The first bidentate phosphanylborohydride: Synthesis, structure, and reactivity towards [CpFe(CO)$_2$I]

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Abstract

Deprotonation of the phosphane-borane adduct *rac/meso*-(HP(BH$_3$)(Ph)CH$_2$)$_2$ (**2**) with KH provides facile access to the bidentate phosphanylborohydride *rac/meso*-K$_2$[(P(BH$_3$)(Ph)CH$_2$)$_2$] (**3**). Treatment of **3** with two equivalents of [CpFe(CO)$_2$I] gives the dinuclear complex *rac/meso*-[(CpFe(CO)$_2$)$_2$-μ-(P(BH$_3$)(Ph)CH$_2$)$_2$] (**4**). Single crystals of the pure diastereomers *meso*-**2**, *meso*-**3**(thf)$_4$, and *rac*-**4** have been grown from toluene/pentane, diethyl ether/thf, and benzene/pentane, respectively. The molecular structures of all three compounds have been determined by X-ray crystallography.
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1. Introduction

The ready availability of versatile toolboxes of ligands with smoothly varying electron donor properties is a prerequisite for the rational design of novel homogeneous catalysts. One such toolbox with highly promising potential for development consists of the series of isoelectronic molecules **A**–**C** (Fig. 1) [1–3]. In moving from the generic methyldiorganyl phosphane **A** to the phosphanylborohydride **B**, a BH$_3$ moiety is substituted for the phosphane methyl group. This leaves the central atom unchanged, but results in a negatively charged ligand. In the corresponding silyl compound **C**, the substitution pattern is conserved, but the central phosphorus atom is replaced by silicon, again introducing a negative charge.

Phosphanes **A** have found extensive use as ligands in coordination chemistry [4,5]. Silanides **C**, while not as widespread as phosphanes, are also generating increasing interest as ancillary ligands, because they are strongly electron-releasing and display a pronounced *trans*-effect [6–9].

The chemistry of phosphanylborohydrides **B**, in contrast, is still largely undeveloped [1–3,10–15].

Our group has recently assessed the relative Lewis basicities of [P(BH$_3$)Ph$_2$]$^-$ and P(CH$_3$)Ph$_2$ with respect to the main group Lewis acids H$^+$, CH$_3^+$ and BH$_3$. Based on NMR spectroscopy, X-ray crystal structure analyses and displacement experiments, we came to the conclusion that the phosphanylborohydride [P(BH$_3$)Ph$_2$]$^-$ forms dative bonds of higher *p* character, is thus better suited to direct its electron lone pair towards the acceptor orbital of the coordinated Lewis acid and consequently forms more stable σ adducts than its neutral counterpart P(CH$_3$)Ph$_2$ [1]. A similar picture was obtained from a study of the chalcogenated phosphanylborohydrides K[EP(BH$_3$)R$_2$] (E = O–Te; R = Ph, *t*Bu), for which a certain degree of E=P multiple-bond character has to be assumed [2]. For example, the tellurium derivative K[TeP(BH$_3$)Ph$_2$] is isolable in good yield whereas from a THF solution of P(CH$_3$)Ph$_2$ and Te$_\infty$ compound TeP(CH$_3$)Ph$_2$ forms only in trace amounts in a dynamic equilibrium. Moreover, the reaction between K[P(BH$_3$)Ph$_2$] and EP(CH$_3$)Ph$_2$ (E = S, Se) resulted in the quantitative formation of K[EP(BH$_3$)Ph$_2$] and P(CH$_3$)Ph$_2$. In a subsequent study [3], we have investigated the complexes [CpFe(CO)$_2$–P(CH$_3$)Ph$_2$]$^+$, [CpFe(CO)$_2$–P(BH$_3$)Ph$_2$],

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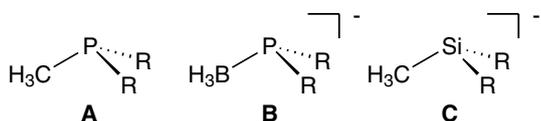Fig. 1. A series of isoelectronic ligands: Phosphanes (**A**), phosphanyl-borohydrides (**B**), and silanides (**C**).

and [CpFe(CO)$_2$–Si(CH$_3$)Ph$_2$] in order to quantify the ligand-to-metal charge transfer, using the ^{13}C-NMR shifts of the cyclopentadienyl rings and the carbonyl ligands as well as the CO IR stretching frequencies as diagnostic tools. Our results clearly show that phosphanes are the weakest donors, silanides are the strongest donors and the gap between them is nicely filled by the phosphanyl-borohydrides.

