CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201000571

Unprecedented Zinc–Borane Complexes

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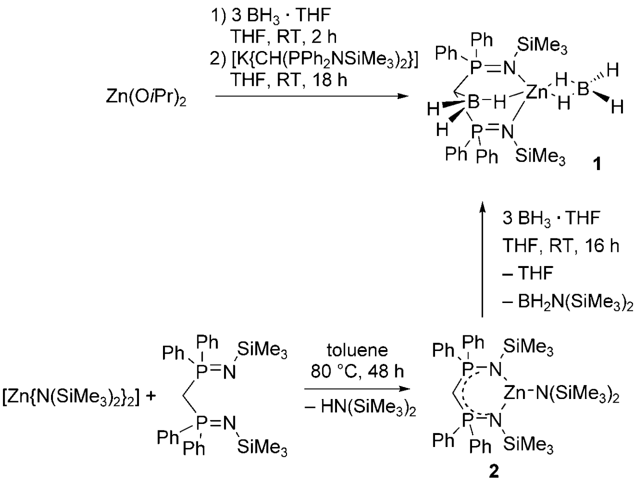
In general, borohydride compounds of various metals have been investigated recently as potential hydrogen storage materials.[1] In zinc chemistry the homoleptic borohydrides [Zn(BH_4)$_2$] were mentioned for the first time in 1951[2] and later investigated in more detail by H. Nöth et al.[3] Although [Zn(BH_4)$_2$] has not been structurally characterized it has numerous applications in organic synthesis.[4] In this context the reduction of carboxylic acids, amino acids, and amides and the hydroboration of simple olefins, dienes, cyclic olefins, and alkynes has been reported,[4] although it is not clear if [Zn(BH_4)$_2$] is really formed under the conditions described. Although the borohydride chemistry of zinc has been known for about half a century the number of structurally characterized Zn−BH_4 compounds is still very limited. To the best of our knowledge, besides the [Zn(BH_4)$_3$]$^-$ anion[5] and methylzinc tetrahydroborate ($MeZnBH_4$)[6] only four other Zn−BH_4 compounds have been reported. These are [(η^5-C_5H_5)$_2$NB(CO)−H−Zn(BH_4)$_2$],[7] [Zn(η^2-BH_4)Cl(tmen)] (tmen = *N,N,N′,N′*-tetramethylenediamine),[8] the bimetallic vanadium(I) polyhydride [($PMePh_2$)$_4$$V_2H_4${Zn($BH_4$)}$_2$][9] and the β-diketoiminate complex [(dipp)NacNacZn(η^2-BH_4)] ((dipp)NacNac = 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]-pent-2-enyl).[10] Besides these Zn−BH_4 compounds, the methylzinc hydroborate derivative [(MeZn)$_2$$B_3H_7$]$_2$[11] and the adduct $ZnCl_2$·B_2H_4·2P(CH_3)$_3$[12] are known. Herein, we now report on the coordination of the borane BH_3 onto a zinc atom.

Since bis(phosphinimino)methanide zinc complexes with alkoxide, amide, and alkyl ligands show some activity as catalysts in the ring-opening polymerization of *rac*-lactide[13] our original intention was the preparation of a bis(phosphinimino)methanide zinc borohydride with the composition [{CH($Ph_2PNSiMe_3$)$_2$}$ZnBH_4$]. In our hands, [Zn(BH_4)$_2$] was too labile for further derivatization with [K{CH(PPh_2NSiMe_3)$_2$}].[14] Therefore, according to a procedure described by H. Nöth et al.[3] [Zn(O*i*Pr)$_2$] was treated with BH_3·THF in THF first, followed by the addition of [K{CH(PPh_2NSiMe_3)$_2$}]. To our surprise, we did not obtain the expected simple borohydride complex [{CH($Ph_2PNSiMe_3$)$_2$}$ZnBH_4$], but instead a borohydride–borane complex of the composition [{CH($Ph_2PNSiMe_3$)$_2$}(κ^1-BH_3)Zn(BH_4)] (**1**, Scheme 1). Besides the BH_4^- group an additional BH_3 molecule is coordinated to the metal atom in compound **1**. The BH_3 molecule is attached to the methine carbon atom of the bis(phosphinimino)methanide ligand and the zinc atom. In the ^{1}H NMR spectrum the signals of the methanide group, which usually is split into a triplet as a result of the coupling to the two phosphorus atoms is split into a multiplet (δ = 2.74 ppm) in compound **1**. This is a result of the additional coupling to the boron atom and the hydrogen atoms of the BH_3 molecule. Moreover two broad signals are observed in the ^{1}H NMR spectrum for the BH_3



Scheme 1.

