Synthesis and crystal structures of bis(diphenylphosphanyl)methanides of lithium and calcium as well as of their borane adducts[†]

Jens Langer, Katja Wimmer, Helmar Görls and Matthias Westerhausen*

Received 15th December 2008, Accepted 9th February 2009 First published as an Advance Article on the web 27th February 2009 DOI: 10.1039/b822530c

The reaction of Li{HC(PPh₂)₂}, which forms [(tmeda)(thf)Li{HC(PPh₂)₂}] (1) in the presence of appropriate Lewis bases, with KOtBu and CaI₂ in THF yields [(thf)₃Ca{CH(PPh₂)₂}] (2). In complexes 1 and 2 the bis(diphenylphosphanyl)methanide anions act as bidentate ligands *via* the phosphorus atoms. Lithiation of H₂C(PPh₂-BH₃)₂ in diethyl ether leads to the formation of [(Et₂O)₂Li{CH(PPh₂-BH₃)₂] (3) which can be recrystallized from 1,2-dimethoxyethane (DME) leading to the formation of solvent-separated [(dme)₃Li]⁺ [HC(PPh₂-BH₃)₂]⁻ (3'). The reaction of 3 with KOtBu and then with anhydrous CaI₂ yields [(thf)Ca{CH(PPh₂-BH₃)₂] (4). In compound 4 a Ca–C bond of 2.754(3) Å is observed in the solid state to only one of the anions whereas the other anion only binds *via* the borane units.

Introduction

The synthesis of alkylcalcium compounds poses several challenges which have to be overcome. Calcium metal itself is rather inert whereas the organylcalcium compounds exhibit an enormous reactivity which often leads to ether cleavage reactions.¹⁻³ Metal activation, which was achieved via cocondensation of calcium vapour with bromo-bis(trimethylsilyl)methane, and addition of 1,4dioxane led to the formation of the first structurally characterized dialkylcalcium derivative, $[(diox)_2Ca{CH(SiMe_3)_2}_2]$.⁴ In order to circumvent difficulties arising from the low reactivity of the metal, the metathesis reaction of alkyl potassium with calcium diiodide offers a promising procedure. This reaction pathway allowed the isolation and structural characterization of $[Ca{C(SiMe_3)_3}_2]$ with a bent C–Ca–C fragment,⁵ of $[(thf)_2Ca{CH(SiMe_3)_2}_2]$,⁶ and of the calciate $[Ca{CH(SiMe_3)_2}_3]^-$ with a calcium atom in a pyramidal environment.7 In order to stabilize the organocalcium compounds in ether the nucleophilicity of the carbanion has to be reduced via delocalization of anionic charge by phenyl groups (leading to benzyl derivatives)8-13 or via backdonation of charge into a $\sigma^*(Si-C)$ bond of a trialkylsilyl group (negative hyperconjugation).⁴⁻⁶ Even a combination of both concepts was applied in order to isolate soluble trialkylsilylbenzyl calcium derivatives.8,14

In carbene adducts such as complexes of CaR₂ with imidazol-2-ylidenes often dissociation equilibria were observed.¹⁵ Nevertheless, crystallization of these adducts could be performed and short calcium–C bonds were observed.^{16–18} Stabilization of anionic charge was also performed by phosphoranyl substituents as in calcium bis[bis(trimethylsilylimino-diphenylphosphoranyl)methanide] and in dimeric calcium bis(trimethylsilylimino-diphenylphosphoranyl)methanediide¹⁹ as well as in calcium bis[bis-(arylimino-diphenylphosphoranyl)methanide] and in calcium bis(arylimino-diphenylphosphoranyl)methanediide.^{20,21} The synthesis of calcium bis[trimethylsilyl-bis(dimethylphosphanyl)methanide] succeeded *via* the metathesis reaction of Li{C(PMe₂)₂-SiMe₃} with CaCl₂ in THF. The anions in [(thf)₃Ca{C(PMe₂)₂-SiMe₃}₂] bind as bidentate ligands *via* the phosphorus bases to the calcium atom leading to a seven-coordinate calcium center with an average Ca–P bond length of 3.043 Å.²² Here we report on the synthesis and characterization of [(thf)₃Ca{CH(PPh₂)₂}₂] and its borane adduct.

Results and discussion

Synthesis

Lithium bis(diphenylphosphanyl)methanide has been wellknown for nearly forty years.²³ Its 1,2-bis(dimethylamino)ethane (TMEDA) adduct is monomeric in the solid state with the lithium atom binding to the phosphorus atoms of the anion and to the nitrogen atoms of the bidentate TMEDA ligand.²⁴ The Li-P distances are 2.582(4) Å. Substitution of the TMEDA molecule by a THF molecule leads to dimerization and the formation of a lithium-carbon bond with a length of 2.242(8) Å.²⁵ A similar relation is observed for monomeric $[(tmeda)Li{C(PMe_2)_2SiMe_3}]$ and dimeric [(thf)Li{C(PMe₂)₂SiMe₃}]²⁵ as well as for dimeric $[(thf)Li{C(PMe_2)_3}]$.²⁶ The enhancement of the coordination number of lithium in [(tmeda)(thf)Li{HC(PPh₂)₂}](1) leads to two significantly different Li-P bond lengths of 2.653(4) and 3.018(4) Å. This lithium complex 1 was reacted with KOtBu [giving potassium bis(diphenylphosphanyl)methanide]27 and then with anhydrous calcium diiodide yielding [(thf)₃Ca{CH(PPh₂)₂}₂] (2) according to eqn (1). In this complex the calcium atoms show a comparable coordination sphere as in $[(thf)_3Ca\{C(PMe_2)_2SiMe_3\}_2]$ of Karsch and Reisky.22



