ELSEVIER

Influence of aromatic ring substituents and co-ligand on the binding mode of a phosphine–borane-stabilized carbanion; crystal structures of $[[(Me_3Si)_2\{Ph_2P(BH_3)\}C]KL_n]_2[L_n = (OEt_2)_2,$ pmdeta; pmdeta = N,N,N',N'',N''-pentamethyldiethylenetriamine]

Keith Izod *, Corinne Wills, William Clegg, Ross W. Harrington

Main Group Chemistry Laboratories, Department of Chemistry, School of Natural Sciences, Bedson Building, University of Newcastle, Newcastle upon Tyne NE1 7RU, UK

Abstract

The phosphine–borane adduct $(Me_3Si)_2CHPPh_2(BH_3)$ (**1**) is readily prepared from the reaction between $(Me_3Si)_2CHPCl_2$ and 2 equiv of PhMgBr in refluxing THF, followed by treatment with $BH_3 \cdot SMe_2$. The reaction between **1** and MeK in cold diethyl ether proceeds cleanly to give $[[(Me_3Si)_2\{Ph_2P(BH_3)\}C]K]$ (**2**), which may be crystallized in the presence of pmdeta to give the corresponding adduct $[[(Me_3Si)_2\{Ph_2P(BH_3)\}C]K(pmdeta)]_2$ (**2a**) [pmdeta = N,N,N',N'',N''-pentamethyldiethylenetriamine]. Treatment of **1** with MeK, followed by crystallization from cold diethyl ether, gives $[[(Me_3Si)_2\{Ph_2P(BH_3)\}C]K(OEt_2)_2]_2$ (**2b**). X-ray crystallography reveals that in both **2a** and **2b** the phosphine–borane-stabilized carbanion ligand binds to the metal centers via its BH_3 hydrogen atoms; there are no short contacts between the potassium ions and the carbanion centers. In **2b** the ligand also binds the potassium ion through an η^5-aryl interaction; in **2a** this contact is absent.
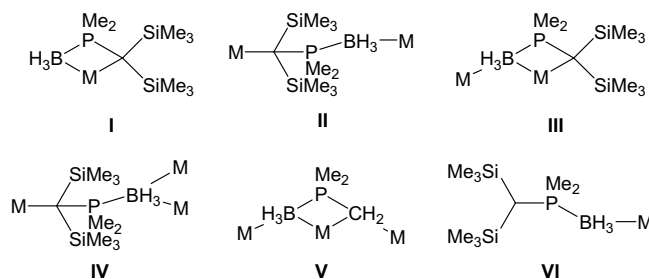© 2007 Elsevier B.V. All rights reserved.

Keywords: Alkali metal; Organometallic; Crystal structure; Carbanion

1. Introduction

In spite of the frequent application of phosphine–borane-stabilized carbanions for the synthesis of both chiral and achiral mono- and polyphosphines [1,2], little is known about the structures of these species. In a recent extended study we have shown that alkali and alkaline earth metal complexes of these ligands exhibit a remarkable structural diversity; these compounds crystallize as molecular species, ate complexes, one-dimensional polymers, ribbon-type polymers and two-dimensional sheets [3–8]. There is also a remarkable diversity of ligand binding modes in these compounds; we have observed a chelating mode (**I**), a variety of bridging modes (**II–V**), and a terminal BH_3-donor

mode (**VI**). In addition, Schmidbaur and co-workers have reported the separated ion pair compound [Li(tmeda)2][CH{PMe2(BH3)}2], in which there are no close contacts between the cation and the carbanion [9], and Kobayashi and co-workers have reported a phosphine–borane-stabilized carbanion complex of lithium in which there is a C–Li contact but no B–H···Li contacts [10].

* Corresponding author.
  E-mail address: k.j.izod@ncl.ac.uk (K. Izod).

It is well known that alkali metal cations are able to form moderately strong interactions with aromatic rings [11]. This has important consequences both for the structural chemistry of alkali metal complexes, where metal–aryl contacts compete with more traditional metal-lone pair interactions [12], and in biology, where alkali metal–arene contacts are thought to play a significant role in the molecular conformation of proteins [13]. Alkali metal–arene contacts are a frequent feature of organo-alkali metal compounds and so we were interested to see whether such interactions would have any significant effect on the coordination behavior of phosphine–borane-stabilized carbanions with these metals. We report herein the synthesis of a new phenyl-substituted phosphine–borane adduct, and the synthesis and structural characterization of two potassium derivatives of this compound.