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and the BH_4^- group. These signals are well resolved in the $^1H\{^{11}B\}$ NMR spectrum into a singlet for the BH_4^- group ($\delta = 0.77$ ppm) and a doublet of triplets for the BH_3 molecule ($\delta = 1.03$ ppm). The splitting of the latter signals is a result of the coupling to the methine hydrogen atom and the two phosphorus atoms. In the ^{11}B NMR spectrum a broad signal is seen for the BH_3 molecule ($\delta = -27.9$ ppm) and a quintet is observed for the BH_4^- group ($\delta = -45.9$ ppm; $^1J(B,H) = 80.1$ Hz). In the EI-MS spectrum a molecular peak of compound **1** was observed with low intensity (1%).

The solid-state structure of compound **1** was established by single-crystal X-ray diffraction (Figure 1). All hydrogen atoms were located in the difference Fourier map and subsequently refined. The zinc atom is coordinated by the two imine nitrogen atoms of the bis(phosphinimino)methanide ligand, the BH_4^- group, and the BH_3 molecule. Most interesting is the hitherto unobserved κ^1-coordination of the BH_3 molecule between the methine carbon atom and the zinc atom. The methine carbon atom coordinates directly to the boron atom with a distance of C1–B2 1.687(3) Å. Moreover, one three-center two-electron B–H–Zn bond is formed with a Zn–B2 bond length of 2.704(2) Å. Thus, the BH_3 molecule binds with just one hydrogen atom to the zinc atom. The angle of the bridge displayed by C1-B2-Zn is 78.82(2)°. The bis(phosphinimino)methanide coordinates as a bidentate ligand onto the zinc atom forming a six-membered metallacycle (N1-P1-C1-P2-N2-Zn), which adopts a twist-boat conformation. The BH_4^- ligand binds in an η^2-fashion to the zinc atom showing a bond length of Zn–B1 2.274(3) Å. This kind of coordination is in agreement with the few other known Zn–BH_4 compounds, such as [Zn(η^2-BH_4)Cl(tmen)][8] and [(dipp)NacNacZn(η^2-BH_4)].[10]

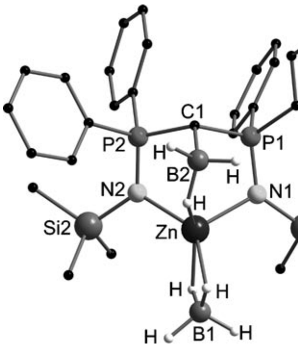


Figure 1. Solid-state structure of **1** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] or angles [°]: Zn–B1 2.274(3), Zn–B2 2.7035(5), Zn–N1 2.027(2), Zn–N2 2.042(2), C1–B2 1.687(3), N1–P1 1.598(2), N2–P2 1.600(2); B1-Zn1-N1 116.74(9), B1-Zn1-N2 124.79(10), B2-Zn1-N1 80.620(7), B2-Zn1-N2 87.574(7), N1-Zn1-N2 108.24(7), C1-B2-Zn 78.816(7).

