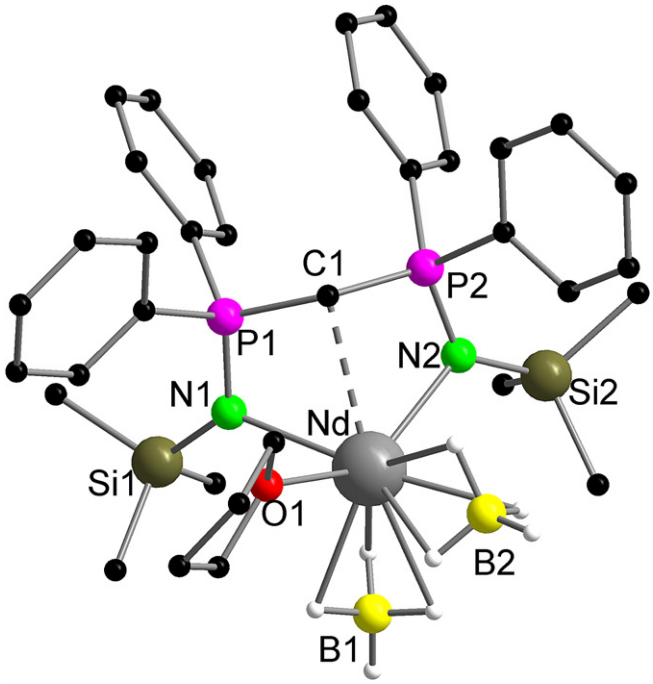


Fig. 1. Solid state structure of **1**, omitting hydrogen atoms, except for the freely refined B–H atoms. Selected bond lengths [Å] or angles [°]: Nd–N1 2.499(2), Nd–N2 2.477(2), Nd–O1 2.4940(15), Nd–B1 2.642(3), Nd–B2 2.653(3), Nd–C1 2.711(2), N1–P1 1.599(2), N1–Si1 1.734(2), N2–P2 1.603(2), N2–Si2 1.736(2), C1–P2 1.750(2), C1–P1 1.754(2); N1–Nd–N2 91.40(6), N1–Nd–O1 80.29(5), N2–Nd–O1 141.07(5), N1–Nd–B1 93.65 (9), N2–Nd–B1 106.64(8), N1–Nd–B2 159.69(8), N2–Nd–B2 98.75(8), N1–Nd–C1 62.93(6), N2–Nd–C1 62.65(5), O1–Nd–B1 111.78(8), O1–Nd–B2 80.78(7), B1–Nd–B2 100.15(11), O1–Nd–C1 79.99(5), B1–Nd–C1 152.47(9), B2–Nd–C1 106.42(8), P1–C1–P2 124.53(11).

$\{CH(PPh_2NSiMe_3)_2\}^-$ ligand as tridentate a five-fold coordination sphere around the metal atom is formed. This coordination polyhedron can be described as a distorted tetragonal pyramidal geometry (e.g. B1–Sc–B2 102.9(2)°). As observed for all other bis(phosphinimino)methanide complexes of the trivalent lanthanides [30,49–58] a six membered metallacycle (N1–P1–C1–P2–N2–Sc) is formed by coordination of the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand showing Sc–N bond distances of Sc–N1 2.134(3) Å and Sc–N2 2.160 (3) Å [49]. Moreover a long interaction between the central carbon atom (C1) and the scandium atom (Sc–C1 2.471(3) Å) is observed. The hydrogen atoms of the BH_4^- groups could be located despite their proximity to the transition metal atom and were freely refined. In contrast to all other bis(phosphinimino)methanide borohydride complexes of the rare earth elements only one of the two BH_4^- anions is η^3-coordinated and the other one coordinates in an η^2-mode. The coordination mode is confirmed by the different Sc–B distances of the η^3-coordinated borohydride (Sc–B1 2.310 (5) Å) and the η^2-coordinated borohydride (Sc–B2 2.526(5) Å). η^2-Coordinated BH_4^- anions are rare in scandium compounds but have been reported earlier, e.g. in the scandium monoborohydride complex $[\{C_5H_3(SiMe_3)_2\}_2Sc(BH_4)]$ [59]. The Sc–H (2.03(4) Å) and the Sc–B (2.52(3) Å) distances in this complex are similar to the values found for the η^2-coordinated BH_4^- group in **2** (Sc–H 2.12(4)/ 2.04(5) Å).