Dalton Trans., 2009, 2951-2957 | 2951

Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, August-Bebel-Str. 2, D-07743, Jena, Germany. E-mail: m.we @ uni-jena.de; Fax: +49 (0) 3641 9-48102

[†] CCDC reference numbers 712109 for 1, 712110 for 2, 712111 for 3, 712112 for 3', and 712113 for 4. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b822530c

In order to prevent Ca–P bonds the lone pairs at the P atoms were blocked with borane units. The well-known²⁸⁻³⁰ borane adduct $H_2C(PPh_2-BH_3)_2$ [which is isoelectronic to $H_2C(SiPh_2-CH_3)_2$] was metallated in diethyl ether with butyl lithium, yielding [(Et₂O)₂Li{CH(PPh₂-BH₃)₂] (**3**) with the lithium atom coordinating to the B-bound hydrides. Recrystallization from 1,2-dimethoxyethane (DME) gave the solvent-separated ion pair [(dme)₃Li]⁺ [HC(PPh₂-BH₃)₂]⁻ (**3'**). The reaction of **3** with KOtBu and then with anhydrous CaI₂ led to the formation of [(thf)Ca{CH(PPh₂-BH₃)₂]₂] (**4**) with moderate yield as shown in eqn (2). This compound is isoelectronic to yet unknown [(thf)Ca{CH(SiPh₂-CH₃)₂}₂] but the bis(trimethylsilyl)methanides of calcium contain quite similar structural motifs.^{4,6}



NMR investigations

The NMR data of these bis(diphenylphosphanyl)methanides are summarized in Table 1. For comparison reasons the parameters of bis(diphenylphosphanyl)methane **A** and its borane adduct A·2BH₃ are included. The borane addition leads to a low field shift of the ³¹P NMR resonance due to the enlarged coordination number and the formation of a Lewis acid–base complex. The P–CH₂–P unit shows a low field shift for the protons and a slight high field shift in the ¹³C{¹H} NMR experiment. Deprotonation of the methylene moieties leads to significant low field shifts of these resonances in the NMR spectra in agreement with larger shielding due to anionic charge on these P–CH–P fragments. The delocalization and formation of partial double bonds also enhances the ¹J(P,C) coupling constants of the P–CH–P units.

The *ipso*-carbon atoms of the P-bound phenyl groups are also affected by borane addition as well as deprotonation of the methylene groups. In the borane adduct drastically larger ${}^{1}J(P,i-C)$ coupling constants are observed.

Molecular structures

The coordination behaviour of the bis(diphenylphosphanyl)methanide ligand is diverse. Mercury bis[bis(diphenylphosphanyl)methanide] shows Hg–C bonds and no short Hg–P contacts.³¹ These ligands can also bind *via* the carbon and the phosphorus atoms as found in dimeric lithium derivatives^{25,26} as well as in [Cr₂(Cl){CH(PPh₂)₂}₃] and [Sm{ η^3 -CH(PPh₂)₂}₃].³² Cas well as P-coordination of this ligand was also observed for main group elements such as *e.g.* Sn, Pb,³³ Al, and Ga.³⁴ In dinuclear gold(1) complexes, the bis(diphenylphosphanyl)methanide anion is in a bridging position and binds *via* the P-atoms.³⁵

In compounds 1 and 2 the bis(diphenylphosphanyl)methanide ligand binds exclusively *via* the phosphorus atoms. Fig. 1 and 2 display molecular structures and numbering schemes of 1 and 2, respectively. The anion of lithium derivative 1 shows comparable parameters as in $[(\text{tmeda})\text{Li}\{\text{CH}(\text{PPh}_2)_2\}]$.²⁴ The negative charge is delocalized in the PCP fragment leading to

Table 1Selected NMR data of bis(diphenylphosphanyl)methane derivatives. Starting $H_2C(PPh_2)_2$ (A) and $H_2C(PPh_2BH_3)_2$ (A·2 BH₃) are included for comparison reasons

	Α	1	2	$A \cdot 2BH_3$	3	$K\{HC(PPh_2BH_3)_2\}$	4
ιН							
δ (PCHP)	2.88	1 56	2.02	3 23	0.74	0.61	1 53
$^{2}J(\mathrm{H,P})$	1.9	8.6	6.8	10.7	<1	6.6	14
¹³ C{ ¹ H}							
$\delta(PCP)$	28.7	17.9	16.5	23.9	5.1	6.6	5.6
J(C,P)	23.3	19.4	31.1	24.8	77.4	76.7	51.0
$\delta(i-C)$	140.3	152.3	149.1	129.1	142.8	143.4	138.0
J(C,P)	4.5	4.0	Broad	55.7	56.7	59.8	66.1
$\delta(o-C)$	133.6	132.0	131.9	132.9	133.1	132.7	131.9
$^{2}J(C.P)$	21.0	7.8	6.4	9.9	9.2	8.7^a	9.6
δ(<i>m</i> -C)	128.9	127.4	127.8	129.1	127.2	127.4	128.1
$^{3}J(C,P)$	7.1	Broad	< 1	10.7	9.4	8.8^{a}	b
$\delta(p-C)$	129.1	125.4	126.6	132.0	127.9	128.1	129.2
${}^{31}\mathbf{P}(\{^{1}\mathbf{H}\})$							
$\delta(PCP)$	-20.4	+2.9	+1.0	+14.9	+16.3	+18.1	+11.1
¹¹ B{ ¹ H}							
$\delta(\dot{BH}_3)$	_	_	_	-56.1°	-33.6	-33.9	-31.5
Ref.				28			

^{*a*} Observation of a pseudo-triplet of a AA'X spectrum type. ^{*b*} Coupling constant cannot be assigned due to overlap with solvent signals. ^{*c*} Chemical shift given relative to BMe₃; chemical shift given relative to BF₃·OEt₂: $\delta = -36.6$.