Since the reaction leading to compound **1** may raise some questions about the in situ formed zinc precursor, we additionally established a second synthetic pathway to compound **1**. In this approach we started from the new compound [{CH($Ph_2PNSiMe_3$)$_2$}Zn{N($SiMe_3$)$_2$}] (**2**), which was prepared by the reaction of bis(phosphinimino)methane {CH_2($Ph_2PNSiMe_3$)$_2$} and [Zn{N($SiMe_3$)$_2$}$_2$]. The bis(phosphinimino)methane ligand was deprotonated during the course of the reaction. Further treatment of complex **2** with BH_3·THF in THF resulted, as expected, in the formation of the borohydride–borane complex **1** (Scheme 1). During the course of the reaction the {N($SiMe_3$)$_2$}$^-$ group was replaced by a BH_4^- group and an additional BH_3 molecule was coordinated to the metal center.[15] This result may be of some further interest because transition-metal–amine–borane complexes attracted some attention for the catalytic dehydrocoupling of amine boranes.[16–20]

The analytical data for compound **2** is as expected. The room temperature ^1H and $^{31}P\{^1H\}$ NMR spectra of compound **2** show a symmetrical pattern for the {CH($Ph_2PNSiMe_3$)$_2$}$^-$ ligand. In the ^1H NMR spectrum for the P–C*H*–P resonance ($\delta = 2.10$ ppm) a significant upfield shift is observed compared with the neutral ligand ($\delta = 3.42$ ppm).[21] Compound **2** shows one signal in the $^{31}P\{^1H\}$ NMR spectrum ($\delta = 29.1$ ppm), which is significantly downfield shifted compared with the starting material ($\delta = -5.9$ ppm),[21] but is in the range of the analogous mesityl bis(phosphinimino)methanide complex [{CH($Ph_2PNC_6H_2$-Me_3-2,4,6)$_2$}ZnN($SiMe_3$)$_2$] ($^{31}P\{^1H\}$ NMR: $\delta = 33.1$ ppm).[13] The solid-state structure of **2** is in agreement with the NMR spectroscopy data obtained in solution (Figure 2). In the solid state, the pseudo triangular coordination sphere around the zinc atom is defined by the two phosphinimine nitrogen atoms (Zn–N1 1.994(2) Å and Zn–N2 2.050(2) Å) and the nitrogen atom of the N($SiMe_3$)$_2$ group (Zn–N3 1.914(2) Å). The N1-Zn-N2 angle of the phosphinimine anion is 103.16(7)°, whereas the angles to the N($SiMe_3$)$_2$ group are N1-Zn-N3 132.00(8)° and N2-Zn-N3 124.67(8)°. A six-membered metallacycle (N1-P1-C1-P2-N2-Zn) is formed by the ligand and the zinc atom. The ring adopts a twist-

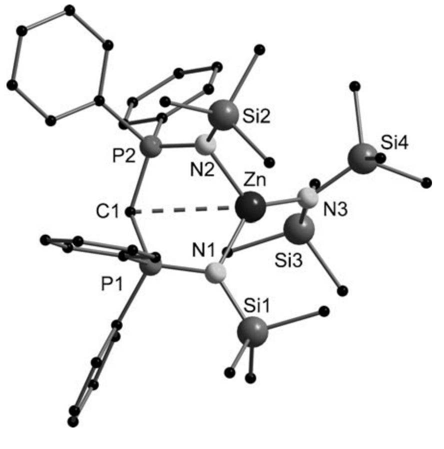
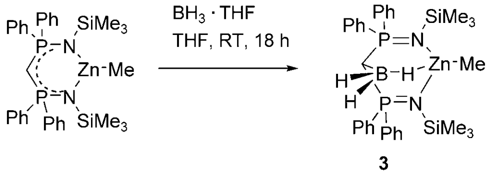


Figure 2. Solid-state structure of **2** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] or angles [°]: Zn–N1 1.994(2), Zn–N2 2.050(2), Zn–N3 1.914(2), Zn–C1 2.981(2); N1-Zn1-N2 103.16(7), N1-Zn1-N3 132.00(8), N2-Zn1-N3 124.67(8), P1-C1-P2 123.72(12).

boat conformation in which the central carbon atom and the zinc atom are displaced from the N_2P_2 least-square plane. A long interaction between the methine carbon atom and the zinc atom of 2.981(2) Å is observed. This distance is longer than usual Zn–C distances. The observed conformation of the six-membered metallacycle is typical for bis(phosphinimino)methanide complexes.[22]