The suggestion that the energy barrier for a change from an η^2/η^3-coordination to an η^3/η^3-coordination of the two BH_4^- ions is indeed low is supported by the fact that a conformational polymorph of **2** was identified by a low temperature (9 K) single crystal X-ray diffraction experiment: Racemic crystals of compound **2** crystallize in the centrosymmetric monoclinic space group $P2_1/c$ with four molecules of **2** and four molecules of toluene in the unit cell. Obviously due to the different packing of the molecules in the centrosymmetric crystal lattice both BH_4^- groups are now η^3-coordinated (Sc–B1 2.350(3) Å and Sc–B2 2.355(2) Å) (Fig. 3). Apart

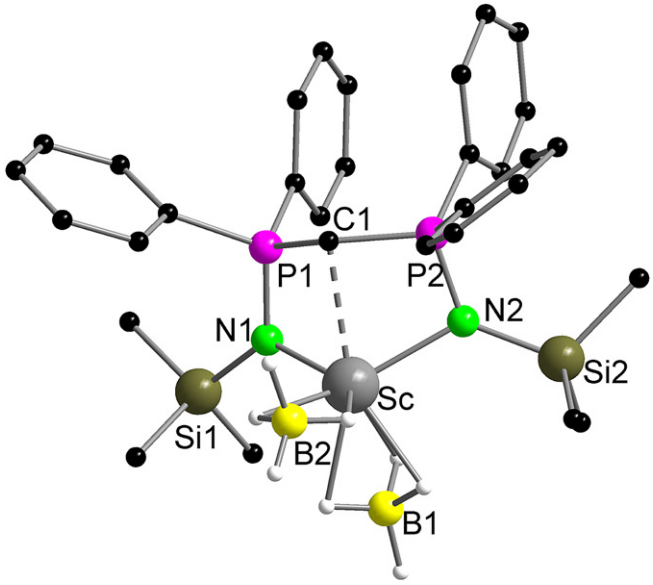


Fig. 2. Solid state structure of **2**, measured at 200 K, omitting the solvent molecule and the hydrogen atoms, except for the freely refined B–H atoms. Selected bond lengths [Å] or angles [°]: Sc–N1 2.134(3), Sc–N2 2.160(3), Sc–C1 2.471(3), Sc–B1 2.310(5), Sc–B2 2.526(5), N1–P1 1.609(3), N1–Si1 1.757(3), N2–P2 1.615(3), N2–Si2 1.755(3), C1–P2 1.737(4), C1–P1 1.748(4); N1–Sc–N2 111.97(12), N1–Sc–B1 103.3(2), N2–Sc–B1 102.3(2), N1–Sc–B2 114.1(2), N2–Sc–B2 119.6(2), N1–Sc–C1 70.66(12), N2–Sc–C1 69.58(12), B1–Sc–B2 102.9(2), B1–Sc–C1 165.8(2), B2–Sc–C1 91.3(2), P1–C1–P2 126.3(2).