Notwithstanding the encouraging perspectives, one has to face the fact that silanide as well as phosphanylborohy-dride complexes tend to be significantly less stable than phosphane complexes. Possible decomposition pathways include one-electron reduction processes ([SiR$_3$]$^-$) or hydride transfer from boron to the metal atom ([P(BH$_3$)R$_2$]$^-$) [3]. The unwanted cleavage of the metal–silicon bond in silanide complexes has been suppressed by the introduction of a chelating ether into the ligand molecule (e.g. [R$_2$Si–(CH$_2$)$_n$–PR$_2'$]$^-$; $n = 1, 2$) [9]. Corresponding coordination compounds are readily accessible upon treatment of appropriate metal complex fragments with R$_2$(H)Si–(CH$_2$)$_n$–PR$_2'$. The reaction occurs via binding of the phosphane moiety and subsequent oxidative addition of the Si–H bond.

We suggest adopting a similar strategy for the stabilization of phosphanylborohydride complexes. To this end, we require either (phosphanoalkyl)phosphanylborohydrides [R(H$_3$B)P–(CH$_2$)$_n$–PR$_2'$]$^-$ or bidentate phosphanylborohy-dride ligands [R(H$_3$B)P–(CH$_2$)$_n$–P(BH$_3$)R]$^{2-}$.

The purpose of this paper is to describe the preparation of the potentially bidentate donor molecule K$_2$-[(P(BH$_3$)(Ph)CH$_2$)$_2$] (**3**)[16] (Scheme 1) along with the full characterization of the phosphane-borane adduct (HP(BH$_3$)-(Ph)CH$_2$)$_2$ (**2**). The latter molecule not only serves as the precursor of **3**, but may also be employed directly for metal complexation via the oxidative addition of its H–P bonds [13]. Moreover, we will report the results of salt metathesis reactions between **3** and the iron carbonyl complex [CpFe-(CO)$_2$I] (**4**; Scheme 1).

2. Results and discussion

2.1. Synthesis and spectroscopical characterization

Note: Pure diastereomers will be designated as *rac* or *meso* whereas mixtures of diastereomers will not explicitly be designated as *rac/meso*.

Treatment of (HP(Ph)CH$_2$)$_2$ (**1**) with a solution of BH$_3$ · thf in thf yields the borane adduct (HP(BH$_3$)-(Ph)CH$_2$)$_2$ (**2**; Scheme 1). The pure diastereomer *meso*-**2**
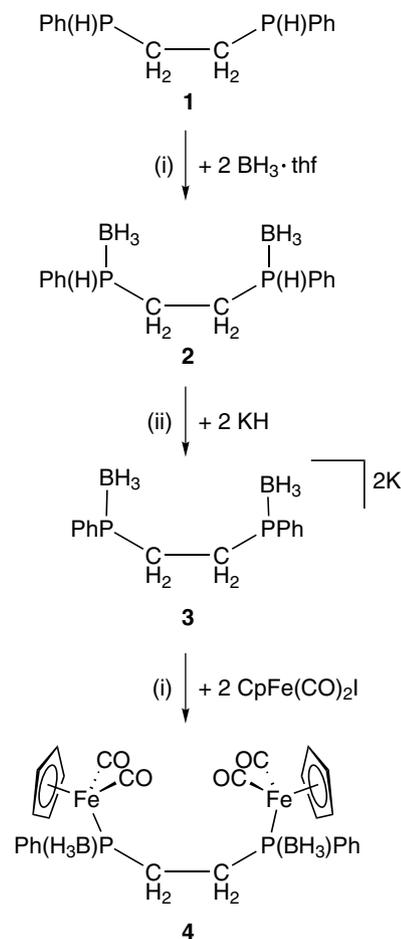
Scheme 1. Synthesis of the phosphane-borane adduct **2**, the corresponding bidentate phosphanylborohydride **3**, and the dinuclear iron complex **4**. (i) −78 °C to rt, thf; (ii) 0 °C to rt, thf.