To extend our studies, the previously reported zinc methyl compound [{CH($Ph_2PNSiMe_3$)$_2$}ZnMe][23] was treated with BH_3·THF in THF to give the borane–zinc complex [{CH($Ph_2PNSiMe_3$)$_2$}Zn(κ^1-BH_3)ZnMe] (**3**, Scheme 2). As observed for compound **1** the BH_3 molecule is bound to the methine carbon atom of the bis(phosphinimino)methanide ligand and the zinc atom. In contrast to compound **1** no reaction was observed at the zinc atom. Thus, instead of a borane–borohydride zinc complex a borane–methyl zinc complex was obtained. The strength and inertness of Zn–Me bonds has been well investigated.[24] In the ^{1}H NMR spectrum of compound **3** the proton of the methine group is split into a multiplet ($\delta = 2.66$ ppm), whereas the signal of the zinc methyl group is a sharp singlet ($\delta = -0.43$ ppm), which is about 0.6 ppm high-field shifted compared with the starting material.[23] In the ^{1}H{^{11}B} NMR spectrum the resonance of the BH_3 molecule is split into a doublet of triplets ($\delta = 1.02$ ppm; ^3J(H,H) = 5.0 Hz and ^3J(H,P) = 15.5 Hz). The chemical shifts of the BH_3 protons in compounds **1** and **3** are almost identical. In the ^{11}B NMR spectrum one broad signal for the boron atom is observed ($\delta = -30.1$ ppm). As expected one signal is also found in the ^{31}P{^{1}H} NMR spectrum ($\delta = 34.5$ ppm). As was observed for compound **1**, a molecular peak for compound **3** could also be detected in the EI-MS spectrum (*m*/*z* 651; 5 %).



Scheme 2.

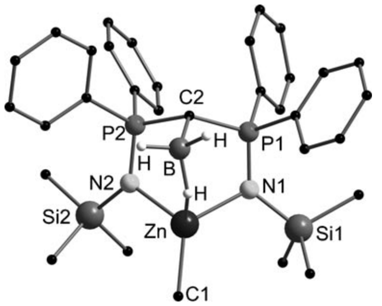


Figure 3. Solid-state structure of **3** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] or angles [°]: Zn–B 2.7640(5), Zn–N1 2.077(2), Zn–N2 2.054(2), Zn–C1 1.995(2), C2–B 1.687(3), N1–P1 1.591(2), N2–P2 1.598(2); N1-Zn-C1 124.56(10), N2-Zn-C1 122.52(10), N1-Zn-N2 103.76(7), C2-B-Zn 79.693(8).

The structure of compound **3** was confirmed by single-crystal X-ray diffraction in the solid state (Figure 3). The hydrogen atoms of the BH_3 molecule were located in the difference Fourier map and subsequently refined. As observed for compound **1** a BH_3 molecule is bound in a κ^1-fashion between the methine carbon atom of the bis(phosphinimino)methanide ligand and the zinc atom. Although the methine carbon atom is directly bound to the boron atom (C2–B 1.687(3) Å) a three-center two-electron B–H–Zn bond is formed with a Zn–B distance of 2.764(2) Å. The Zn–C2 distance of 2.969(1) Å is significantly elongated compared with the starting material [{CH($Ph_2PNSiMe_3$)$_2$}ZnMe][23] (Zn–C 2.527(4) Å). Only one hydrogen atom of the BH_3 molecule is coordinated to the zinc atom. Moreover the methyl group (Zn–C1 1.995(2) Å) and the imine functionality of the bis(phosphinimino)methanide are coordinated onto the zinc atom (Zn–N1 2.077(2) Å and Zn–N2 2.054(2) Å) forming an almost mirror-symmetrical coordination polyhedron.

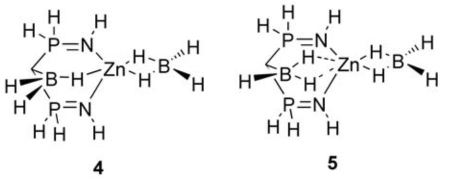
To obtain a deeper understanding of the bonding of BH_3 in [{CH($Ph_2PNSiMe_3$)$_2$}(κ^1-BH_3)ZnX] (X = Me, BH_4), we investigated the molecules by means of quantum chemical methods. The bonding situation in these compounds remains comparable, independent of the ligand X. Therefore, we focused on the discussion of the special nature of the BH_3 bonding to the molecule [{CH($Ph_2PNSiMe_3$)$_2$}(κ^1-BH_3)Zn(BH_4)]. The structural data obtained by theoretical calculations at the RI-DFT level[25–28] (symmetry C_1, program system TURBOMOLE,[29,30] basis sets of def-SV(P) quality for all atoms)[31] are in sound agreement with the experimentally deduced values (Table 1). The reaction enthalpy for the formation of **1** is calculated to be -140 kJ mol^{-1}. We were especially interested in the roles that the C–B and the

