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Synthesis and dehydrocoupling reactivity of iron and ruthenium phosphine–borane complexes†‡

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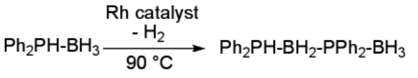
The Fe and Ru phosphine–borane complexes $CpM(CO)_2PPh_2{\cdot}BH_3$ (**1**, M = Fe, **4**, M = Ru) were synthesized utilizing the reaction of the phosphine–borane anion $Li[PPh_2{\cdot}BH_3]$ with the iodo complexes $CpM(CO)_2I$. The Fe complex **1** reacted with PMe_3 to yield $CpFe(CO)(PMe_3)(PPh_2{\cdot}BH_3)$ (**2**) and $CpFe(PMe_3)_2(PPh_2{\cdot}BH_3)$ (**3**) whereas the Ru species **4** gave only $CpRu(CO)(PMe_3)(PPh_2{\cdot}BH_3)$ (**5**). The complexes **1–5** were characterized by ^1H, ^{11}B, ^{13}C and ^{31}P NMR spectroscopy, MS, IR and X-ray crystallography for **1** to **4**, and EA for **1**, **2** and **4**. The reactivity of **1** and **4** towards $PPh_2H{\cdot}BH_3$ was explored. Although no stoichiometric reactions were detected under mild conditions, both **1** and **4** were found to function as dehydrocoupling catalysts to afford $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ in the melt at elevated temperature (120 °C). The carbonyl $Fe_2(CO)_9$ also functioned as a dehydrocoupling catalyst under similar conditions. Complex **1** and $Fe_2(CO)_9$ represent the first reported active Fe complexes for the catalytic dehydrocoupling of phosphine–borane adducts.

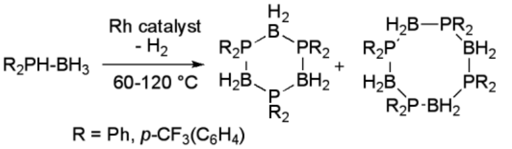
Introduction

Metal-catalyzed dehydrocoupling to form bonds between inorganic elements is emerging as a convenient, mild and versatile synthetic method.[1] Since the initial reports of Si–Si and B–B bond formation *via* catalytic dehydrocoupling in the mid 1980s[2], many other bonds between main group elements have been successfully mediated by transition metal catalysts.[3] Both homo-and heterodehydrocoupling reactions involving main-group hydride species have been demonstrated with early and late transition metal catalysts.[1–3]

The catalytic dehydrocoupling of phosphine–borane and amine–borane adducts has been developed to produce rings, chains and high molecular weight polymers under relatively mild reaction conditions. For example, using Rh catalysts, such processes proceed at 60–120 °C for secondary phosphine–borane adducts such as $Ph_2PH{\cdot}BH_3$.[4] In contrast, in the absence of catalyst, thermal dehydrocoupling of phosphine–borane adducts requires temperatures of 180–200 °C.[5] Dehydrocoupling of primary and secondary phosphine–borane adducts catalyzed by late transition metals has been shown to yield linear oligomeric species, six- and eight-membered rings, and high molecular weight polyphosphinoboranes (eqn (1)–(3)).[4] For example, $PhPH_2{\cdot}BH_3$ can be polymerized using Rh^I complexes at 130 °C whereas in the absence of catalyst only low molecular weight materials are formed (eqn (3)).[4] With electron-withdrawing substituents at phosphorus in the phosphine–borane, the catalytic dehydrocoupling reaction proceeded at 60 °C.[4d] Early and late transition metal-catalyzed dehydrocoupling of primary and secondary amine–borane adducts results in cyclic aminoboranes and borazines under mild reaction conditions (eqn (4) and (5)).[6] This process has been applied to transfer hydrogenation using Rh catalysts and $Me_2NH{\cdot}BH_3$ as a stoichiometric hydrogen source for the hydrogenation of alkenes at 25 °C.[7] Recently, in addition to the Rh, Ir, and Ru catalysts described earlier, other (and in some cases more efficient) metal catalysts for the dehydrocoupling of amine–boranes have been reported as well.[8] The ammonia–borane adduct $NH_3{\cdot}BH_3$ has recently attracted great interest for hydrogen storage applications as a result of possessing one of the highest densities of hydrogen available (*ca.* 20% by weight).[9]



$$Ph_2PH\text{-}BH_3 \xrightarrow[90\ °C]{\text{Rh catalyst}\ -H_2} Ph_2PH\text{-}BH_2\text{-}PPh_2\text{-}BH_3 \qquad (1)$$