was isolated after repeated recrystallization of **2** from toluene/pentane in 26% yield. Compound **2** is readily deprotonated by KH in thf to give the bidentate phosphanylborohydride K$_2$[(P(BH$_3$)(Ph)CH$_2$)$_2$] (**3**). Single crystals grown by gas-phase diffusion of diethyl ether into a solution of **3** in thf consisted exclusively of the *meso*-diastereomer *meso*-**3**(thf)$_4$. The dinuclear iron complex **4** (Scheme 1) is obtained by addition of a solution of **3** in thf to a solution of [CpFe(CO)$_2$I] (2 equiv.) in thf at −78 °C. Recrystallization of **4** from benzene/pentane gave single crystals of *rac*-**4**. Attempts to synthesize the corresponding mononuclear iron complex [CpFe(CO)-η^2-(P(BH$_3$)(Ph)CH$_2$)$_2$] with a chelating phosphanylborohydride ligand from 1 equiv. of [CpFe(CO)$_2$I] and 1 equiv. of **3** under similar conditions resulted in a complex mixture of various unidentifiable boron- and phosphorus-containing products. Addition of 18-crown-6 to the reaction mixture and layering with diethyl ether led to the deposition of a small number of red crystals. An X-ray crystal structure analysis revealed cations [{K(18-c-6)}$_2$-µ:η^5-C$_5$H$_5$]$^+$ together with [CpFe-(CO)$_2$]$^-$ anions [17]. It is important to note in this context that chelate complexes [CpFe(CO)-η^2-dppe]$^+$ are well-known for the neutral diphosphane ligand (P(Ph)$_2$CH$_2$)$_2$

(dppe) [18–27]. A special feature of our ligand **3** that could be responsible for the fact that **3** does not readily adopt a chelating coordination mode, is its reducing power [3]. Liu et al. have recently demonstrated that the reaction of [CpFe(CO)$_2$I] and dppe selectively leads to the bridged complexes [(CpFe(CO)$_2$)$_2$-μ-dppe]I$_2$ when [Cp$_2$Co] or dilute MeLi are present as redox catalysts (17e–19e pathway) [28]. Electron-transfer chain processes thus appear to suppress the formation of the chelate complex [CpFe(CO)-η^2-dppe]I, and a similar effect may be operative also in our case.

The ^{11}B{^{1}H} NMR spectrum of *meso*-**2** is characterized by a resonance at −41.6 ppm, testifying to the presence of tetracoordinated boron nuclei [29]. Upon deprotonation, the signal is shifted by 10.8 ppm to lower field (**3**: δ(^{11}B) = −30.8). A similar effect has been observed in the case of HP(BH$_3$)Ph$_2$ (δ(^{11}B) = −40.0) [1] as compared to K[P(BH$_3$)Ph$_2$] (δ(^{11}B) = −30.1) [2]. No significant further shift of the ^{11}B resonance occurs upon formation of the dinuclear iron complex *rac*-**4** (δ(^{11}B) = −30.9; cf. [CpFe(CO)$_2$–P(BH$_3$)Ph$_2$]: δ(^{11}B) = −28.0 [3]).

In contrast to the ^{11}B nuclei, the ^{31}P nuclei are less shielded in *meso*-**2** (δ(^{31}P) = −2.1) than in **3** (δ(^{31}P) = −49.2; cf. PMe$_2$Ph: δ(^{31}P) = −47.6[30]). The chemical shift of −49.2 ppm represents the mean value of two signals at −48.7 ppm and −49.7 ppm (intensity ratio 1:1) which arise from *rac*- and *meso*-**3**. Interestingly, this ^{31}P NMR spectrum is obtained irrespective of whether *rac/meso*-**2** or *meso*-**2** are used in the deprotonation reaction. The fact that enantiomerically pure phosphanylborohydrides can racemize in solution already within 5 min at rt is well documented [31]. Imamoto et al. reported evidence that race-

mization does not occur via borane transfer but rather via pyramidal inversion [31]. In our special case, however, borane transfer would be an intramolecular rather than an intermolecular process making it a potentially competitive racemization pathway that should not be excluded from consideration. Iron complexation leads to a shift of the ^{31}P resonance back to lower field (*rac*-**4**: δ(^{31}P) = 29.4). This trend qualitatively agrees with the development of the ^{31}P chemical shifts along the series HP(BH$_3$)Ph$_2$, K[P(BH$_3$)Ph$_2$], and [CpFe(CO)$_2$–P(BH$_3$)Ph$_2$] (1.7 ppm [1], −28.8 ppm [2], 34.3 ppm [3], respectively).

None of the ^{11}B/^{31}P NMR signals is sufficiently well resolved to determine the $^1J_{BP}$ coupling constants.

All ^{1}H- and ^{13}C NMR signals of *meso*-**2**, **3**, and *rac*-**4** appear in the expected regions. Importantly, the CO carbon nuclei of *rac*-**4** give rise to two signals in the ^{13}C NMR spectrum (δ(^{13}C) = 213.2, 213.3). This is a result of the presence of the chiral phosphanylborohydride ligand which renders the two CO molecules of each CpFe(CO)$_2$ fragment diastereotopic.