2. Results and discussion

The reaction between $\{(Me_3Si)_2CH\}PCl_2$ and 2 equiv of PhMgBr in refluxing THF yields the tertiary phosphine $\{(Me_3Si)_2CH\}PPh_2$ [14]. Treatment of this compound with $BH_3 \cdot SMe_2$ in THF gives the phosphine–borane adduct $\{(Me_3Si)_2CH\}P(BH_3)Ph_2$ (1) as a colorless solid in good yield and purity, after a straightforward aqueous work-up (Scheme 1). The ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of 1 are as expected; the BH_3 group gives rise to a broad quartet at 1.22 ppm, which collapses to a broad doublet ($J_{PH} = 15.3$ Hz) on decoupling the ^{11}B nucleus. The $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ spectra consist of a broad doublet and a poorly resolved quartet at -37.1 and 14.0 ppm, respectively ($J_{PB} = 66.1$ Hz).

Compound 1 reacts cleanly with a small excess of MeK in diethyl ether to give the corresponding potassium salt $[(Me_3Si)_2\{Ph_2P(BH_3)\}C]K$ (2). Complete metalation of 1 was confirmed by a $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture, which exhibited a single poorly-resolved quartet at 16.0 ppm ($J_{PB} = 107.3$ Hz), and by the lack of a signal due to the PSi_2CH group in the $^1H\{^{11}B\}$ NMR spectrum of 2 [cf. 1.39 ppm (d, $^2J_{PH} = 19.2$ Hz) for this group in 1]. As observed in previous cases, metalation of the neutral phosphine–borane adduct leads to a near doubling of the ^{31}P–^{11}B coupling constant [3–8].

Treatment of 2 with pmdeta followed by recrystallization from hot toluene yields the corresponding complex $[[(Me_3Si)_2\{Ph_2P(BH_3)\}C]K(pmdeta)]_2$ (2a) as pale yellow needles [pmdeta = N,N,N',N'',N''-pentamethyldiethylenetriamine]. In contrast, recrystallization of 2 from cold

diethyl ether in the absence of co-ligands gives pale yellow blocks of the complex $[[(Me_3Si)_2\{Ph_2P(BH_3)\}C]K(OEt_2)_2]_2$ (2b) in moderate yield. The coordinated diethyl ether in 2b is slowly lost under vacuum, although solid samples of 2b are stable enough that, by careful manipulation of the crystalline solid, accurate elemental analyses could be obtained. However, despite repeated attempts, ^1H NMR spectra of 2b consistently show low, but variable, amounts of diethyl ether present.

The solid state structures of 2a and 2b were determined by X-ray crystallography; the molecular structures of 2a and 2b are shown in Figs. 1 and 2, respectively, and selected bond lengths and angles for both 2a and 2b are given in Table 1.

Both 2a and 2b crystallize as discrete centrosymmetric dimers. The potassium ions in 2a are coordinated by the three nitrogen atoms of the pmdeta co-ligand, and by two η^2-BH_3 groups, one from each ligand in the dimer. Thus the BH_3 group in each phosphine–borane-stabilized carbanion ligand forms a μ_2-η^2:η^2 bridge between the two potassium ions in the dimer. The coordination sphere of each potassium ion is completed by three short agostic-type interactions with three of the methyl groups in the pmdeta co-ligand, one on each nitrogen; the $K \cdots C(Me)$ distances [3.222(8)–3.458(8) Å] are typical for this type of contact, which usually falls in the range 3.30–3.70 Å [15]. There are no short contacts between the potassium ions and the essentially planar carbanion centers [sum of angles

Fig. 1. Molecular structure of 2a with 40% probability ellipsoids and with H atoms bonded to carbon omitted for clarity.