Table 1. Experimental and theoretical (RI-DFT/def-SV(P)) results of [{CH($Ph_2PNSiMe_3$)$_2$}(κ^1-BH_3)Zn(BH_4)] (**1**), [{CH(H_2PNH)$_2$}(κ^1-BH_3)Zn(BH_4)] (**4**), and [{CH(H_2PNH)$_2$}(BH_3)Zn(BH_4)] (**5**) (distances *r* [Å]).

	1		**4**		**5**	
	exptl[a]	theory	theory		theory	
	r	*r*	*r*	SEN	*r*	SEN
C1–B2	1.687(3)	1.670	1.685	1.35	1.717	1.25
B2–H	1.24(3)	1.273	1.266	1.29	1.237	1.40
Zn–H(B2)	1.82(2)	1.905	1.910	0.49	3.220	0.01
Zn–B1	2.274(3)	2.254	2.206	1.30	2.174	1.39
Zn–H(B1)	1.84(3), 1.96(3)	1.873/1.887	1.800/1.894	0.72/0.59	1.802/1.833	0.72/0.74
Zn–B2	2.704(2)	2.811	2.879	0.49	3.460	0.04
Zn–C	2.897(2)	2.983	3.094	0.05	3.344	0.01
Zn-H-B2	–	–	–	0.41	–	–0.01
Zn-H-B1	–	–	–	0.55/0.49	–	0.55/0.57

[a] All hydrogen atoms were located in the difference Fourier map and subsequently refined.

Zn–H connections play. To calculate the energy belonging to the Zn–H connection the energy difference between the C_s symmetrical model compounds $[\{CH(H_2PNH)_2\}(\kappa^1\text{-}BH_3)Zn(BH_4)]$ (**4**) and $[\{CH(H_2PNH)_2\}(BH_3)Zn(BH_4)]$ (**5**) was calculated (Scheme 3). By this means the bonding energy of the Zn–H–B2 bond was estimated to be around 22 kJ mol^{-1}. From the comparison of the Zn–B2 distances in **4** and **5** we conclude that in **5** this connection is of nonbonding or repulsive nature and that an η^2-bridged connection to BH_3 cannot be realized.


4 **5**

Scheme 3.

On the grounds of a population analysis based on occupation numbers (Ahlrichs–Heinzmann population analysis)[32] the shared electron numbers as a measure of the covalent bond strength were determined. We found that on one hand the covalent bonds in Zn–H–B1 and Zn–H–B2 mainly belong to three-center two-electron bonds and are of similar strength. On the other hand the partial atomic charges q indicate that the ionic bond strengths are also of comparable size: $q(Zn)=0.70$, $q(H\text{-}(BH_3))=0.03$, $q(H\text{-}(BH_4))=0.04$, $q(B1)=-0.52$, $q(B2)=-0.57$.

In conclusion, two different borane complexes of zinc were synthesized by different synthetic pathways. In both compounds the borane molecule is κ^1-coordinated to the zinc atom. To the best of our knowledge this unusual coordination was not reported previously in zinc chemistry, although BH_3 complexes of other metals were reported by us and other groups (e.g., scandium,[33,34] lutetium,[34,35] and uranium[36]). The reported results show that simple borane chemistry still shows some surprising reactions.[37]

Experimental Section

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

$[\{CH(Ph_2PNSiMe_3)_2\}(\kappa^1\text{-}BH_3)Zn(BH_4)]$ (1)