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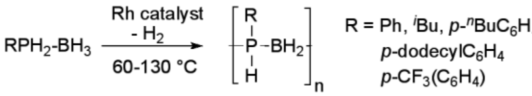

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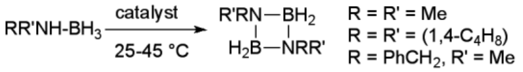

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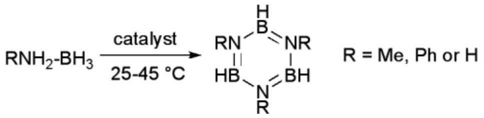

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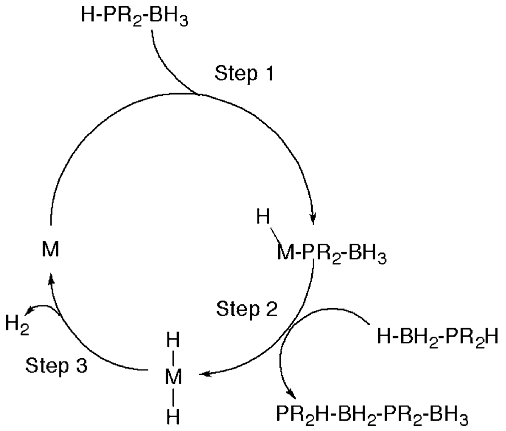
† Dedicated to Prof. Ken Wade on the occasion of his 75th birthday.

‡ Electronic supplementary information (ESI) available: ^1H, $^{13}C\{^1H\}$ and proton-coupled ^{11}B NMR spectra of compound **5** in $CDCl_3$. CCDC reference numbers 670259–670262. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718918d

It has also been reported that $B(C_6F_5)_3$ can catalyze formation of B–P bonds by dehydrocoupling of phosphine–borane adducts at 20 °C; however, the molecular weight of the polymer was low and the reaction time was 3 days.[10]

Mechanistic studies have indicated that the dehydrocoupling of phosphine–borane adducts using $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ involves a homogeneous process whereas that for amine–borane adducts is predominantly heterogeneous.[11] It has also been suggested that the dehydrocoupling of amine–borane adducts involves a key homogeneous catalytic component according to XAFS studies.[12] Further insights into the mechanism of the Rh catalyzed dehydrocoupling of phosphine–borane adducts such as $Ph_2PH{\cdot}BH_3$ can be anticipated from studies of model complexes related to the proposed intermediates in the catalytic cycle. A possible first step in the dehydrocoupling of phosphine–borane adducts may involve insertion of the transition metal into either the P–H or B–H bond of the adduct. The following steps may involve σ-bond metathesis and/or oxidative addition/reductive elimination processes.[13] One of the plausible processes involving initial P–H bond activation is shown in Scheme 1.[14]