$\{(Me_3Si)_2CH\}PCl_2$ $\xrightarrow[\text{2. } BH_3 \cdot SMe_2/THF]{\text{1. 2PhMgBr/THF}}$ $\{(Me_3Si)_2CH\}P(BH_3)Ph_2$ (1) $\xrightarrow[\text{MeK/} Et_2O]{\text{MeK/} pmdeta}$ $[[(Me_3Si)_2\{Ph_2P(BH_3)\}C]K(pmdeta)]_2$ (2a)

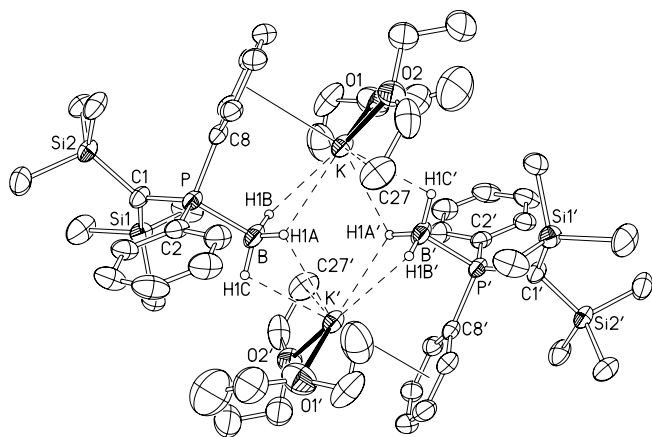$[[(Me_3Si)_2\{Ph_2P(BH_3)\}C]K(Et_2O)_2]_2$ (2b)

Scheme 1.

Fig. 2. Molecular structure of **2b** with 40% probability ellipsoids and with minor disorder components and H atoms bonded to carbon omitted for clarity.

in the $PCSi_2$ skeleton = 359.8°]. In contrast, the potassium ions in **2b** are coordinated by two η^2-BH_3 groups, one from each ligand in the dimer, two oxygen atoms from the ether ligands, a short agostic-type K···C(Me) contact to one of the ether ligands [K···C(Me) 3.510(3) Å], and an η^5-phenyl group from the carbanion ligand. The K···C distances to the η^5-phenyl rings in **2b** range from 3.194(2) to 3.524(2) Å [the typical range for K···η^5-phenyl distances is 2.96–3.30 Å [12]; the K–C12 distance is greater than 3.56 Å]. Once again, there are no short contacts between the potassium ions and the essentially planar carbanion centers [sum of angles in the $PCSi_2$ skeleton = 359.49°].

The C1–P distances of 1.718(5) and 1.7084(19) Å in **2a** and **2b**, respectively, are significantly shorter than the C1–P distances in the closely related compounds [[(Me₃Si)₂{Me₂P (BH₃)}C]K]∞ (**3**) [4], [[(Me₃Si)₂{Me₂P(BH₃)}C]K (THF)₀.₅]∞ (**4**) [8], and [[(Me₃Si)₂{Me₂P(BH₃)}C]K(pmdeta)]₂ (**5**) [8] which are 1.735(5) and 1.735(5) Å (for the two crystallographically different carbanions in the asymmetric unit), 1.750(2) and 1.745(2) Å, and 1.742(2) Å, respectively. The shorter C1–P distances in **2a** and **2b** are clearly associated with increased delocalization of charge from the carbanion center via negative hyperconjugation in these compounds and the change in hybridization of the carbanion center from sp^3 to sp^2.

The K–H distances of 2.64(7) and 2.88(7) Å in **2a** and 2.77(2) and 2.91(3) Å in **2b** are similar to K–H distances found in potassium salts of borohydride anions; for example, the K–H distances in [K(H₂B-*t*-Bu₂)(pmdeta)]₂ are 2.56(2), 2.67(1) and 3.06(2) Å [15].

The structures of **2a** and **2b** are markedly different from those adopted by the potassium salts of the closely related carbanion (Me₃Si)₂{Me₂P(BH₃)}C⁻, in which methyl groups replace the phenyl rings found in (Me₃Si)₂{Ph₂P (BH₃)}C⁻. The solvent-free compound **3** crystallizes with a complex two-dimensional sheet structure, whereas the THF adduct **4** crystallizes as a ribbon-type polymer; in both compounds there are both K–H(B) and K–C contacts. The pmdeta adduct **5** crystallizes as a centrosymmetric dimer related to **2a** and **2b**, however, in **5** the phosphine–borane-stabilized carbanion ligands bind the potassium ions via both their BH₃ groups (in a μ_2-η^2:η^2 fashion) and their carbanion centers, generating pseudo-four-membered chelate rings. The different coordination behavior of these two closely related ligands may be attributed to a combination of steric and electronic effects. In **2a** and **2b**, the phenyl rings engender greater steric hindrance about the carbanion center, favoring coordination by the