a strong shortening of the P–C bonds. However, the coordination mode of the anion in the complexes $[(tmeda)Li{CH(PPh_2)_2}]$ and $[(tmeda)(thf)Li{CH(PPh_2)_2}]$ differ significantly. Whereas in $[(tmeda)Li{CH(PPh_2)_2}]$ an average Li–P bond length of 2.582(6) Å was observed,²⁴ the enhanced strain due to the addition of another Lewis base leads to enhanced Li–P distances and to significantly different Li–P bond lengths of 2.653(4) and 3.018(4) Å in **1**. Thus the penta-coordination, which can best be described as



Fig. 1 Molecular structure and numbering scheme of $[(tmeda)(thf)-Li{HC(PPh_2)_2}]$ (1). The ellipsoids represent a probability of 40%. The H atoms are omitted for clarity reasons with the exception of the PC(H)P units. Intercalated solvent molecules are not shown. Selected bond lengths (Å): Li1–P1 2.653(4), Li1–P2 3.018(4), Li1–N1 2.172(5), Li1–N2 2.143(4), Li1–O1 1.946(4), C1–P1 1.733(2), C1–P2 1.736(2), P1–C2 1.845(2), P1–C8 1.858(2), P2–C14 1.852(2), P2–C20 1.844(2). Angles (°): P1–Li1–P2 61.07(8), P1–C1–P2 113.3(1), Li1–P1–C1 95.5(1), Li1–P2–C1 83.5(1).



Fig. 2 Molecular structure and numbering scheme of $[(thf)_3Ca{HC-(PPh_2)_2}_2]$ (2). The ellipsoids represent a probability of 40%. The H atoms are omitted for clarity reasons with the exception of the P–C(H)–P units. Selected bond lengths (Å): Ca1–P1 3.146(1), Ca1–P2 3.0654(9), Ca1–P3 3.0589(9), Ca–P4 3.107(1), Ca1–O1 2.394(2), Ca1–O2 2.428(2), Ca1–O3 2.370(2), C1–P1 1.730(3), C1–P2 1.728(3), P1–C2 1.841(3), P1–C8 1.849(3), P2–C14 1.860(3), P2–C20 1.854(3), C26–P3 1.724(3), C26–P4 1.734(3), P3–C27 1.856(3), P3–C33 1.846(3), P4–C39 1.851(3), P4–C45 1.846(3). Angles (°): P1–Ca1–P2 55.55(2), P3–Ca1–P4 55.95(2), P1–C1–P2 113.7(2), P3–C26–P4 113.5(2), P1–Ca1–P3 89.51(3), P1–Ca1–P4 144.92(3), P2–Ca1–P3 142.24(3), P2–Ca1–P4 153.32(3).

a coordination number of 4 + 1 for lithium in 1, also causes an elongation of the Li–N bonds of approximately 0.1 Å.

The calcium derivatives **2** and $[(thf)_3Ca\{C(SiMe_3)(PMe_2)_2\}_2]^{22}$ are very similar. The Ca–O distances of these complexes are nearly identical. However, the different bulk of methyl and phenyl groups leads to a distortion of the binding mode of the anions. On the one hand and in contrast to $[(thf)_3Ca\{C(SiMe_3)(PMe_2)_2\}_2]^{22}$ with an average Ca–P bond length of 3.043 Å, larger Ca–P bond lengths of 3.062 and 3.126 Å are observed. On the other hand, the P–C distances of the PCP backbone are shorter in **2** (av. C–P 1.729 Å) than in $[(thf)_3Ca\{C(SiMe_3)(PMe_2)_2\}_2]$ (av. C–P 1.758 Å).²² The steric pressure of the trimethylsilyl group leads to a narrower PCP angle of 106.0° whereas in **2** an average PCP bond angle of 113.6° is observed.

The addition of borane formally leads to the insertion of BH₃ units into the Li–P bonds. In $[(Et_2O)_2Li{CH(PPh_2-BH_3)_2}]$ (3) the hexa-coordinate lithium atom is in a distorted trigonal prismatic environment of two oxygen (av. Li–O 1.977 Å) and four hydrogen atoms (av. Li–H 2.06 Å). Molecular structure and numbering scheme are given in Fig. 3. The coordination of BH₃ to the P atoms leads to a strong widening of the PCP angle to 130.8° and to a slight shortening of the P–C bonds (av. P–C 1.713 Å). In H₂C(PPh₂BH₃)₂ a characteristic P–C single bond of 1.833 Å is observed with a PCP angle of 118.2°.³⁰



Fig. 3 Molecular structure and numbering scheme of $[(Et_2O)_2Li-{HC(PPh_2BH_3)_2}]$ (3). The ellipsoids represent a probability of 40%. The H atoms are omitted for clarity reasons with the exception of the P–C(H)–P and borane units. Selected bond lengths (Å): Li1–O1 1.971(7), Li1–O2 1.983(7), Li1–H1_{B1} 2.08(4), Li1–H2_{B1} 2.10(4), Li1–H1_{B2} 2.02(4), Li1–H2_{B2} 2.05(4), C1–P1 1.710(3), C1–P2 1.716(3), P1–B1 1.926(4), P1–C2 1.830(3), P1–C8 1.833(3), P2–B2 1.922(4), P2–C14 1.839(3), P2–C20 1.832(3). Angles (°): P1–C1–P2 130.8(2), C1–P1–B1 121.6(2), C1–P2–B2 120.3(2).