Scheme 1

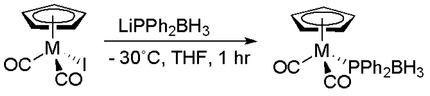
As an illustration of the first step in Scheme 1, we have previously studied the oxidative-addition of the P–H bond in the adducts $RPhPH{\cdot}BH_3$ (R = H or Ph) at Pt(0) centers on addition of $Pt(PEt_3)_3$.[15a] However, upon treatment of the resulting complexes with a further equivalent of adduct, phosphine–borane ligand-exchange reactions rather than dehydrocoupling (step 2 in Scheme 1) were detected at the Pt centre of *cis*-$[PtH(PPh_2{\cdot}BH_3)(depe)]$ (depe = 1,2-bis(diethylphosphino)ethane).[15a] Model complexes such as *cis*-$[PtH(PPhH{\cdot}BH_3)(dcype)]$ (dcype = 1,2-bis(dicyclohexylphosphino)ethane) were also successfully prepared *via* dehydrocoupling reactions between the Pt–H and P–H bonds of *cis*-$[PtH_2(dcype)]$ and $PhPH_2{\cdot}BH_3$, respectively.[15b] The absence of dehydrocoupling reactivity with Pt phosphine–borane complexes[15] has prompted us to explore the corresponding chemistry of other metals. In this paper we describe our analogous studies of Fe and Ru phosphine–borane complexes.

Results and discussion

As step 1 in Scheme 1 involving the oxidative-addition of a P–H bond of a phosphine–borane adduct at a metal center has been amply demonstrated in the case of Pt, in this work we focussed on the subsequent steps. In particular, we were interested in detecting a stoichiometric reaction of a phosphine borane complex with a phosphine–borane adduct (*i.e.* step 2 in Scheme 1) rather than the ligand exchange reactions observed in the case of Pt.[15a] We prepared the Fe and Ru complexes utilized in this study *via* a convenient nucleophilic substitution route. The targeted phosphine–borane complexes were chosen such that the generation of additional vacant coordination sites around the metal *via* ligand dissociation would be possible. This was anticipated to facilitate further reactivity towards phosphine–borane adducts within the metal coordination sphere.

Synthesis of $CpFe(CO)_2PPh_2BH_3$ (1)

The iron phosphine–borane complex $CpFe(CO)_2(PPh_2{\cdot}BH_3)$ (**1**) was targeted to utilize the CO ligands that might dissociate to generate vacant coordination space around the central metal atom to enable subsequent reaction with phosphine–borane adducts. Complex **1** was synthesized by reacting $CpFe(CO)_2I$ and $LiPPh_2{\cdot}BH_3$ at −30 °C in THF for 1 h (eqn (6)). The product **1** was purified by column chromatography and recrystallization from toluene at −40 °C to yield amber crystals (50% yield).



(6)

1: M = Fe
4: M = Ru

Complex **1** was characterized by EA, IR, NMR, MS and X-ray crystallography. The $^{31}P\{^1H\}$ spectrum showed a quartet at δ 31.5 at 60 °C which appears as a broad doublet at 25 °C. The broad signal is characteristic of P bound to B with the broadening arising from unresolved quadrupolar coupling. The $^{11}B\{^1H\}$ NMR spectrum showed a doublet at δ −30.4 ppm ($^1J_{PB} = 45$ Hz). This doublet also resolved better like the broad signal in the $^{31}P\{^1H\}$ NMR spectrum at higher temperature. The ^1H NMR showed multiplets for phenyl resonances around δ 7.75 ppm and δ 7.33 ppm as well as a singlet for the Cp resonance at δ 4.99 ppm and a broad quartet for a boron hydride resonance at δ 1.45 ppm ($^1J_{HB}$ = *ca.* 100 Hz). The IR spectrum showed carbonyl peaks at 2029 and 1980 cm^{-1} which are lower frequency than those for $CpFe(CO)_2I$ at 2037 and 1994 cm^{-1}.[16] This data indicated that the phosphine–borane substituent is more electron donating compared to iodide and increases the back-bonding of the electron density from the Fe centre to the CO ligand. Complex **1** was reported recently by Wagner and co-workers who similarly treated $CpFe(CO)_2I$ with $KPPh_2BH_3$ in THF at −78 °C.[17] The X-ray structure (Fig. 1) is in monoclinic crystal system with a $P2_1/n$ space group whereas Wagner and co-workers reported a structure in orthorhombic crystal system with $P2_12_12_1$ space group. The bond length and bond angle data are comparable for the two structures. The same group also recently reported the first bidentate phosphanylborohydride Fe complex, *rac*/*meso*-$[(CpFe(CO)_2)_2\{\mu\text{-}(P(BH_3)(Ph)CH_2)_2\}]$, using a similar synthetic method.[18]