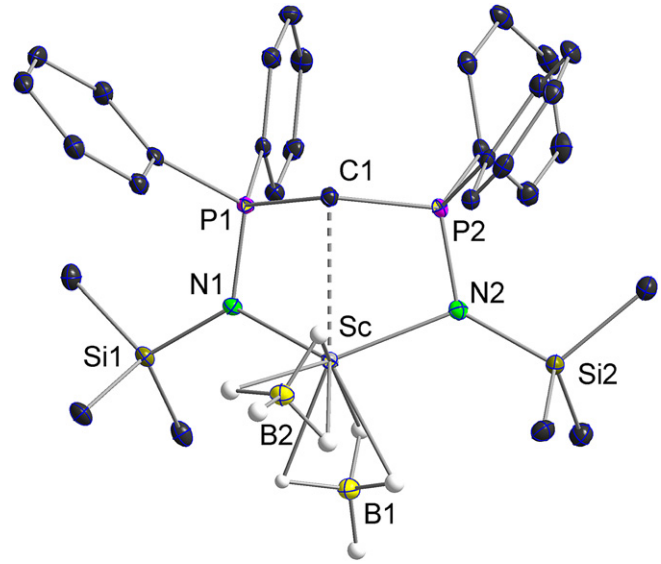


Fig. 3. ORTEP representation (50% probability) of the solid state structure of **2**, obtained from a racemic crystal at 9 K, omitting the solvent molecule and hydrogen atoms, except for B–H atoms (all hydrogen atoms are freely refined). Selected bond lengths [Å] or angles [°]: Sc–N1 2.152(2), Sc–N2 2.148(2), Sc–C1 2.543(3), Sc–B1 2.350 (3), Sc–B2 2.355(2), N1–P1 1.609(2), N1–Si1 1.749(2), N2–P2 1.607(2), N2–Si2 1.751 (2), C1–P2 1.738(2), C1–P1 1.731(2); N1–Sc–N2 117.91(7), N1–Sc–B1 96.88(8), N2–Sc–B1 98.90(9), N1–Sc–B2 114.54(8), N2–Sc–B2 116.01(8), N1–Sc–C1 69.02(7), N2–Sc–C1 68.98(7), B1–Sc–B2 108.65(9), B1–Sc–C1 151.39(8), B2–Sc–C1 99.92(8), P1–C1–P2 130.97(14).

from this qualitative difference the two conformers of **2** mainly show variations of the torsion angles of the phenyl-rings whereas the coordination geometry of the tridentate $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand is not changed significantly (Figs. 2 and 3).

3. Summary

In summary we have prepared the bis(phosphinimino)methanide bis(borohydrides) of neodymium $[\{(Me_3SiNPPh_2)_2CH\}Nd(BH_4)_2(THF)]$ and scandium $[\{(Me_3SiNPPh_2)_2CH\}Sc(BH_4)_2]$ from $[Ln(BH_4)_3(THF)_n]$ and $K\{CH(PPh_2NSiMe_3)_2\}$. While both BH_4^- groups in compound **1** are η^3-coordinated, an η^3- and an η^2-coordination mode is observed for compound **2** at 200 K. A second conformational polymorph of **2** was found, in which both BH_4^- groups coordinate in an η^3-fashion.

4. Experimental section

4.1. General

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} torr) line, or in an argon-filled MBraun glove box. THF was distilled under nitrogen from potassium benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were dried using an MBraun solvent purification system (SPS-800). All solvents for vacuum line manipulations were stored *in vacuo* over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Aldrich (99 atom % D). NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 15% BF_3 Et_2O (^{11}B NMR), respectively. IR spectra were obtained on a Shimadzu FTIR-8400. Mass spectra were recorded at 70 eV on Varian Mat SM 11. Elemental analyses were carried out with an Elementar vario EL. $LnCl_3$ [60], $[Ln(BH_4)_3(THF)_n]$ [34], and $K\{CH(PPh_2NSiMe_3)_2\}$ [47], were prepared according to literature procedures.

4.2. $[\{(Me_3SiNPPh_2)_2CH\}Nd(BH_4)_2(THF)]$ (**1**)

THF (25 ml) was condensed at −78 °C onto a mixture of $[Nd(BH_4)_3(THF)_3]$ (740 mg, 1.83 mmol) and $[K\{CH(PPh_2NSiMe_3)_2\}]$ (1.09 g, 1.50 mmol) and the resulting blue reaction mixture was stirred for 16 h at 60 °C. The blue solution was filtered off, concentrated and layered with *n*-pentane. The product was obtained as purple crystals after 16 h at room temperature. Yield: 704 mg, 0.80 mmol, 44% (single crystals). IR (ν/cm^{-1}): 708 (s), 750 (w), 833 (s), 930 (m), 1016 (w), 1070 (s), 1093 (s), 1125 (s), 1159 (w), 1248 (m), 1433 (w), 1729 (w), 1995 (w), 2078 (m), 2121 (m), 2204 (w), 2334 (m), 2418 (w), 2924 (w). EI/MS (70 eV, 180 °C) *m/z* (%): 717 ($M^+ - THF - BH_4$, 9), 702 ($\{(Me_3SiNPPh_2)_2CH\}Nd^+$, 2), 569 (81), 558 ($CH(PPh_2NSiMe_3)_2^+$, 94), 543 ($CH(PPh_2NSiMe_3)_2^+ - CH_3$, 100), 493 (44), 481 (21), 455 (58) 394 (34), 345 ($[M^+ - CH_3 - 2\ BH_4]/2$, 29), 287 (26), 272 ($Ph_2PNSiMe_3$, 40), 264 (25), 256 (19), 199 (26), 183 (30), 135 (53), 121 (82), 73 ($SiMe_3$, 38). (**1** + 1 THF) $C_{39}H_{63}B_2N_2O_2Si_2P_2Nd$ (875.91): calcd. C, 53.48, H, 7.25, N, 3.20; found C, 53.87, H, 7.10, N, 2.92%.