Route A: A stirred suspension of $[Zn(OiPr)_2]$ (70 mg, 0.42 mmol) in THF (5 mL) was cooled to 0 °C. $BH_3\cdot THF$ (1.4 mL, 1 M in THF, 1.40 mmol) was added dropwise by using a syringe. The reaction mixture was allowed to warm to RT and stirred for 2 h. After cooling to 0 °C $[K\{CH(PPh_2NSiMe_3)_2\}]$[14] (250 mg, 0.42 mmol) in THF (5 mL) was added and the mixture was stirred overnight at ambient temperature. The volatile components were evaporated in vacuum and the residue was extracted with toluene (10 mL). After filtration the solvent was evaporated. The residue was washed with *n*-pentane (10 mL) and dried in vacuum. Single crystals suitable for single-crystal X-ray diffraction studies were obtained by slow diffusion of *n*-pentane into a concentrated THF solution. Yield: 145 mg (54 %).

Route B: $BH_3\cdot THF$ (1.12 mL, 1 M in THF, 1.12 mmol) was added at RT by syringe to a stirred solution of $[\{(Me_3SiNPPh_2)_2CH\}ZnN(SiMe_3)_2]$ (250 mg, 0.32 mmol) in THF (10 mL). The solution was stirred for 16 h and the volatile components were evaporated in vacuum. The colorless residue was washed with *n*-pentane (10 mL) and dried in vacuum. Colorless crystals were obtained by slow diffusion of *n*-pentane into a THF solution. Yield: 147 mg (70 %). ^1H NMR ($[D_8]THF$, 300 MHz): $\delta=0.12$ (s, 18 H, $SiMe_3$), 0.30–1.50 (br, 7 H, BH_3+BH_4), 2.74 (m, 1 H, P–CH–P), 7.04–7.09 (m, 4 H, PPh), 7.21–7.27 (m, 2 H, PPh), 7.38–7.53 (m, 10 H, PPh), 7.76–7.84 ppm (m, 4 H, PPh); $^1H\{^{11}B\}$ NMR ($[D_8]THF$, 300 MHz): $\delta=0.12$ (s, 18 H, $SiMe_3$), 0.77 (s, 4 H, BH_4), 1.03 (dt, 3 H, BH_3, $^3J(H,H)=5.0$ Hz, $^2J(H,H)=15.1$ Hz), 2.74 (m, 1 H, P–CH–P), 7.04–7.09 (m, 4 H, PPh), 7.21–7.27 (m, 2 H, PPh), 7.38–7.53 (m, 10 H, PPh), 7.76–7.84 ppm (m, 4 H, PPh); $^{13}C\{^1H\}$ NMR ($[D_8]THF$, 100 MHz): $\delta=4.6$ (t, $^3J=1.8$ Hz, $SiMe_3$), 128.7 (PPh), 129.1 (PPh), 132.6 (PPh), 133.9 ppm (PPh); $^{31}P\{^1H\}$ NMR ($[D_8]THF$, 121 MHz): $\delta=39.0$ ppm; ^{11}B NMR ($[D_8]THF$, 96 MHz): $\delta=-30.1$ (br, BH_3), -45.9 ppm (br quint, BH_4, $^1J(B,H)=80.1$ Hz); Attenuated total reflection (ATR)-IR: $\tilde{\nu}=3053$ (w), 2950 (w), 2414 (sh), 2393 (s), 2316 (m), 2299 (m), 2100 (sh), 2056 (m), 1437 (m),1263 (m), 1251 (m), 1117 (s), 1088 (m), 1070 (m), 835 (s), 741 (s), 688 (s), 501 cm^{-1} (s); MS (EI; 70 eV): m/z (%): 651 ($[M]^+$, 1), 636 ($[M]^+-BH_3$, 1), 622 ($[M]^+-B_2H_6$, 86), 569 ($[CH(PPh_2NSiMe_3)_2BH]^+$, 22), 558 ($[CH_2(PPh_2NSiMe_3)_2]^+$, 8), 543 ($[CH_2(PPh_2NSiMe_3)_2-Me]^+$, 43), 471 ($[CH_2(PPh_2)(PPh_2NSiMe_3)]^+$, 9), 455 ($[CH_2(PPh_2)(PPh_2NSiMe_2)]^+$, 16); HRMS: calcd for $C_{31}H_{46}B_2N_2P_2Si_2Zn$: 650.21523; found: 650.21529.