Reaction of 1 with PMe_3

Next, we explored the reactivity of **1** with PMe_3 in order to examine if the P–B bond was stable to the presence of a strong donor ligand and also to explore if the CO ligands are easy to

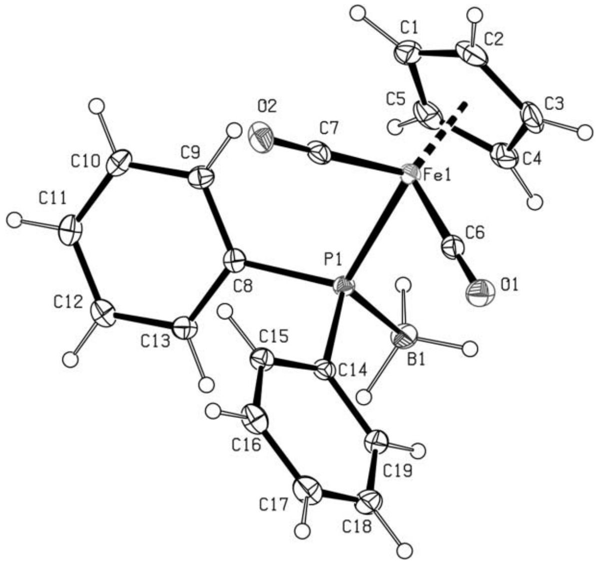
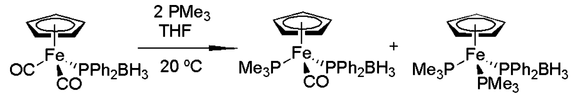


Fig. 1 Molecular structure of $CpFe(CO)_2(PPh_2{\cdot}BH_3)$ **1**. Selected bond lengths (Å) and angles (°): C5–Fe1 2.102(2), C6–O1 1.145(3), C6–Fe1 1.766(2), C7–O2 1.144(3), P1–C8 1.837(2), P1–C14 1.831(2), P1–B1 1.953(3), P1–Fe1 2.2822(6); C6–Fe1–P1 89.22(7), C7–Fe1–P1 92.33(7), C8–P1–C14 101.89(9), C8–P1–B1 107.23(11), C8–P1–Fe1 113.26(7), C14–P1–B1 109.26(11), C14–P1–Fe1 107.58(7).

displace. The latter situation would facilitate further reaction with phosphine–borane adducts at the metal center, as required for step 2 in Scheme 1. Upon the addition of two equivalents of PMe_3 to a THF solution of **1** at 20 °C, the CO-substitution products $CpFe(CO)(PMe_3)(PPh_2{\cdot}BH_3)$ (**2**) and $CpFe(PMe_3)_2(PPh_2{\cdot}BH_3)$ (**3**) were formed (eqn (7)). The $^{31}P\{^1H\}$ NMR spectrum of the reaction solution showed two resonances consistent with these products: a doublet at δ 31.2 and a broad multiplet at δ 26.9 for **2** and a doublet at δ 24.1 and a broad multiplet at δ 18.8 for **3**. Complex **2** was isolated in pure form by column chromatography and recrystallization from THF. Both compounds were characterized by X-ray crystallography (Fig. 2 and 3). The complexes **2** and **3** crystallize in the monoclinic crystal system with *Cc* and $P2_1/n$ space group respectively. The P–B bond length of **2** is not significantly different to that of **1**. However, the P–B bond length of **3** is significantly (0.03 Å) longer than that of **2**. In addition, the Fe–P($Ph_2{\cdot}BH_3$) bond length of **2** and that of **1** are similar whereas the Fe–P($Ph_2{\cdot}BH_3$) bond length of **3** is significantly (0.04 Å) longer.