Table 1
Selected bond lengths (Å) and angles (°) for **2a** and **2b**

2a					
K–H1A	2.64(7)	K–H1B	2.88(7)	K–H1B′	2.95(7)
K–H1C′	2.67(5)	K···B	3.215(7)	K···B′	3.269(7)
K–N1	2.900(5)	K–N2	2.865(5)	K–N3	2.883(5)
K···C24	3.222(8)	K···C27	3.411(7)	K···C21	3.458(8)
P–C1	1.718(5)	P–C8	1.837(5)	P–C14	1.848(5)
P–B	1.951(6)	C1–Si1	1.831(5)	C1–Si2	1.823(5)
N1–K–N2	61.98(15)	N2–K–N3	62.39(14)		
B···K···B′	87.73(16)	P–C1–Si2	120.1(3)		
P–C1–Si1	120.4(3)	Si1–C1–Si2	119.3(3)		
2b					
K–H1A	2.77(2)	K–H1B	2.91(3)	K–H1A′	2.90(2)
K–H1C′	2.64(3)	K···B	3.296(3)	K···B′	3.094(2)
K–O1	2.675(2)	K–O2	2.7021(18)	K–C8	3.2316(19)
K–C9	3.194(2)	K–C10	3.339(2)	K–C11	3.524(2)
K–C12	3.568(2)	K–C13	3.421(2)	K···C27	3.510(3)
P–C1	1.7084(19)	P–C2	1.839(2)	P–C8	1.843(2)
C1–Si1	1.826(2)	C1–Si2	1.826(2)	P–B	1.939(2)
O1–K–O2	106.07(7)	B···K···B′	85.98(7)		
P–C1–Si2	120.17(11)	P–C1–Si1	118.93(11)		
Si1–C1–Si2	120.39(10)				

BH$_3$ groups; in addition, the phenyl rings are likely to facilitate the delocalization of charge away from the carbanion center, making this center less nucleophilic and a poorer donor in comparison to the BH$_3$ group.

3. Conclusions

The ready availability of the phosphine–borane adduct **1** and its facile metalation provide a useful opportunity to study the effect of phenyl substituents on the structures adopted by phosphine–borane-stabilized carbanions. We find that such substituents have a marked effect on the structural preferences of these carbanions, leading, in the example studied, to a BH$_3$-donor coordination mode with no metal–carbanion center contacts. In addition, it appears that, in the presence of weaker, monodentate ligands such as diethyl ether, there is significant competition for coordination of the potassium ions by the aryl rings of the phosphine–borane-stabilized carbanion. This clearly has important implications for the use of such carbanions for the synthesis of chiral phosphines, since there is the possibility that, where a BH$_3$-donor mode is adopted, the presence of chiral diamines such as (−)-sparteine at the metal center will have little influence on the stereochemical outcome of any reaction at the carbanion center.

4. Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. THF, diethyl ether and toluene were distilled under nitrogen from sodium, potassium or sodium/potassium alloy. THF was stored over activated 4 A molecular sieves; all other solvents were stored over a potassium film. Deuterated toluene was distilled from potassium and CDCl$_3$ was distilled from CaH$_2$; both deuterated solvents were deoxygenated by three freeze–pump–thaw cycles and were stored over activated 4 A molecular sieves. Pmdeta was dried over CaH$_2$ and was distilled under nitrogen before use; MeK [16] and (Me$_3$Si)$_2$CHPCl$_2$ [17] were prepared by previously published procedures. PhMgBr was supplied by Aldrich as a 2.45 M solution in THF; BH$_3$·SMe$_2$ was supplied by Aldrich as a 2.0 M solution in THF.