The IR spectrum of *rac*-**4** is characterized by two carbonyl stretching frequencies at $\tilde{v}$ = 2027, 1978 cm^{-1} (cf. [CpFe(CO)$_2$–P(BH$_3$)Ph$_2$]: $\tilde{v}$ = 2030, 1982 cm^{-1} [3]).

2.2. X-ray crystal structure determinations

Details of the X-ray crystal structure analyses of *meso*-**2**, *meso*-**3**(thf)$_4$, and *rac*-**4** are summarized in Table 1.

The borane adduct *meso*-**2** (Fig. 2) possesses crystallographically imposed inversion symmetry. The P–B (1.923(2) Å) and P–C(phenyl) bond lengths (1.817(1) Å) of *meso*-**2** are in good agreement with the corresponding

Table 1
Selected crystallographic data of *meso*-**2**, *meso*-**3**(thf)$_4$, and *rac*-**4**

|	*meso*-**2**	*meso*-**3**(thf)$_4$	*rac*-**4**
Formula	C$_{14}$H$_{22}$B$_2$P$_2$	C$_{30}$H$_{52}$B$_2$K$_2$O$_4$P$_2$	C$_{28}$H$_{30}$B$_2$Fe$_2$O$_4$P$_2$ × C$_6$H$_6$
F_w	273.88	638.48	703.89
Color, shape	Colorless, plate	Colorless, block	Yellow, rod
Temperature (K)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	8.7354(7)	15.154(2)	9.4084(6)
b (Å)	9.8498(6)	7.9144(13)	14.4270(9)
c (Å)	9.7027(8)	16.439(3)	14.6089(9)
α (°)	90	90	106.626(5)
β (°)	95.606(7)	111.232(11)	107.000(5)
γ (°)	90	90	97.300(5)
V (Å^3)	830.85(11)	1837.8(5)	1768.32(19)
Z	2	2	2
$D_{calcd.}$ (g cm^{-3})	1.095	1.154	1.322
$F(000)$	292	684	728
μ (mm^{-1})	0.243	0.374	0.945
Crystal size (mm)	0.50 × 0.46 × 0.26	0.12 × 0.08 × 0.06	0.24 × 0.11 × 0.10
Reflections collected	16030	11836	27772
Independent reflections (R_{int})	1829 (0.0474)	3351 (0.1418)	6602 (0.0377)
Data/restraints/parameters	1829/0/87	3351/0/183	6602/18/491
Goodness-of-fit on F^2	1.091	0.893	1.034
R_1, wR_2 ($I > 2\sigma(I)$)	0.0306, 0.0849	0.0802, 0.1234	0.0257, 0.0622
R_1, wR_2 (all data)	0.0315, 0.0858	0.1982, 0.1588	0.0308, 0.0643
Largest difference in peak and hole (e Å^{-3})	0.245 and −0.251	0.295 and −0.432	0.243 and −0.271
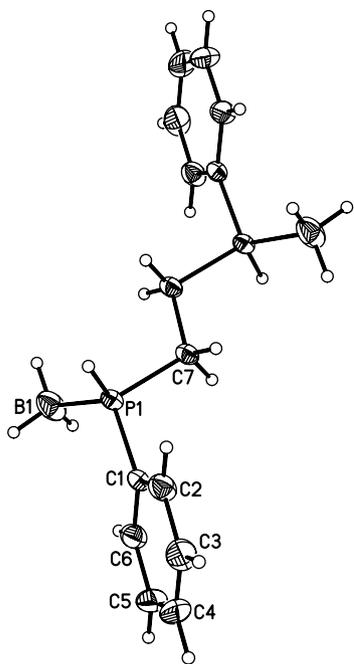
Fig. 2. Molecular structure of *meso*-**2** in the crystal. Selected bond lengths (Å) and bond angles (°): P(1)–B(1) = 1.923(2), P(1)–C(1) = 1.817(1), P(1)–C(7) = 1.832(1); B(1)–P(1)–C(1) = 115.0(1), B(1)–P(1)–C(7) = 114.9(1), C(1)–P(1)–C(7) = 106.5(1). Symmetry transformation used to generate equivalent atoms: −x + 1, −y + 1, −z.

values in the related adduct K(18-crown-6)[(BH₃)₂PPh₂] (P–B = 1.930(2) Å/1.940(2) Å; P–C(phenyl) = 1.829(2) Å/ 1.831(2) Å) [1]. In line with Bent's rule, [32] the C–P–C angle of 106.5(1)° in *meso*-**2** is significantly smaller than the two B–P–C bond angles (114.9(1)°, 115.0(1)°).