1 2 3 (7)

Synthesis of $CpRu(CO)_2(PPh_2{\cdot}BH_3)$ (4)

We also attempted to prepare a phosphine–borane complex of Ru analogous to **1**. The compound $CpRu(CO)_2(PPh_2{\cdot}BH_3)$ (**4**) was synthesized analogously to **1** by reacting $CpRu(CO)_2I$ and $LiPPh_2{\cdot}BH_3$ at −30 °C in THF (eqn (6)). This compound was also characterized by EA, IR, NMR, MS and X-ray crystallography. The $^{31}P\{^1H\}$ NMR spectrum showed a quartet at δ 18.7 at 60 °C which had the appearance of a broad doublet at 20 °C. The $^{11}B\{^1H\}$ NMR spectrum showed a doublet at δ −28.5 ppm ($^1J_{PB}$ = 42 Hz).

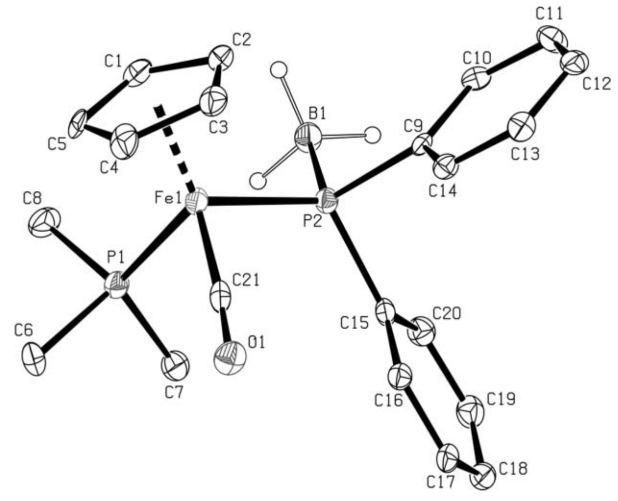


Fig. 2 Molecular structure of $CpFe(CO)(PMe_3)(PPh_2{\cdot}BH_3)$ **2**. Selected bond lengths (Å) and angles (°): C21–Fe1 1.729(5), C21–O1 1.168(5), P1–Fe1 2.2106(13), P2–Fe1 2.2718(12), C21–O1 1.168(5), P2–B1 1.949(5); C21–Fe1–P1 91.95(15), C21–Fe1–P2 98.83(15), P1–Fe1–P2 94.23(5), C9–P2–B1 108.7(2), C9–P2–C15 96.87(18).

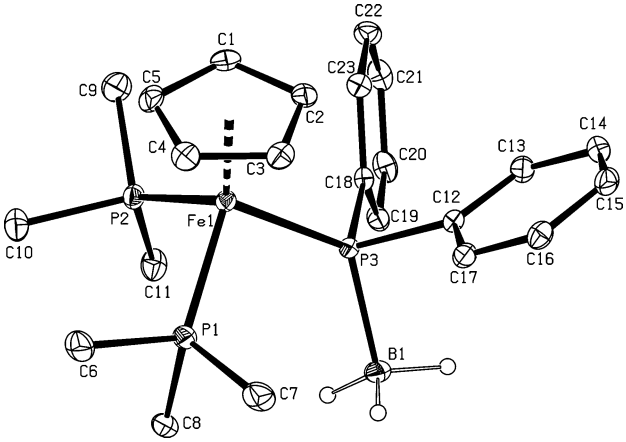


Fig. 3 Molecular structure of $CpFe(PMe_3)_2(PPh_2{\cdot}BH_3)$ **3**. Selected bond lengths (Å) and angles (°) P1–Fe1 2.2124(6), P2–Fe1 2.2160(6), P3–Fe1 2.3119(6), P3–B1 1.980(3); P3–Fe1–P1 94.99(2), P3–Fe1–P2 95.39(2), C18–P3–C12 100.70(9), B1–P3–Fe1 127.34(8).