The solvent-separated ion pair $[(dme)_3Li]^+$ $[HC(PPh_2-BH_3)_2]^-$ (3') crystallized with two crystallographically independent molecules in the asymmetric unit which are distinguished by the letters "A" and "B". Molecular structure and numbering scheme of molecule A is shown in Fig. 4. No short contacts exist between anion and cation. Whereas in the contact ion pair 3 a cisoid arrangement of the BH₃ units was observed, a transoid conformation is realized in solvent-separated 3'. Due to this fact repulsion between the B2A borane moiety and the P1A diphenylphosphanyl fragment leads to a widening of the P1A–C1A–P2A (133.5(2)°) and C1A–P2A–B2A angles (121.1(2)°).



Fig. 4 Structure representation and numbering scheme of molecule A of solvent-separated [(dme)₃Li]⁺ [HC{PPh₂BH₃}₂]⁻ (3'). The other ion pair B of the asymmetric unit is omitted. The ellipsoids represent a probability of 40%. The phenyl and DME hydrogen atoms are neglected for clarity reasons. Selected bond lengths of the anion (Å): C1A–P1A 1.704(4), C1A–P2A 1.725(4), C1A–H1A 0.84(4), P1A–B1A 1.934(4), P1A–C2A 1.839(4), P1A–C8A 1.833(4), P2A–B2A 1.937(4), P2A–C14A 1.834(4), P2A–C20A 1.840(4). Angles (°): P1A–C1A–P2A 133.5(2), P1A–C1A–H1A 112(3), P2A–C1A–H1A 114(3), C1A–P1A–B1A 108.9(2), C1A–P2A–B2A 121.1(2). Selected bond lengths of the cation (Å): Li1A–O1A 2.214(8), Li1A–O2A 2.045(7), Li1A–O3A 2.131(7), Li1A–O4A 2.244(8), Li1A–O5A 2.068(7), Li1A–O6A 2.145(7).

In [(thf)Ca{CH(PPh₂-BH₃)₂] (4) the nine-coordinate calcium atom binds to an oxygen (Ca–O 2.359 Å) and one carbon atom (Ca–C 2.754 Å) as well as seven hydrogen atoms (av. Ca–H 2.42 Å). Despite the rather large coordination number, a small Ca–O distance is observed. The Ca–H bond lengths are in the expected region and larger than bridging hydride ions between two calcium cations.³⁶ Molecular structure and numbering scheme of 4 is displayed in Fig. 5. The Ca–C bond is longer than observed in the bis(trialkylsilyl)methyl derivatives of calcium,^{4.6} the carbene adducts,^{16–18} and in [(thf)₂Ca{C₃H₃(SiMe₃)₂]₂],³⁷ however, similar Ca–C bond lengths were found in [Ca{C(PPh₂=NSiMe₃)₂]₂.¹⁹

The fact that one anion shows a Ca1–C1 bond whereas the other does not offers the opportunity to elucidate the influence on the structural parameters of the anions. The formation of the Ca–C bond leads to a pyramidalization of the HCP₂ moiety (angle sum at C1 341°, at C26 358°) and to a smaller P1–C1–P2 bond angle of 125.0° compared to P3–C26–P4 with 129.7°. This structural change hinders charge delocalization leading to larger P–C1 bonds (av. C1–P1/2 1.762 Å, C26–P3/4 1.712 Å).

The metal–boron distances in the contact ion pairs **3** (Li1–B1 2.478(7) and Li1–B2 2.467 Å) and **4** (Ca1–B1 2.754(3), Ca1–B2 2.908(4), Ca1–B3 2.813(3), and Ca1–B4 2.833(3) Å) are comparable to those observed in other compounds. In LiBH₄³⁸ and LiNH₂BH₃³⁹ lithium–boron distances of 2.37 to 2.62 Å and 2.50 to 2.69 Å, respectively, were found. In calcium boranate Ca(BH₄)₂ Ca–B distances between 2.89 and 2.96 Å were determined.^{40,41} Furthermore in Ca(NH₂BH₃), which attracts some interest as a hydrogen storage material, similar values between 2.87 and 3.03 Å were observed.³⁹ In [(thf)₄Ca{(Me₃Si)₂C–PMe₂BH₃]₂] the calcium atom binds to the oxygen atoms of the THF bases and to four boron-bound hydride groups of two borane units with a Ca–B distance of 2.751(2) Å.⁴² Comparable values were also observed in [(dme)₂Ca(BH₄)₂]⁴³ whereas in [{(Me₃Si)₃C₅H₂}Ca(thf)₂(HBEt₃)]⁴⁴ a rather loose contact be-



Fig. 5 Molecular structure and numbering scheme of $[(thf)Ca{HC-PPh_2BH_{3})_2}_2]$ (4). The ellipsoids represent a probability of 40%. The phenyl and THF hydrogen atoms are neglected for clarity reasons. Selected bond lengths (Å): Ca–C1 2.754(3), Ca1–O1 2.359(2), Ca1–H1_{B1} 2.37(3), Ca1–H3_{B1} 2.62(3), Ca1–H2_{B2} 2.37(3), Ca1–H1_{B3} 2.41(3), Ca1–H3_{B3} 2.34(3), Ca1–H1_{B4} 2.37(3), Ca1–H3_{B4} 2.47(3), C1–P1 1.764(3), C1–P2 1.759(3), P1–B1 1.933(3), P1–C2 1.825(3), P1–C8 1.821(3), P2–B2 1.919(3), P2–C14 1.828(3), P2–C20 1.823(3), C26–P3 1.712(3), C26–P4 1.712(3), P3–B3 1.926(3), P3–C27 1.825(3), P3–C33 1.834(3), P4–B4 1.930(3), P4–C39 1.830(3), P4–C45 1.825(3). Angles (°): Ca1–C1–P1 91.3(1), Ca1–C1–P2 92.3(1), P1–C1–P2 125.0(2), C1–P1–B1 113.5(2), C1–P2–B2 113.7(2), P3–C26–P4 129.7(2), C26–P3–B3 120.4(1), C26–P4–B4 120.8(2).

tween the $[\{(Me_3Si)_3C_5H_2\}Ca(thf)_2]$ unit and the $[HBEt_3]$ anion was found.