^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{11}B{^{1}H} NMR spectra were recorded on a JEOL Lambda500 spectrometer operating at 500.16, 125.65, 202.35 and 160.35 MHz, respectively; ^{1}H, and ^{13}C chemical shifts are quoted in ppm relative to tetramethylsilane, ^{31}P and ^{11}B chemical shifts are quoted in ppm relative to 85% H$_3$PO$_4$ and BF$_3$OEt$_2$, respectively. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

{(Me$_3$Si)$_2$CH}PPh$_2$: This compound was prepared by an alternative, higher yielding procedure to that previously reported [14]. To a solution of {(Me$_3$Si)$_2$CH}PCl$_2$ (8.94 g, 34.2 mmol) in THF (50 mL) was added PhMgBr (27.9 mL, 68.4 mmol), dropwise. The resulting solution was heated under reflux for 1 h, and then stirred for 16 h at room temperature, during which time a white solid formed. Deoxygenated water (50 mL) was cautiously added; the organic layer was decanted and dried over activated 4 Å molecular sieves. The solution was filtered and the solvent was removed *in vacuo* from the filtrate to yield {(Me$_3$Si)$_2$CH}PPh$_2$ as an off-white solid. Isolated yield 10.32 g, 87.6%. NMR data for this compound were essentially identical to those reported previously [14].

{(Me$_3$Si)$_2$CH}P(BH$_3$)Ph$_2$ (**1**): To a solution of {(Me$_3$Si)$_2$CH}PPh$_2$ (4.25 g, 12.3 mmol) in THF (40 mL) was added BH$_3$·SMe$_2$ (6.17 mL, 12.3 mmol). The resulting solution was stirred for 16 h then the solvent was removed *in vacuo* to yield **1** as a white solid. Isolated yield 4.31 g, 97.8%. ^{1}H{^{11}B} NMR (CDCl$_3$): δ −0.02 (s, 18H, SiMe$_3$), 1.22 (d, $^2J_{PH}$ = 15.3 Hz, 3H, BH$_3$), 1.39 (d, $^2J_{PH}$ = 19.2 Hz, 1H, CH), 7.36–7.84 (m, 10H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 2.67 (SiMe$_3$), 10.57 (CH), 128.47 (d, $^3J_{PC}$ = 9.9 Hz, *m*-Ph), 130.57 (*p*-Ph), 132.19 (d, $^2J_{PC}$ = 9.4 Hz, *o*-Ph), 133.61 (d, $^1J_{PC}$ = 52.6 Hz, *ipso*-Ph). ^{11}B{^{1}H} NMR (CDCl$_3$): δ −37.1 (d, J_{PB} = 66.1 Hz). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 14.0 (q, J_{PB} = 66.1 Hz).

[[(Me$_3$Si)$_2${Ph$_2$P(BH$_3$)}C]K(OEt$_2$)$_2$]$_2$ (**2b**): A solution of {(Me$_3$Si)$_2$CH}P(BH$_3$)Ph$_2$ (1.97 g, 5.50 mmol) in cold (−10 °C) diethyl ether (30 mL) was added to solid MeK (0.34 g, 6.28 mmol). The mixture was allowed to attain room temperature and was stirred for 16 h. The slightly turbid solution was filtered to give a yellow solution and cooling of this filtrate (−30 °C) for several hours yielded pale yellow blocks of [[(Me$_3$Si)$_2${Ph$_2$P(BH$_3$)}C]K(OEt$_2$)$_2$]$_2$ (**2b**) suitable for X-ray crystallography. Isolated yield 1.01 g, 46%. Anal. Calc. for C$_{27}$H$_{51}$BKO$_2$PSi$_2$ (544.74): C, 59.53; H, 9.44. Found: C, 59.39; H, 9.52%. ^{1}H{^{11}B} NMR (toluene-d_8): δ 0.20 (s, 18H, SiMe$_3$), 0.65 (d, J_{PH} = 14.0 Hz, 3H, BH$_3$), 0.99 (t, 4H, CH$_2$CH$_3$), 3.15 (q, 2H, OCH$_2$CH$_3$), 6.99 (m, 2H, *p*-Ph), 7.10 (m, 4H, *m*-Ph), 7.94 (m, 4H, *o*-Ph). ^{13}C{^{1}H} NMR (toluene-d_8): δ 7.98 (SiMe$_3$), 11.74 (Si$_2$CP), 16.37 (OCH$_2$CH$_3$), 66.70 (OCH$_2$CH$_3$), 128.94 (*m*-Ph), 131.64 (*p*-Ph), 133.64 (d, $^2J_{PC}$ = 8.3 Hz, *o*-Ph), 144.08 (d, $^1J_{PC}$ = 49.6 Hz, *ipso*-Ph). ^{11}B{^{1}H} NMR (toluene-d_8): δ -27.5 (d, J_{PB} = 107.3 Hz). ^{31}P{^{1}H} NMR (toluene-d_8): δ 16.0 (q, J_{PB} = 107.3 Hz).