The ^1H NMR spectrum showed multiplets for phenyl resonances around δ 7.95 ppm and δ 7.10 ppm as well as a singlet for the Cp resonance at δ 4.54 ppm and a broad quartet for the boron hydride resonance at δ 2.39 ppm ($^1J_{HB}$ = *ca.* 100 Hz). The IR spectrum showed carbonyl peaks at 2040 and 1985 cm^{-1} which, as for the case of **1**, are at lower wavenumber than the peaks for $CpRu(CO)_2I$ at 2044 and 1995 cm^{-1}.[16] This is attributed to the more electron donating phosphine–borane ligand. In comparison with the IR data of compound **1** of 2037 and 1994 cm^{-1}, the values were similar. Complex **4** crystallized in the monoclinic crystal system with $P2_1/n$ space group (Fig. 4).

Reaction of 4 with PMe_3

As with the case of Fe complex **1**, the reactivity of **4** with PMe_3 was investigated. Upon the addition of two equivalents of PMe_3 to a THF solution of **4**, $CpRu(CO)(PMe_3)(PPh_2{\cdot}BH_3)$ (**5**) was formed at 20 °C. The product was found to be not as soluble in THF as

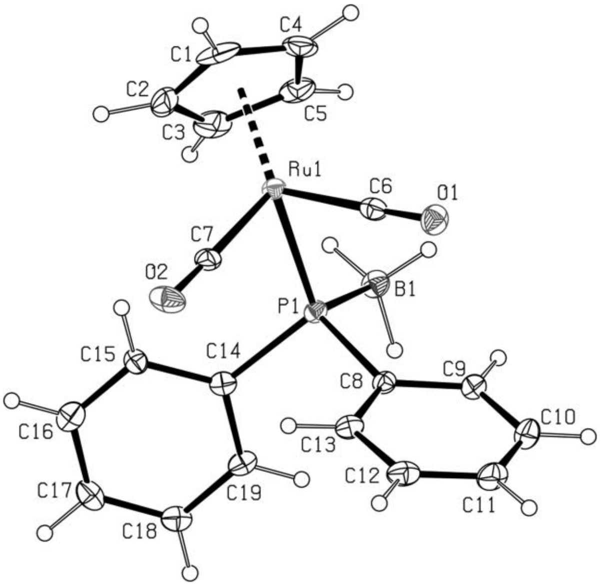


Fig. 4 Molecular structure of CpRu(CO)$_2$(PPh$_2$·BH$_3$) **4**. Selected bond lengths (Å) and angles (°): C5–Ru1 2.251(5), C6–O1 1.150(5), C6–Ru1 1.875(5), C7–O2 1.139(5), P1–C8 1.835(4), P1–C14 1.846(4), P1–B1 1.965(5), P1–Ru1 2.3760(11); C6–Ru1–P1 87.47(13), C7–Ru1–P1 91.51(12), C8–P1–C14 102.28(19), C8–P1–B1 110.0(2), C8–P1–Ru1 108.40(13), C14–P1–B1 107.4(2), C14–P1–Ru1 112.87(14).

CpRu(CO)$_2$(PPh$_2$·BH$_3$), and gradually precipitated out as a white solid. Unlike the reactivity of **1** with PMe$_3$, the bisphosphine Ru analogue of **3** was not detectable. The ^{31}P{^{1}H} NMR spectrum of **5** showed two resonances as expected: a broad multiplet at δ 13.5 and a doublet at δ 9.5. The ^{1}H NMR spectrum resembled that of **4** along with a doublet at δ 1.23 for the PMe$_3$ ligand. The IR peak of 1939 cm^{-1} for complex **5** is at lower frequency than the stretching vibrations at 2039 and 1985 cm^{-1} for complex **4**, consistent with additional back-bonding to the CO moiety due to the electron-donating PMe$_3$ ligand.

Dehydrocoupling reactivity of Fe and Ru complexes 1 and 4 with Ph$_2$PH·BH$_3$

The dehydrocoupling reactivity of complexes **1** and **4** toward Ph$_2$PH·BH$_3$ was explored both in the melt and in solution (Table 1). We have previously shown that the conversion of Ph$_2$PH·BH$_3$ to Ph$_2$PH·BH$_2$·PPh$_2$·BH$_3$ (eqn (8)), is less than 5% at 120 °C in the melt after 15 h (Table 1, entry 3).[4b] In toluene solution at 110 °C the conversion was also very low but was detectable with a value of *ca.* 10% after 15 h by ^{11}B{^{1}H} and ^{31}P{^{1}H} NMR in toluene (entry 1). A significant amount of free PPh$_2$H was also observed.