Conclusion

The rich coordination chemistry of the ligand [HC(PPh₂-BH₃)₂] was investigated varying from a free anion to a ligand binding via the borane moieties and via the methine carbon atom. The metathesis reaction of $K{CH(PPh_2)_2}$ and $K{CH(PPh_2-BH_3)_2}$ with anhydrous calcium diiodide yields corresponding $[(thf)_3Ca{CH(PPh_2)_2}_2]$ (2) and $[(thf)Ca{CH(PPh_2-BH_3)_2}]$ (4), respectively. In compound 2 the bis(diphenylphosphanyl)methanide anions act as bidentate ligands via the phosphorus atoms leading to a seven-coordinate calcium atom. The coordination mode of the $[RC(PR'_2)_2]^{-1}$ anions in main group45 and f-block27 chemistry depends on the metal atom, the presence of donor ligands, and the nature of the substituents R and R' at carbon and phosphorus.⁴⁵ Due to similar Pauling electronegativities and a valence isoelectronic situation the anionic carbon and phosphorus centers can compete as Lewis bases making it difficult to foresee the coordination mode. The formal insertion of borane into the Ca-P bonds of 2 leads to compound 4 which is isoelectronic to [(thf)Ca{CH(SiPh₂- $(CH_3)_2$]. In 4 one anion exclusively binds *via* the boron-bound hydrides whereas the other ligand also shows an additional Ca-C bond. However, in solution both these anions are chemically and magnetically equivalent as a consequence of flexibility of the molecule. The free anion was observed in the solvent-separated ion pair $[(dme)_{3}Li]^{+}$ $[HC(PPh_{2}-BH_{3})_{2}]^{-}$ (3').

The compounds $[(thf)Ca{CH(PPh_2-BH_3)_2}_2]$ (4) and yet unknown $[(thf)Ca{CH(SiPh_2-CH_3)_2}_2]$ are isoelectronic complexes. However, the coordination behaviour of the ligands shows significant differences. Bis(triorganylsilyl)methyl groups form Ca–C bonds as found in $[(diox)_2Ca{CH(SiMe_3)_2}_2]^{46}$ (diox = 1,4-dioxane) whereas the CH(PPh₂-BH₃)₂ group prefers a coordination to calcium *via* the borane units due to significant basicity of B-bound hydrogen atoms.

Experimental section

General considerations

All manipulations were carried out by using Schlenk techniques under an atmosphere of argon. Prior to use, tetrahydrofuran, dimethoxyethane, and diethyl ether were dried over potassium hydroxide and distilled over Na/benzophenone in an argon atmosphere. Starting [LiCH(PPh₂)₂],²³ [KCH(PPh₂)₂],²⁷ and H₂C(PPh₂BH₃)₂³⁰ were prepared according to literature procedures using toluene instead of benzene. ¹H NMR and ¹³C NMR spectra were recorded at ambient temperature on a Bruker AC 200 or AC 400 MHz spectrometer. All spectra were referenced to TMS or deuterated solvent as an internal standard.

[(tmeda)(thf)Li{CH(PPh₂)₂}] (1). Recrystallization of Li-{CH(PPh₂)₂} from a mixture of THF and 1,2-bis(dimethylamino)ethane (tmeda) gave crystals of [(tmeda)(thf)Li{CH(PPh₂)₂}]. THF (1), suitable for X-ray diffraction studies. ¹H NMR (200 MHz, [D₈]THF, 25 °C): δ 1.56 (t, ²J_{H,P} = 8.6 Hz, 1H, PCHP), 2.12 (s, 12H, CH₃ tmeda), 2.27 (s, 4H, CH₂ tmeda), 6.85–7.1 (m, 12H, CH-Ph), 7.45–7.58 (m, 8H, CH Ph). ¹³C NMR (50.3 MHz, [D₈]THF, 25 °C): δ 17.9 (t, ¹J_{C,P} = 19.4 Hz, 1C, PCP), 46.1 (s, 4C, CH₃ tmeda), 58.8 (s, 2H, CH₂ tmeda), 125.4 (s, 4C, *p*-CH Ph), 127.4 (br, 8C, CH Ph), 132.0 (t, ³J_{C,P} = 7.8 Hz, 8C, CH Ph), 152.3 (t, ¹J_{C,P} = 4 Hz, 4C, *i*-C Ph). ³¹P NMR (81 MHz, [D₈]THF, 25 °C): δ 2.9 (s).

Synthesis of $[(thf)_3Ca{CH(PPh_2)_2}_2]$ (2). Solid KOtBu (0.17 g, 1.52 mmol) was added to a stirred solution of LiCH(PPh₂)₂ (0.70 g, 1.75 mmol) in diethyl ether (35 ml). The resulting yellow solution was stored for 2 days at -20 °C. Afterwards the formed pale yellow precipitate was isolated by filtration and dried in vacuo (yield: 0.41 g). This K{CH(PPh₂)₂} (0.25 g, 0.59 mmol) was added to a stirred solution of (thf)₄CaI₂ (0.16 g, 0.275 mmol) in 5 ml of THF, resulting in the precipitation of KI. The suspension was stirred for 30 min and the solid was removed. The clear vellow solution was stored for 3 days at -40 °C in order to precipitate crystalline CaI₂(thf)₄ which was removed by decantation afterwards. The solution was concentrated in vacuo until the remaining yellow oil started to crystallize. Crystallization was complete after 1 day at 0 °C and the obtained solid, consisting of 2 and traces of H₂C(PPh₂)₂, was dried in vacuum. ¹H NMR (200 MHz, [D₈]THF, 25 °C): δ 2.02 ² $J_{\text{H,P}}$ = 6.8 Hz, 2H, PCHP), 6.95–7.2 (m, 24H, CH-Ph), 7.55–7.70 (m, 16H, CH Ph). ¹³C NMR (50.3 MHz, [D₈]THF, 25 °C): δ 16.5 (t, ${}^{1}J_{C,P}$ = 31.1 Hz, 2C, PCP), 126.6 (s, 8C, *p*-CH Ph), 127.8 (s, 16C, CH Ph), 131.9 (t, ${}^{3}J_{CP} = 6.4$ Hz, 16C, CH Ph), 149.1 (br, 8C, *i*-C Ph). ³¹P NMR (81 MHz, [D₈]THF, 25 °C): δ 1.0 (s).