$[\{CH(Ph_2PNSiMe_3)_2\}Zn\{N(SiMe_3)_2\}]$ (2): Toluene (10 mL) was added to a mixture of $[CH_2(PPh_2NSiMe_3)_2\}]$ (280 mg, 0.5 mmol) and $[Zn\{N(SiMe_3)_2\}_2]$ (0.5 mmol). The mixture was heated at 80 °C for 48 h. The solvent was evaporated under vacuum and the compound was crystallized from toluene at 0 °C. Colorless crystals were obtained after one week. Yield: 250 mg, (64 %). ^1H NMR (C_6D_6, 300 MHz) $\delta=0.21$ (s, 18 H, $SiMe_3$), 0.52 (s, 18 H, $SiMe_3$), 2.12 (t, $^2J=3.9$ Hz, 1 H, P–CH–P), 6.98–7.09 (m, 12 H, PPh), 7.58–7.65 (m, 8 H, PPh); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) $\delta=4.7$ (t, $^3J=1.8$ Hz, $SiMe_3$), 6.9 ($SiMe_3$), 31.9 (t, $^1J=121.2$ Hz, P-CH-P), 128.1 (PPh), 130.5 (PPh), 131.9 (PPh), 136.6 (PPh), 137.9 ppm (PPh); $^{31}P\{^1H\}$ NMR (C_6D_6, 161.7 MHz, 25 °C) $\delta=29.1$; IR (KBr): $\tilde{\nu}=3055$ (m), 2960 (m), 2893 (m), 1961 (m), 1899 (w), 1589 (w), 1573 (w), 1485 (m), 1434 (s), 1411 (m), 1263 (m), 1240 (m), 1174 (w), 1157 (br), 1103 (w), 1068 (m), 1039 (w), 1026 (m), 968 (m), 935 (s), 864, 829 (m), 802 (s), 777 (m), 740 (s), 730 (m), 709 (m), 696 cm^{-1} (s); elemental analysis calcd (%) for $C_{37}H_{57}N_3P_2Si_4Zn$ (783.53): C 56.72, H 7.33, N 5.36; found: C 55.92, H 7.24, N 5.15.

$[\{CH(Ph_2PNSiMe_3)_2\}Zn(\kappa^1\text{-}BH_3)ZnMe]$ (3): $BH_3\cdot THF$ (1.12 mL, 1 M in THF, 1.12 mmol) was added at room temperature, by syringe, to a stirred solution of $[\{(Me_3SiNPPh_2)_2CH\}ZnMe]$[22] (319 mg, 0.50 mmol) in THF (10 mL). The solution was stirred for 16 h. The volatiles were evaporated in vacuum and the residue was extracted with toluene (10 mL). After filtration the solvent was evaporated to obtain a colorless foam. Colorless crystals suitable for X-ray analysis were obtained from a THF/*n*-pentane solution at −30 °C. Yield: 128 mg (39 %). ^1H NMR ($[D_8]THF$, 300 MHz): $\delta=-0.43$ (s, 3 H, Zn–Me), 0.08 (s, 18 H, $SiMe_3$), 0.4–1.4 (br, 3 H, BH_3), 2.66 (m, 1 H, P–CH–P), 6.98–7.05 (m, 4 H, PPh), 7.15–7.22 (m, 2 H, PPh), 7.27–7.47 (m, 10 H, PPh), 7.75–7.82 ppm (m, 4 H, PPh); $^1H\{^{11}B\}$ NMR ($[D_8]THF$, 300 MHz): $\delta=-0.43$ (s, 3 H, Zn–Me), 0.08 (s, 18 H, $SiMe_3$), 1.02 (dt, 3 H, BH_3, $^3J(H,H)=5.0$ Hz, $^2J(H,H)=15.5$ Hz), 2.66 (m, 1 H, P–CH–P), 6.98–7.05 (m, 4 H, PPh), 7.15–7.22 (m, 2 H, PPh), 7.27–7.47 (m, 10 H, PPh), 7.75–7.82 ppm (m, 4 H, PPh); $^{13}C\{^1H\}$ NMR ($[D_8]THF$, 75 MHz): $\delta=-6.8$ (s, Zn–Me), 4.7 (t, $^3J=1.7$ Hz, $SiMe_3$), 128.5 (PPh), 128.9 (PPh), 132.1 (PPh), 133.8 ppm (PPh); $^{31}P\{^1H\}$ NMR ($[D_8]THF$, 121 MHz): $\delta=34.5$ ppm; ^{11}B NMR ($[D_8]THF$, 128 MHz): $\delta=-30.6$ ppm (br, BH_3); ATR-IR): 3043 (w), 2960 (m), 2368 (sh), 2324 (m), 2100 (sh), 2079 (s), 1984 (m), 1433 (m), 1259 (m), 1244 (m), 1116 (s), 1085 (vs), 1016 (s), 827 (vs), 737 (s), 688 (vs), 501 cm^{-1} (vs); MS (EI, 70 eV): m/z (%): 651 ($[M-H]^+$, 5), 636 ($[M]^+-BH_3$, 6), 622 ($[M]^+-BH_3\text{-}Me$, 100), 569 ($[CH(PPh_2NSiMe_3)_2BH]^+$, 38), 558 ($[CH_2(PPh_2NSiMe_3)_2]^+$, 20), 543 ($[CH_2(PPh_2NSiMe_3)_2-Me]^+$, 100), 471 ($[CH_2(PPh_2)(PPh_2NSiMe_3)]^+$, 8), 455 ($[CH_2(PPh_2)(PPh_2NSiMe_2)]^+$, 17); HRMS: calcd for $C_{32}H_{45}BN_2P_2Si_2Zn$: 650.19810; found: 650.19812.