[[(Me$_3$Si)$_2${Ph$_2$P(BH$_3$)}C]K(pmdeta)]$_2$ (**2a**): A solution of {(Me$_3$Si)$_2$CH}P(BH$_3$)Ph$_2$ (0.82 g, 2.29 mmol) in cold (−10 °C) diethyl ether (30 mL) was added to solid MeK (0.12 g, 2.29 mmol). The mixture was allowed to attain room temperature and was stirred for 16 h. The slightly turbid solution was filtered, then pmdeta (0.48 mL, 2.29 mmol) was added. The resulting solution was stirred for 30 min, and then the solvent was removed *in vacuo* to yield a yellow oil. The oil was dissolved in hot toluene, and allowed to cool to room temperature to give pale yellow needles of [[(Me$_3$Si)$_2${Ph$_2$P(BH$_3$)}-C]K(pmdeta)]$_2$ (**2a**) suitable for X-ray crystallography. Isolated yield 0.60 g, 49%. Anal. Calc. for C$_{28}$H$_{54}$BKN$_3$PSi$_2$ (569.80): C, 59.02; H, 9.55; N, 7.37. Found: C, 58.89; H,

Table 2
Crystallographic data for **2a** and **2b**

Compound	2a	2b
Formula	$C_{56}H_{108}B_2K_2N_6P_2Si_4$	$C_{54}H_{102}B_2K_2O_4P_2Si_4$
M	1139.6	1089.5
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	17.495(3)	12.773(2)
b (Å)	10.1310(16)	14.652(3)
c (Å)	19.931(3)	18.649(4)
β (°)	90.117(2)	106.181(3)
V (Å^3)	3532.7(10)	3351.8(11)
Z	2	2
μ (mm^{-1})	0.283	0.298
Data collected	29 649	29 180
Unique data	4628	8081
R_{int}	0.064	0.028
Data with $F^2 > 2\sigma$	4350	6214
Refined parameters	349	346
R (on F, $F^2 > 2\sigma$)	0.061	0.048
R_w (on F^2, all data)	0.132	0.130
Goodness of fit on F^2	1.318	1.055
Minimum, maximum electron density (e Å^{-3})	0.35, −0.41	0.54, −0.32

9.43; N, 7.24%. ^{1}H{^{11}B} NMR (toluene-d_8): δ 0.32 (s, 18H, SiMe$_3$), [BH$_3$ protons not observed], 1.76 (s, 3H, NMe), 1.83 (s, 12H, NMe$_2$), 1.84 (m, 4H, NCH$_2$), 1.85 (m, 4H, NCH$_2$), 7.00 (m, 2H, p-Ph), 7.14 (m, 4H, m-Ph), 8.13 (m, 4H, o-Ph). ^{13}C{^{1}H} NMR (toluene-d_8): δ 8.23 (SiMe$_3$), 15.27 (Si$_2$CP), 42.82 (NMe), 46.20 (NMe$_2$), 56.58 (NCH$_2$), 58.17 (NCH$_2$), 128.39 (d, $^3J_{PC} = 8.3$ Hz, m-Ph), 133.44 (d, $^4J_{PC} = 8.3$ Hz, p-Ph), 133.90 (d, $^2J_{PC} = 8.8$ Hz, o-Ph), 145.32 (d, $^1J_{PC} = 51.64$ Hz, $ipso$-Ph). ^{11}B{^{1}H} NMR (toluene-d_8): δ −27.2 (d, $J_{PB} = 104.8$ Hz). ^{31}P{^{1}H} NMR (toluene-d_8): δ 18.1 (q, $J_{PB} = 104.8$ Hz).