Synthesis of $[(Et_2O)_2Li{HC(PPh_2BH_3)_2}]$ (3) and $[(dme)_3Li]$ -[HC(PPh_2BH_3)_2] (3'). Solid H₂C(PPh_2BH_3)_2 (0.65 g, 1.58 mmol) was suspended in 30 ml of diethyl ether and a solution of *n*-butyllithium (1.0 ml of 1.6M hexane solution, 1.6 mmol) was added slowly to the stirred suspension at room temperature. The resulting clear, pale yellow solution was stirred for 0.5 h and then stored at 0 °C over night. Afterwards the supernatant solution was decanted from the colorless crystals of 3. Yield: 0.53 g. The product loses ether on drying in vacuo. ¹H NMR (400 MHz, [D₈]THF, 25 °C): δ 0.50–1.40 (br, 6H, BH₃), 0.74 (s, 1H, PCHP), 1.16 (CH₃ Et₂O), 3.42 (CH₂ Et₂O), 7.15 (br s, 12H, Ph), 7.76 (m, 8H, Ph). ⁷Li NMR (155.6 MHz, [D₈]THF, 25 °C): δ –0.8 (s). ¹¹B NMR (128.4 MHz, [D₈]THF, 25 °C): δ –33.6 (s). ¹³C NMR (50.3 MHz, $[D_8]$ THF, 25 °C): δ 5.12 (t, ${}^1J_{C,P} = 77.4$ Hz, 1C, PCP), 15.7 (s, CH₃ Et₂O), 66.2 (s, CH₂ Et₂O), 127.2 (d, $J_{CP} = 9.4$ Hz, 8C, CH Ph), 127.9 (s, 4C, *p*-CH Ph), 133.1 (d, *J*_{C,P} = 9.2 Hz, 8C, CH Ph), 142.8 (d, ${}^{1}J_{CP} = 56.7$ Hz, 4C, *i*-C Ph). ${}^{31}P$ NMR (81 MHz, $[D_8]$ THF, 25 °C): δ 16.3 (br). Recrystallization of 3 from 1,2dimethoxyethane yielded compound [(dme)₃Li][CH(PPh₂)₂] (3') which was used for elemental analysis: $C_{37}H_{57}B_2LiO_6P_2$ (688.37), calcd.: C 64.56, H 8.35%; found: C 64.26, H 8.24%.

Synthesis of $[(thf)Ca{HC(PPh_2BH_3)_2}_2]$ (4). Solid KOtBu (0.18 g, 1.61 mmol) was added to a stirred solution of 3 in 35 ml of diethyl ether, prepared from $H_2C(PPh_2BH_3)_2$ (0.72 g, 1.75 mmol) and a solution of n-butyllithium (1.1 ml of 1.6M hexane solution, 1.76 mmol). The resulting reaction mixture was stirred for 2 h. Afterwards the formed pale yellow solid of $K{HC(PPh_2BH_3)_2}$ (0.73 g) was isolated by filtration and dried in vacuo. This pottassium salt was used without characterization or further purifications. Solid K{ $HC(PPh_2BH_3)_2$ } (0.60 g, 1.33 mmol) was added to a stirred solution of (thf)₄CaI₂ (0.31 g, 0.53 mmol) in 15 ml of THF, leading to the precipitation of colorless KI. The reaction mixture was stirred for an additional hour and reduced to dryness. The remaining colorless residue was dried in vacuo for 5 min and afterwards suspended in 15 ml of toluene. After 30 min the remaining solids were removed by filtration. The colorless solution was concentrated in vacuo to 8 ml and stored at -20 °C for 2 days. The formed colorless crystals were isolated by filtration and dried in vacuo. Yield: 0.27 g (54%). Elemental analysis (C₅₄H₆₂CaB₄OP₄, 934.307): calcd.: C 69.42, H 6.69%; found: C 67.15, H 6.50%. ¹H NMR (400 MHz, [D₆]benzene, 25 °C): δ 1.08 (t, ${}^{3}J_{H,H} = 6.4$ Hz, 4H, thf), 1.2–2.2 (br, 12H, BH₃), 1.53 (t, ${}^{2}J_{H,P} = 14$ Hz, 2H, PCHP), 3.76 (t, ${}^{3}J_{H,H} = 6.4$ Hz, 4H, thf), 6.9-7.05 (m, 24H, Ph), 7.65-7,75 (m, 16H, Ph). ¹¹B NMR (128.4 MHz, [D₆]benzene, 25 °C): δ –31.5 (br). ¹³C NMR (100.6 MHz, [D₆]benzene, 25 °C): δ 5.56 (t, ${}^{1}J_{CP} = 51$ Hz, 2C, PCP), 25.0 (s, 2C, thf), 69.7 (s, 2C, thf), 128.1 (signal overlaps with the solvent signal, 16C, CH Ph), 129.2 (s, 8C, p-CH Ph), 131.9 (d, $J_{CP} = 9.6$ Hz, 8C, CH Ph), 138.0 (d, ${}^{1}J_{CP} = 66.1$ Hz, 4C, *i*-C Ph). ³¹P NMR (162 MHz, [D₈]THF, 25 °C): δ 11.1 (br).