4.3. $[\{(Me_3SiNPPh_2)_2CH\}Sc(BH_4)_2]$ (**2**)

THF (25 ml) was condensed at −78 °C onto a mixture of $[Sc(BH_4)_3(THF)_2]$ (97 mg, 0.41 mmol) and $[K\{CH(PPh_2NSiMe_3)_2\}]$ (191 mg, 0.32 mmol) and the resulting reaction mixture was stirred for 16 h at 60 °C. The colorless solution was filtered and the solvent evaporated *in vacuo*. Then, toluene (20 ml) was condensed onto the residue. The solution was filtered again and concentrated until a colorless precipitate appears. The mixture was heated carefully until the solution became clear. The solution was allowed to stand at room temperature to obtain the product as colorless crystals after 16 h. Yield: 129 mg, 0.18 mmol, 56% (single crystals). ^1H NMR (THF-d_8, 400 MHz, 25 °C): $\delta = 1.09$ (s, 18 H, $SiMe_3$), 0.99–1.41 (br, 8 H, BH_4), 2.06 (t, 1 H, CH, $J_{H,P} = 3.4$ Hz), 2.42 (s, toluene), 7.19–7.24 (m, 4 H, Ph), 7.28–7.31 (m, toluene), 7.39–7.43 (m, 6 H, Ph), 7.57–7.67 (m, 6 H, Ph), 7.98–8.03 (m, 4 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (THF-d_8, 100.4 MHz, 25 °C): $\delta = 3.1$ ($SiMe_3$), 16.3 (t, CH, $J_{C,P} = 98$ Hz), 21.2 (toluene), 125.7 (toluene), 128.6 (toluene), 128.7, 128.9 (2 t, m-Ph, $J_{C,P} = 6.0$ Hz), 129.3 (toluene), 131.7 (p-Ph), 132.0 (t, o-Ph, $J_{C,P} = 5.2$ Hz), 132.4 (p-Ph), 132.7 (t, o-Ph, $J_{C,P} = 5.2$ Hz), 134.4 (m, i-Ph), 135.4 (m, i-Ph), 138.1 (toluene) ppm. $^{31}P\{^1H\}$ NMR (THF-d_8, 101.3 MHz, 25 °C): $\delta = 17.6$ ppm. ^{11}B NMR (THF-d_8, 128.15 MHz, 25 °C): $\delta = -17.6, -22.4$ ppm. IR (ν/cm^{-1}): 715 (s), 740 (m), 835 (vs), 950 (m), 1057 (m), 1106 (m), 1157 (w), 1246 (w), 1436 (m), 1589 (w), 1870 (w), 1991 (w), 2078 (m), 2291 (w), 2352 (w), 2495 (w), 2922 (w). EI/MS (70 eV, 180 °C) *m/z* (%): 675 (13), 638 (12), 632 (M^+, 1), 618 ($M^+ - BH_4$, 67), 603 ($\{(Me_3SiNPPh_2)_2CH\}Sc^+$, 17), 569 (42), 562 (12), 558 ($CH(PPh_2NSiMe_3)_2^+$, 14), 543 ($CH(PPh_2NSiMe_3)_2^+ - CH_3$, 100), 493 (22), 455 (13), 394 (6), 301 ($[M^+ - 2\ BH_4]/2$, 7), 272 ($Ph_2PNSiMe_3$, 26), 197 (10), 135 (17), 121 (14), 73 ($SiMe_3$, 25), 43 (13). (**2** + 1/2 toluene) $C_{34.5}H_{51}B_2N_2Si_2P_2Sc$ (678.49): calcd. C, 61.07, H, 7.58, N, 4.13; found C, 60.84, H, 7.57, N, 3.90%.

4.4. X-ray crystallographic studies of **1** and **2**

Crystals of **1** and **2** were grown from THF. A suitable crystal of compounds **1** and **2** was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C or −123 °C N_2 cold stream of a Stoe IPDS II diffractometer. Subsequent computations were carried out on a Pentium Core2Duo.