Crystal data for 1: $C_{31}H_{46}B_2N_2P_2Si_2Zn$; $M=651.81$; monoclinic; $a=19.947(4)$, $b=10.481(2)$, $c=17.950(4)$ Å; $\beta=111.01(3)°$; $V=3503.1(12)$ Å^3; $T=153(2)$ K; space group $P2_1/c$; $Z=4$; $\mu(Mo_{K\alpha})=0.884$ mm^{-1}; 20679 reflections measured; 7291 independent reflections ($R_{int}=0.0547$). The final R_1 values were 0.0350 ($I>2\sigma(I)$). The final $wR(F^2)$ values were 0.0850 (all data). The goodness of fit on F^2 was 1.034.

Crystal data for 2: $C_{37}H_{57}N_3P_2Si_4Zn$; $M=783.53$; monoclinic; $a=10.3376(9)$, $b=20.5001(17)$, $c=19.9775(17)$ Å; $\beta=93.006(7)°$; $V=4227.8(6)$ Å^3; $T=173(2)$ K; space group $P2_1/n$; $Z=4$; 22751 reflections measured; 11213 independent reflections ($R_{int}=0.0596$). The final R_1 values were 0.0336 ($I>2\sigma(I)$). The final $wR(F^2)$ values were 0.0658 (all data). The goodness of fit on F^2 was 0.695.

Crystal data for 3: $C_{32}H_{45}BN_2P_2Si_2Zn{\cdot}C_4H_8O$; $M=724.10$; monoclinic; $a=12.289(3)$, $b=12.637(3)$, $c=25.807(5)$ Å; $\beta=99.41(3)°$; $V=3953.8(14)$ Å^3; $T=203(2)$ K; space group $P2_1/c$; $Z=4$; $\mu(Mo_{K\alpha})=0.792$ mm^{-1}; 37638 reflections measured; 10463 independent reflections ($R_{int}=0.0400$). The final R_1 values were 0.0449 ($I>2\sigma(I)$). The final $wR(F^2)$ values were 0.1289 (all data). The goodness of fit on F^2 was 1.053.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with The Cambridge Crystallographic Data Centre as a supplementary publication CCDC-765518 (**1**), 765802 (**2**), and 765519 (**3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft, the Leibniz Rechenzentrum der Bayrischen Akademie der Wissenschaften (project h 1191), and the Fonds der Chemischen Industrie.

Keywords: boranes · borohydride · coordination compounds · coordination modes · zinc

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Received: March 4, 2010