Crystal structure determinations

The intensity data for the compounds 1, 2, 3 and 4 were collected on a Nonius KappaCCD diffractometer using graphitemonochromated Mo K α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.^{47,48} The structures were solved by direct methods (SHELXS)⁴⁹ and refined by full-matrix least squares techniques against F_o² (SHELXL-97) (Table 2).⁵⁰ The hydrogen atoms for all CH fragments and for the borane of 3 and 4 were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal

Compound	1	2	3	3'	4
Formula	$C_{35}H_{45}LiN_2OP_2, C_4H_7O$	$C_{62}H_{66}CaO_3P_4$	$C_{33}H_{47}B_2LiO_2P_2$	$[C_{25}H_{27}B_2P_2]^- [C_{12}H_{30}LiO_6]^+$	C54H62B4CaOP4
Fw/g mol ⁻¹	649.71	1023.11	566.21	688.33	934.24
T∕°Č	-90(2)	-90(2)	-90(2)	-90(2)	-90(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_{1}/c$	$P2_1/c$	$P\overline{1}$	$P\overline{1}$	$P2_{1}/c$
a/Å	21.3975(6)	12.2090(4)	10.0747(8)	11.2500(2)	13.4163(4)
b/Å	9.8321(2)	16.6792(5)	11.1578(7)	12.3814(2)	13.8646(4)
c/Å	18.8821(6)	27.0731(6)	16.7869(13)	29.6450(5)	28.3332(6)
$\alpha / ^{\circ}$	90.00	90.00	97.819(4)	86.239(1)	90.00
$\beta/^{\circ}$	108.9380(10)	95.218(2)	104.841(3)	81.939(1)	101.003(2)
$\gamma/^{\circ}$	90.00	90.00	106.881(4)	82.513(1)	90.00
$V/Å^3$	3757.43(18)	5490.2(3)	1699.7(2)	4048.91(12)	5173.4(2)
Ζ	4	4	2	4	4
$\rho/\mathrm{g}\mathrm{cm}^{-3}$	1.149	1.238	1.106	1.129	1.199
μ/cm^{-1}	1.50	2.76	1.54	1.47	2.82
Measured data	26018	34850	11602	28533	31260
Data with $I > 2\sigma(I)$	6195	6779	5238	11470	7944
Unique data/ R_{int}	8610/0.0582	12534/0.0900	7587/0.0555	17957/0.0394	11746/0.0644
w R_2 (all data, on F^2) ^{<i>a</i>}	0.1564	0.1498	0.2287	0.2805	0.1457
$R_1 (I > 2\sigma(I))^a$	0.0594	0.0588	0.0834	0.0934	0.0562
S ^b	1.018	0.997	1.067	1.005	1.022
Res. dens./e Å ⁻³	0.689/-0.485	0.581/-0.295	0.665/-0.515	1.642/-0.807	0.467/-0.264
CCDC No.	712109	712110	712111	712112	712113

 Table 2
 Crystal data and refinement details for the X-ray structure determinations of compounds 1 to 4

^{*a*} Definition of the *R* indices: $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ with $w^{-1} = \sigma^2 (F_o^2) + (aP)^2$. ^{*b*} $s = \{\sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p) \}^{1/2}$.

parameters. All non-disordered non-hydrogen atoms were refined anisotropically.⁵⁰ The cation [(dme)₃Li]⁺ of compound **3'** is heavily disordered and therefore the structural discussions are concentrated on the non-disordered part. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Acknowledgements

This work was supported by the *Deutsche Forschungsgemeinschaft* (DFG, Bonn-Bad Godesberg, Germany). We also acknowledge the financial support by the *Fonds der Chemischen Industrie* (Frankfurt/Main, Germany).

References

- M. Westerhausen, M. Gärtner, R. Fischer and J. Langer, Angew. Chem., 2007, 119, 1994–2001, (Angew. Chem., Int. Ed., 2007, 46, 1950– 1956).
- 2 M. Westerhausen, M. Gärtner, R. Fischer, J. Langer, L. Yu and M. Reiher, *Chem.-Eur. J.*, 2007, **13**, 6292–6306.
- 3 M. Westerhausen, Coord. Chem. Rev., 2008, 252, 1516–1531.
- 4 F. G. N. Cloke, P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. Royo, J. Chem. Soc., Chem. Commun., 1991, 724–726.
- 5 C. Eaborn, S. A. Hawkes, P. B. Hitchcock and J. D. Smith, *Chem. Commun.*, 1997, 1961–1962.
- 6 M. R. Crimmin, A. G. M. Barrett, M. S. Hill, D. J. MacDougall, M. F. Mahon and P. A. Procopiou, *Chem.-Eur. J.*, 2008, 14, 11292–11295.
- 7 P. B. Hitchcock, A. V. Khvostov and M. F. Lappert, *J. Organomet. Chem.*, 2002, **663**, 263–268.
- 8 V. Knapp and G. Müller, Angew. Chem., 2001, 113, 187–190, (Angew. Chem., Int. Ed., 2001, 40, 183–186).
- 9 S. Harder, F. Feil and A. Weeber, Organometallics, 2001, 20, 1044–1046.
- 10 S. Harder and F. Feil, Organometallics, 2002, 21, 2268-2274.
- 11 F. Feil, C. Müller and S. Harder, J. Organomet. Chem., 2003, 683, 56-63.
- 12 S. Harder, S. Müller and E. Hübner, Organometallics, 2004, 23, 178– 183.
- 13 M. A. Guino-o, C. F. Campana and K. Ruhlandt-Senge, Chem. Commun., 2008, 1692–1694.