All structures were solved by the Patterson method (SHELXS-97 [61]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97 [61]. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded. The hydrogen atom contributions of all compounds were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

Crystal data for **1**: $C_{35}H_{55}B_2N_2NdOP_2Si_2 \cdot C_4H_8O$, $M = 875.89$, triclinic, $a = 10.0240(11)$ Å, $b = 14.0591(18)$ Å, $c = 16.601(3)$ Å, $\alpha = 100.341(11)°$, $\beta = 92.568(10)°$, $\gamma = 104.573(10)°$, $V = 2217.5(5)$ Å^3, $T = 200(2)$ K, space group *P*-1, $Z = 2$, $\mu(MoK\alpha) = 1.330$ mm^{-1}, 16,352 reflections measured, 7780 independent reflections ($R_{int} = 0.0256$). The final R_1 values were 0.0211 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0529 (all data). The goodness of fit on F^2 was 1.035.

Crystal data for **2** (enantiomerically pure): $C_{31}H_{47}B_2N_2P_2ScSi_2 \cdot C_7H_8$, $M = 724.54$, monoclinic, $a = 10.744(2)$ Å, $b = 11.264(2)$ Å, $c = 18.065(4)$ Å, $\beta = 94.20(3)°$, $V = 2180.4(8)$ Å^3, $T = 200(2)$ K, space group $P2_1$, $Z = 2$, $\mu(MoK\alpha) = 0.323$ mm^{-1}, 19,026 reflections measured, 10,295 independent reflections ($R_{int} = 0.0764$). The final R_1 values were 0.0589 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1365 (all data). The goodness of fit on F^2 was 1.039. Flack parameter = 0.00(4).

For the low temperature (9 K) X-ray diffraction experiment a crystal of **2** was glued to a Capton loop with perfluorinated

polyether and mounted on a Huber four-circle diffractometer equipped with a 4 K Displex closed-cycle helium cryostat. The sample was cooled with maximum cooling power to 9(2) K. Owing to the use of beryllium cooling shields, the Bragg intensities of the sample were contaminated in part by parasitic X-ray scattering from small crystalline beryllium domains. To correct systematically for these modulated powder diffraction rings, an individual background image (with the crystal translated out of the X-ray beam) was recorded for each image. The controlled crystal translation was provided by employing a microstepper motor (AttocubeSystems), which allowed us to translate the sample within the closed sample chamber at a positioning accuracy of ±0.1 nm. During data reduction each image and its corresponding individual background image were subtracted to eliminate the parasitic scattering by the beryllium domains.

Preliminary examination and final data collection were performed with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) generated from a Bruker FR 591 rotating anode running at 50 kV and 60 mA. Intensity data were collected by employing an MAR345 IP Detector and 1° φ-scans with a detector-to-sample distance of 200 mm. One φ-scan set (180 frames in total) were collected (detector offset angle +20.0°; scan time = 600 s per frame, respectively).

For X-ray data reduction, an initial orientation matrix was determined from 10 frames and refined during the integration of the full scan set. Cell refinement and data reduction were performed with the EVAL-14 [62] program package. After integration the symmetry-equivalent or multiple measured reflections were merged and a semiempirical absorption correction was applied by using the "Sortav" program [63]. The structure was solved by direct methods (SIR92) [64] and refined by using full-matrix least-squares techniques on F^2 using the program SHELXL-97 [61]. All hydrogen atoms could be located in the difference Fourier maps and were freely refined.

Crystal data for **2** (racemate): $C_{31}H_{47}B_2N_2P_2ScSi_2 \cdot C_7H_8$, $M = 724.54$, monoclinic, $a = 14.6250(5)$ Å, $b = 12.7346(3)$ Å, $c = 22.3686(7)$ Å, $\beta = 102.939(2)°$, $V = 4060.2(2)$ Å^3, $T = 9(2)$ K, space group $P2_1/c$, $Z = 4$, μ(MoKα) = 0.347 mm^{-1}, 14,577 reflections measured, 7043 independent reflections ($R_{int} = 0.0247$). The final R_1 values were 0.0438 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0838 (all data). The goodness of fit on F^2 was 1.202.

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Appendix. Supplementary material

Positional parameters, hydrogen atom parameters, thermal parameters, bond distances and angles have been deposited as supporting information.

CCDC-775458 (**1**), 775459 (**2**) 775560 (**2** (racemate)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033. E-mail: deposit@ccdc.cam.ac.uk).

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