The phosphanylborohydride *meso*-**3** crystallizes with four thf ligands that are coordinated to its K⁺ ions

(*meso*-**3**(thf)₄; Fig. 3). Moreover, each K⁺ ion establishes short K–B distances to two adjacent anionic moieties (K(1)–B(1)#1 = 3.058(7) Å, K(1)–B(1)#2 = 3.136(8) Å). Each BH₃ group in turn binds to two K⁺ ions such that a polymeric structure is formed in the solid state. Metal–boron distances are a well-established measure of the denticity of borohydride groups [33]. Addition of the ionic radii of bidentate (1.6 ± 0.1 Å [33]) and tridentate borohydride ligands (1.36 ± 0.06 Å [33]) to the ionic radius of K⁺ (1.65 Å [34]) results in K–B distances of 3.25 Å and 3.01 Å for bi- and tridentate coordination modes, respectively. An inspection of the crystal structure of *meso*-**3**(thf)₄ leads to the conclusion that the shorter K–B distance of 3.058(7) Å indeed corresponds to an η³ bonded borohydride ligand. Since the position of the K⁺ ion relative to the second H₃BPR₂ ligand precludes an η³ coordination, this interaction is best described as η² (K–B = 3.136(8) Å). The P–B bonds (1.983(7) Å) as well as the P–C bonds (1.871(6) Å, 1.843(6) Å) in *meso*-**3**(thf)₄ are significantly longer and the corresponding bond angles smaller than in the protonated derivative *meso*-**2**. This observation can easily be rationalized on the basis of fundamental orbital hybridization arguments according to which atomic *s* character concentrates in orbitals representing an electron lone pair [32]. As a consequence, the P–B and P–C bonds in *meso*-**3**(thf)₄ have a higher degree of *p* character than the analogous bonds in *meso*-**2**.

The crystal structure analysis of *rac*-**4** provides conclusive evidence that the compound is indeed a dinuclear iron complex with a bridging phosphanylborohydride ligand rather than a mononuclear chelate complex (Fig. 4). The two Fe–P bond lengths of *rac*-**4** (2.271(1) Å, 2.275(1) Å) are identical to the Fe–P bond length of [CpFe(CO)₂–P(BH₃)Ph₂] (2.271(1) Å [3]). Even the conformations of
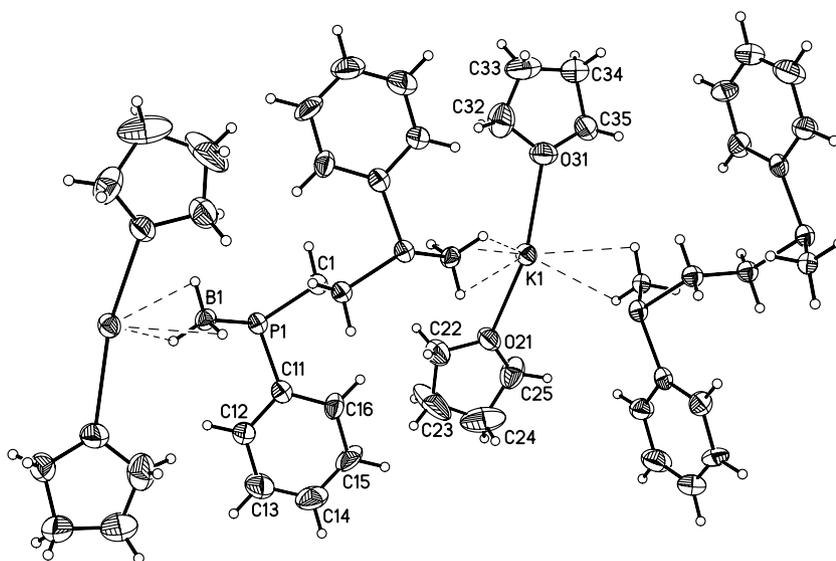