- 14 F. Feil and S. Harder, Organometallics, 2000, 19, 5010-5015.
- 15 W. A. Herrmann and C. Köcher, Angew. Chem., 1997, 109, 2256–2282, (Angew. Chem., Int. Ed., 1997, 36, 2162–2187).
- 16 A. J. Arduengo, F. Davidson, R. Krafczyk, W. J. Marshall and M. Tamm, Organometallics, 1998, 17, 3375–3382.
- 17 H. Schumann, J. Gottfriedsen, M. Glanz, S. Dechert and J. Demtschuk, J. Organomet. Chem., 2001, 617–618, 588–600.
- 18 A. G. M. Barrett, M. R. Crimmin, M. S. Hill, G. Kociok-Köhn, D. J. MacDougall, M. F. Mahon and P. A. Procopiou, *Organometallics*, 2008, 27, 3939–3946.
- 19 L. Orzechowski, G. Jansen and S. Harder, J. Am. Chem. Soc., 2006, 128, 14676–14684.
- 20 (a) M. S. Hill and P. B. Hitchcock, *Chem. Commun.*, 2003, 1758–1759; (b) S. A. Ahmed, M. S. Hill and P. B. Hitchcock, *Organometallics*, 2006, 25, 394–402.
- 21 L. Orzechowski and S. Harder, *Organometallics*, 2007, **26**, 2144–2148.
- 22 H. H. Karsch and M. Reisky, Eur. J. Inorg. Chem., 1998, 905-911.
- 23 K. Issleib and H. P. Abicht, J. Prakt. Chem., 1970, 312, 456-465.
- 24 D. J. Brauer, S. Hietkamp and O. Stelzer, *J. Organomet. Chem.*, 1986, 299, 137–142.
- 25 H. H. Karsch, B. Deubelly and G. Müller, *J. Organomet. Chem.*, 1988, **352**, 47–59.
- 26 H. H. Karsch and G. Müller, J. Chem. Soc., Chem. Commun., 1984, 569–570.
- 27 S. T. Liddle and K. Izod, J. Organomet. Chem., 2006, 691, 2599-2603.
- 28 K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, 1969, 8, 2671– 2674.
- 29 J. Beres, A. Dodds, A. J. Novabito and R. M. Adams, *Inorg. Chem.*, 1971, **10**, 2072–2074.
- 30 H. Schmidbaur, A. Stützer, P. Bissinger and A. Schier, Z. Anorg. Allg. Chem., 1993, 619, 1519–1525.
- 31 M. Lusser and P. Peringer, J. Organomet. Chem., 1986, 312, C61-C63.
- 32 S. Hao, J. I. Song, H. Aghabozorg and S. Gambarotta, J. Chem. Soc., Chem. Commun., 1994, 157–158.
- 33 A. L. Balch and D. E. Oram, Organometallics, 1986, 5, 2159-2161.
- 34 H. Schmidbaur, S. Lauteschläger and G. Müller, J. Organomet. Chem., 1985, 281, 33–43.
- 35 H. Schmidbaur, J. R. Mandl, J. M. Bassett, G. Blaschke and B. Zimmer-Gasser, *Chem. Ber.*, 1981, **114**, 433–440.

- 36 See for example: S. Harder and J. Brettar, Angew. Chem., 2006, 118, 3554–3558, (Angew. Chem., Int. Ed., 2006, 45, 3474–3478).
- 37 M. J. Harvey, T. P. Hanusa and V. G. Young, Angew. Chem., 1999, 111, 241–242, (Angew. Chem., Int. Ed., 1999, 38, 217–219).
- 38 M. R. Hartman, J. J. Rush, T. J. Udovic, R. C. Bowman and S. J. Hwang, J. Solid State Chem., 2007, 180, 1298–1305.
- 39 H. Wu, W. Zhou and T. Yildirim, J. Am. Chem. Soc., 2008, 130, 14834– 14839.
- 40 K. Miwa, M. Aoki, T. Noritake, N. Ohba, Y. Nakamori, S.-i. Towata, A. Züttel and S.-i. Orimo, *Phys. Chem. Rev. B*, 2006, 74, 155122.
- 41 F. Buchter, Z. Łodziana, A. Remhof, O. Friedrichs, A. Borgschulte, P. Mauron, A. Züttel, D. Sheptyakov, G. Barkhordarian, R. Bormann, K. Chłopek, M. Fichtner, M. Søby, M. Riktor, B. Hauback and S. Orimo, J. Phys. Chem. B, 2008, 112, 8042–8048.
- 42 K. Izod, C. Wills, W. Clegg and R. W. Harrington, *Inorg. Chem.*, 2007, 46, 4320–4325.

- 43 E. Hanecker, J. Moll and H. Nöth, Z. Naturforsch., B, 1984, 39, 424–430.
- 44 M. J. Harvey, T. P. Hanusa and M. Pink, J. Chem. Soc., Chem. Commun., 2000, 489–490.
- 45 K. Izod, *Coord. Chem. Rev.*, 2002, **227**, 153–173, and literature cited therein.
- 46 F. G. N. Cloke, P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. Royo, J. Chem. Soc., Chem. Commun., 1991, 724–726.
- 47 COLLECT, Data Collection Software, Nonius B.V., Netherlands, 1998.
- 48 "Processing of X-Ray Diffraction Data Collected in Oscillation Mode" Z. Otwinowski, W. Minor, in C. W. Carter, R. M. Sweet, (eds.): *Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A*, pp. 307–326, Academic Press, San Diego, 1997.
- 49 G. M. Sheldrick, Acta Crystallogr., Sect. A, 1990, 46, 467-473.
- 50 G. M. Sheldrick, SHELXL-97 (Release 97-2), University of Götingen, Germany, 1997.