Crystal structure determinations of **2a** *and* **2b**: Measurements were made at 150 K on a Bruker AXS SMART CCD diffractometer using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). For both compounds cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and were refined on F^2 values for all unique data. Table 2 gives further details. All non-hydrogen atoms were refined anisotropically, and H atoms were constrained with a riding model, except those bound to boron, which were freely refined; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Disorder was resolved for the diethyl ether in **2b**. The crystal of **2a** was twinned (37% minor component) and high angle data were very weak. Programs were Bruker AXS SMART (control) and SAINT (integration), and SHELXTL for structure solution, refinement, and molecular graphics [18].

Acknowledgement

Appendix A. Supplementary material

CCDC 650314 and 650315 contain the supplementary crystallographic data for **2a** and **2b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.07.040.

References

[1] For recent reviews see: (a) M. Ohf, J. Holz, M. Quirmbach, A. Borner, Synthesis (1998) 1391;
(b) J.M. Brunel, B. Faure, M. Maffei, Coord. Chem. Rev. 178–180 (1998) 665;
(c) B. Carboni, L. Monnier, Tetrahedron 55 (1999) 1197;
(d) R.T. Paine, H. Nöth, Chem. Rev. 95 (1995) 343;
(e) A.C. Gaumont, B. Carboni, in: D. Kaufmann, D.S. Matteson (Eds.), Science of Synthesis, Vol. 6, Thieme, Stuttgart, 2004, pp. 485–512.
[2] For examples see: (a) A.R. Muci, K.R. Campos, D.A. Evans, J. Am. Chem. Soc. 117 (1995) 9075;
(b) T. Imamoto, Pure Appl. Chem. 65 (1993) 655.
[3] K. Izod, W. McFarlane, B.V. Tyson, W. Clegg, R.W. Harrington, Chem. Commun. (2004) 570.
[4] K. Izod, C. Wills, W. Clegg, R.W. Harrington, Organometallics 25 (2006) 38.
[5] K. Izod, C. Wills, W. Clegg, R.W. Harrington, Organometallics 25 (2006) 5326.
[6] K. Izod, C. Wills, W. Clegg, R.W. Harrington, Inorg. Chem. 46 (2007) 4320.
[7] K. Izod, C. Wills, W. Clegg, R.W. Harrington, Organometallics 26 (2007) 2861.
[8] K. Izod, C. Wills, W. Clegg, R.W. Harrington, Dalton Trans. (2007) 3669.
[9] H. Schmidbaur, E. Weiss, B. Zimmer-Gasser, Angew. Chem., Int. Ed. Engl. 18 (1979) 782.
[10] X.-M. Sun, K. Manabe, W.W.-L. Lam, N. Shiraishi, J. Kobayashi, M. Shiro, H. Utsumi, S. Kobayashi, Chem. Eur. J. 11 (2005) 361.
[11] (a) J.L. Wardell, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 1, Pergamon, Oxford, 1982, pp. 43–120;
(b) D.S. Wright, M.A. Beswick, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry II, Vol. 1, Pergamon, Oxford, 1995, pp. 1–34.
[12] For examples see: (a) C. Schade, P.vonR. Schleyer, Adv. Organomet. Chem. 27 (1987) 169;
(b) J.D. Smith, Adv. Organomet. Chem. 43 (1999) 267.
[13] (a) D.A. Dougherty, Science. 271 (1996) 163;
(b) D. Sun, V.L. Davidson, Biochemistry. 40 (2001) 12285.
[14] C. Eaborn, N. Retta, J.D. Smith, J. Chem. Soc., Dalton Trans. (1983) 905.
[15] J. Knizek, H. Nöth, J. Organomet. Chem. 614–615 (2000) 168.
[16] (a) E. Weiss, G. Sauermann, Angew. Chem., Int. Ed. Engl. 7 (1968) 133;
(b) E. Weiss, G. Sauermann, Chem. Ber. 103 (1970) 265;
(c) C. Eaborn, P.B. Hitchcock, K. Izod, A.J. Jaggar, J.D. Smith, Organometallics 13 (1994) 753.
[17] M.J.S. Gynane, A. Hudson, M.F. Lappert, P.P. Power, H. Goldwhite, J. Chem. Soc. Dalton Trans. (1980) 2428.
[18] (a) SMART and SAINT software for CCD diffractometers; Bruker AXS Inc., Madison, WI, 2004 and 1997;
(b) Sheldrick, G.M. SHELXTL user manual, version 6; Bruker AXS Inc. Madison, WI, 2001.