Fig. 3. Molecular structure of *meso*-**3**(thf)₄ in the crystal (only part of the polymeric structure is shown). Selected bond lengths (Å), atom-atom distances (Å), and bond angles (°): P(1)–B(1) = 1.983(7), P(1)–C(1) = 1.871(6), P(1)–C(11) = 1.843(6), K(1)–B(1)#1 = 3.058(7), K(1)–B(1)#2 = 3.136(8); B(1)–P(1)–C(1) = 106.6(3), B(1)–P(1)–C(11) = 104.3(3), C(1)–P(1)–C(11) = 103.0(3), O(21)–K(1)–O(31) = 160.9(2). Symmetry transformations used to generate equivalent atoms: #1: x, y + 1, z; #2: −x + 3/2, y + 1/2, −z + 3/2.
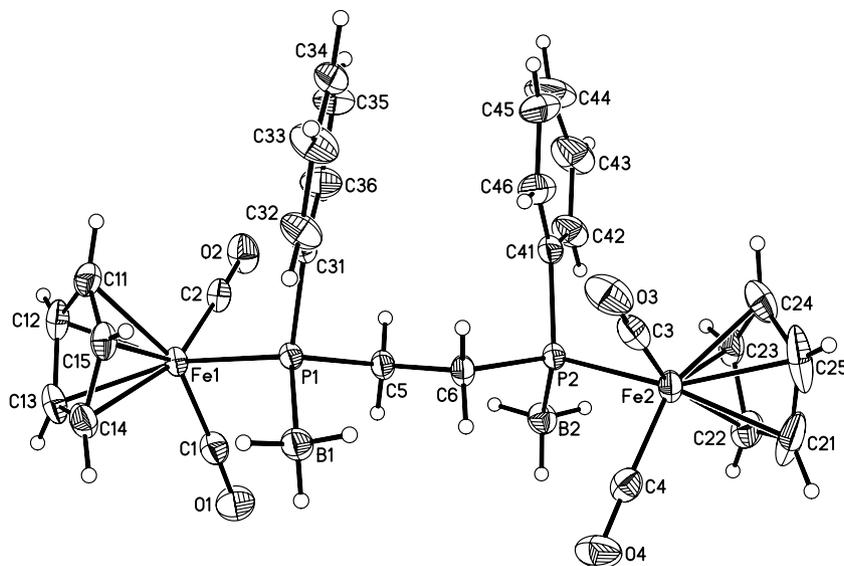
Fig. 4. Molecular structure of *rac*-**4** in the crystal. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): P(1)–Fe(1) = 2.275(1), P(2)–Fe(2) = 2.271(1), P(1)–B(1) = 1.955(2), P(2)–B(2) = 1.948(2), P(1)–C(5) = 1.853(2), P(2)–C(6) = 1.851(2), P(1)–C(31) = 1.840(2), P(2)–C(41) = 1.838(2); B(1)–P(1)–C(5) = 108.3(1), B(2)–P(2)–C(6) = 109.5(1), B(1)–P(1)–C(31) = 111.0(1), B(2)–P(2)–C(41) = 111.8(1), C(5)–P(1)–C(31) = 101.0(1), C(6)–P(2)–C(41) = 102.8(1), B(1)–P(1)–Fe(1) = 114.2(1), B(2)–P(2)–Fe(2) = 114.1(1), C(5)–P(1)–Fe(1) = 111.6(1), C(31)–P(1)–Fe(1) = 109.9(1), C(41)–P(2)–Fe(2) = 109.9(1); P(1)–C(5)–C(6)–P(2) = −166.9(1).

the [CpFe(CO)$_2$–P(BH$_3$)Ph] fragments are the same in both complexes.

3. Conclusion

The bidentate phosphanylborohydride K$_2$[(P(BH$_3$)-(Ph)CH$_2$)$_2$] (**3**) forms upon deprotonation of the corresponding phosphane-borane adduct (HP(BH$_3$)(Ph)CH$_2$)$_2$ (**2**) with KH in a clean and quantitative reaction. A 1:1 mixture of *rac*- and *meso*-**3** is obtained even when diasteriomerically pure *meso*-**2** is employed. This leads to the conclusion that **3** readily racemizes either via pyramidal inversion or via reversible BH$_3$ transfer between the two phosphorus donor sites. Treatment of **3** with two equiv. of [CpFe(CO)$_2$I] gives the dinuclear complex [(CpFe(CO)$_2$)$_2$-μ-(P(BH$_3$)(Ph)CH$_2$)$_2$] (**4**). Attempts at synthesising a corresponding mononuclear compound with chelating phosphanylborohydride ligand led to complex mixtures of decomposition products. One possible solution of this problem would be to replace the highly reactive dianionic ligand [(P(BH$_3$)(Ph)CH$_2$)$_2$]$^{2-}$ by the bidentate molecules Ph(H$_3$B)(H)P–(CH$_2$)$_2$–PPh$_2$ or (HP(BH$_3$)(Ph)CH$_2$)$_2$ (**2**) which could be introduced into the coordination sphere of transition metal ions via an oxidative P–H addition reaction.

4. Experimental

4.1. General considerations

All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were freshly distilled under argon from Na/benzophenone (thf,

diethyl ether, toluene, C$_6$D$_6$) or Na/Pb alloy (pentane, hexane) prior to use. NMR spectra were recorded on Bruker AMX 250, AV 300 or AV 400 spectrometers. ^{1}H- and ^{13}C NMR shifts are reported relative to tetramethylsilane and were referenced against residual solvent peaks (C$_6$D$_5$H: δ = 7.16; C$_6$D$_6$: δ = 128.06; C$_4$D$_7$HO: δ = 1.73, 3.58; C$_4$D$_8$O: δ = 25.3, 67.4). ^{11}B NMR spectra were referenced against external BF$_3$ · OEt$_2$; ^{31}P NMR spectra are reported relative to external H$_3$PO$_4$ (85%). Abbreviations: s = singlet, d = doublet, m = multiplet, br = broad, n.r. = multiplet expected in the NMR spectrum but not resolved, *i* = *ipso*, *o* = *ortho*, *m* = *meta*, *p* = *para*. Elemental analyses were performed by the microanalytical laboratory of the J.W. Goethe-Universität Frankfurt, Germany.

4.2. Materials

Li metal, dppe, BH$_3$ · thf solution (1 mol/L in thf) and [CpFe(CO)$_2$I] were purchased from Aldrich or Fluka and used as received. KH was purchased from Aldrich as a dispersion in mineral oil; prior to use, the oil was washed off with pentane on a Schlenk frit. (HP(Ph)CH$_2$)$_2$ (**1**) was obtained by a modified literature procedure through reductive cleavage of dppe with Li powder in thf and subsequent hydrolysis and distillation [35,36]. (HP(BH$_3$)(Ph)CH$_2$)$_2$ (**2**) has been published by Imamoto et al. [31] We have synthesized **2** via a significantly different route (see below), which we find more convenient.

4.3. Synthesis of (HP(BH$_3$)(Ph)CH$_2$)$_2$ (2)

To a solution of (HP(Ph)CH$_2$)$_2$ (**1**; 3.22 g, 13.08 mmol) in thf (40 mL) was added a calibrated solution of BH$_3$ · thf

in thf (1 mol/L; 26.2 mL, 26.2 mmol) at −78 °C with stirring. After the mixture had warmed to rt overnight, all volatiles were removed in vacuo. The resulting oily residue contained an impurity of HP(BH$_3$)Ph$_2$. The product was purified by column chromatography (90 g silica-gel; eluent: hexane/toluene 1:4, followed by neat toluene; R_f(**2**) = 0.31, R_f(HP(BH$_3$)Ph$_2$) = 0.57). Evaporation of the eluate yielded **2** as a colorless crystalline solid. Yield: 2.36 g (66%). The NMR signals of the two diastereomers of **2** overlap to such an extent that a ratio *rac*:*meso* could not be determined. Repeated recrystallization of **2** from toluene/pentane gave the pure *meso*-diastereomer. Yield of *meso*-**2**: 0.95 g (26%). X-ray quality crystals of *meso*-**2** were obtained by gas-phase diffusion of pentane into a toluene solution of **2**. NMR data of *meso*-**2**: ^{1}H NMR (C$_6$D$_6$, 300.03 MHz): δ = 1.3 (m, 6 H, BH$_3$), 1.69 (n.r., 4 H, CH$_2$) 4.78 (br d, $^1J_{PH}$ = 374 Hz, 2 H, PH), 6.96 (m, 6 H, H-*m*,*p*), 7.33 (m, 4 H, H-*o*).^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.45 MHz): δ = 17.9 (m, CH$_2$), 124.0 (d, $^1J_{PC}$ = 54.0 Hz, C-*i*), 129.2 (m, C-*m*), 131.9 (m, C-*p*), 133.2 (m, C-*o*). ^{11}B{^{1}H} NMR (C$_6$D$_6$, 96.26 MHz): δ = −41.6 (n.r.). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.46 MHz): δ = −2.1 (n.r.). Elemental Anal. Calcd. for C$_{14}$H$_{22}$B$_2$P$_2$ (273.88): C, 61.39; H, 8.10. Found: C, 61.20; H, 7.91%.

4.4. Synthesis of K$_2$[(P(BH$_3$)(Ph)CH$_2$)$_2$] (3)

Solid KH (0.076 g, 1.89 mmol) was added to a solution of (HP(BH$_3$)(Ph)CH$_2$)$_2$ (**2**; 0.241 g, 0.88 mmol) in thf (10 mL) at 0 °C with stirring. After the mixture had warmed to rt overnight, all volatiles were removed in vacuo. The resulting yellowish solid residue was washed with pentane (1 × 10 mL) and thf (1 × 5 mL). The colorless product was dried in vacuo. Yield: 0.288 g (93%) [37]. X-ray quality crystals of *meso*-**3**(thf)$_4$ were obtained by gas-phase diffusion of diethyl ether into a thf solution of **3**. ^{1}H NMR (thf-D$_8$, 400.13 MHz): δ = 0.58 (m, 6 H, BH$_3$), 1.26 (br, 4 H, CH$_2$), 6.76 (m, 2 H, H-*p*), 6.93 (m, 4 H, H-*m*), 7.44 (m, 4 H, H-*o*). ^{13}C{^{1}H} NMR (thf-D$_8$, 100.62 MHz): δ = 122 (n.r., C-*p*), 126 (n.r., C-*m*), 132 (n.r., C-*o*), n.o. (CH$_2$, C-*i*). *Note*: The solubility of **3** is very low even in thf-D$_8$; a decent ^{13}C NMR spectrum was therefore not obtained. ^{11}B{^{1}H} NMR (thf-D$_8$, 128.38 MHz): δ = −30.8 (br). ^{31}P{^{1}H} NMR (thf-D$_8$, 161.98 MHz): δ = −48.7, −49.7 (n.r.).

4.5. Synthesis of [(CpFe(CO)$_2$)$_2$-μ-(P(BH$_3$)(Ph)CH$_2$)$_2$] (4)

A solution of K$_2$[(P(BH$_3$)(Ph)CH$_2$)$_2$] (**3**; 0.165 g, 0.47 mmol) in thf (40 mL) was added to a solution of [CpFe(CO)$_2$I] (0.286 g, 0.94 mmol) in thf (10 mL) at −78 °C with stirring. After the mixture had warmed to rt overnight, all volatiles were removed in vacuo. The resulting brown solid residue was extracted into toluene (10 mL) and the extract was filtered. Pentane (25 mL) was added to the filtrate to precipitate a yellow solid.

Yield: 0.184 g (62%). X-ray quality crystals of *rac*-**4** were obtained by gas-phase diffusion of pentane into a benzene solution of **4**. NMR-data of *rac*-**4**: ^{1}H NMR (C$_6$D$_6$, 400.13 MHz): δ = 2.00 (m, 6 H, BH$_3$), 2.70 (m, 4 H, CH$_2$), 4.07 (s, 10 H, Cp), 7.00 – 7.21 (m, 6 H, H-*m*,*p*), 7.94 (m, 4 H, H-*o*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.45 MHz): δ = 28.4 (d, $^1J_{PC}$ = 11.5 Hz, CH$_2$), 86.4 (n.r., Cp), 128.5 (m, C-*m*), 129.3 (m, C-*p*), 131.9 (m, C-*o*), 140.6 (d, $^1J_{PC}$ = 24.1 Hz, C-*i*), 213.2 (d, $^2J_{PC}$ = 17.9 Hz, CO), 213.3 (d, $^2J_{PC}$ = 19.0 Hz, CO). ^{11}B NMR (C$_6$D$_6$, 128.38 MHz): δ = −30.9 (n.r.). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 161.98 MHz): δ = 29.4 (n.r.). IR (CH$_3$CN): $\tilde{\nu}$ = 2027, 1978 cm^{-1} (CO). Elemental Anal. Calcd. for C$_{28}$H$_{30}$B$_2$Fe$_2$O$_4$P$_2$ (625.78): C, 53.74; H, 4.83. Found: C, 53.74; H, 5.15%.

4.6. X-ray structural characterization

Data collections were performed on a Stoe IPDS-II two circle diffractometer with graphite-monochromated Mo Kα radiation. Empirical absorption corrections with the MULABS option [38] in the program PLATON [39] were performed. Equivalent reflections were averaged. The structures were solved by direct methods [40] and refined with full-matrix least-squares on F^2 using the program SHELXL-97 [41]. Hydrogen atoms bonded to carbon and boron were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. H-atoms bonded to phosphorus were refined isotropically. In the structure of *rac*-**4**, the phenyl ring bonded to P(2) is disordered over two positions with site occupancy factors of 0.649(7) and 0.351(7). The phenyl ring was refined with a restraint to keep the six ring atoms in a common plane. The compound *rac*-**4** crystallizes with 1 equiv. of benzene. Each benzene molecule is disordered over two positions (occupancy factors: 0.61(2)/0.39(2)). Restraints were applied to the benzene ring such that it has similar geometric parameters at both positions.

Appendix A. Supplementary material

CCDC 634049, 634048 and 634050 contain the supplementary crystallographic data for *meso*-**2**, *meso*-**3**(thf)$_4$ and *rac*-**4**. 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.2007.03.006.

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[37] Most of the thf molecules that may be coordinated to the K^+ ions will be removed upon prolonged exposure of the microcrystalline material to a vacuum. Our calculation of the yield of *meso*-**3** is based on the assumption that it contains no residual thf at all.

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