$$Ph_2PH\text{-}BH_3 \xrightarrow[120\ °C]{-\ H_2} Ph_2PH\text{-}BH_2\text{-}PPh_2\text{-}BH_3 \qquad (8)$$

No stoichiometric reaction was detected between equimolar amounts of **1** and Ph$_2$PH·BH$_3$ in solution at 25 °C. However, on heating the 1 : 1 reaction at 110 °C, Ph$_2$PH·BH$_3$ dehydrocoupled to form Ph$_2$PH·BH$_2$·PPh$_2$·BH$_3$ with 75% conversion after 15 h (Table 1, entry 4). Dehydrocoupling also did not proceed when a solution of Ph$_2$PH·BH$_3$ and **1** (10 mol%) was irradiated by UV, which can often promote CO dissociation (entry 6). When 10 mol% of **1** was used at 110 °C (entry 7), the conversion was only slightly higher than when no complex was added in toluene (entry 1). There was only 5% conversion at 60 °C (entry 8). In contrast, in the absence of solvent, the adduct Ph$_2$PH·BH$_3$ dehydrocoupled to Ph$_2$PH·BH$_2$·PPh$_2$·BH$_3$ with 65% conversion using 1.5 mol% of **1** at 120 °C after 15 h (entry 9) whereas only 5% conversion was noted for the reaction at 60 °C and no conversion was detected at 20 °C (entry 10 and 11).

When the Ru complex **4** was treated with a stoichiometric amount of Ph$_2$PH·BH$_3$ at 110 °C for 4 days in toluene, no

Table 1 Dehydrocoupling of Ph$_2$PH·BH$_3$ to Ph$_2$PH·BH$_2$·PPh$_2$·BH$_3$[a]

Entry	Potential catalyst	Mol%	Solvent	*T*/°C	% Conversion[b]
1	—	—	Toluene	110	10
2	—	—	Toluene	5 (UV)	0
3	—	—	None	120	0[c]
4	**1**	100	Toluene	110	75
5	**1**	25	Toluene	110	50
6	**1**	10	Toluene	5 (UV)	0
7	**1**	10	Toluene	110	20
8	**1**	10	Toluene	60	5
9	**1**	1.5	None	120	65[d]
10	**1**	1.5	None	60	5
11	**1**	1.5	Toluene	20	0
12	**4**	100	Toluene	110	0
13	**4**	1.5	None	120	60[d]
14	Ru$_3$(CO)$_{12}$	1.5	None	120	15[c]
15	Ru/Al$_2$O$_3$	1.5	None	120	5[d]
16	[Rh(μ-Cl)(1,5-cod)]$_2$	1.5	None	90	100[c]
17	[Rh(μ-Cl)(1,5-cod)]$_2$	0.3	THF	5 (UV)	0
18	Fe$_2$(CO)$_9$	10	Toluene	110	10
19	Fe$_2$(CO)$_9$	10	Toluene	60	0
20	Fe$_2$(CO)$_9$	1.5	None	120	80[d]
21	Fe$_2$(CO)$_9$	1.5	None	60	0

[a] A *ca.* 0.10 M solution of PPh$_2$H·BH$_3$ was used where appropriate. [b] After 15 h reaction and estimated by ^{11}B{^{1}H} NMR spectroscopy and averaged from 2 or 3 trials. [c] See ref. 4*b*. [d] These are upper limit estimates due to sublimation effects outlined in the Experimental section. The true values may be *ca.* 10% lower.

dehydrocoupled product was observed (entry 12), but no unreacted $Ph_2PH{\cdot}BH_3$ was detected either. However, when 1.5 mol% of **4** was used without solvent at 120 °C, there was 60% conversion to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ (entry 13). In comparison, with 1.5 mol% of $Ru_3(CO)_{12}$ or Ru/Al_2O_3 under the same conditions, 15 or 5% conversion was observed, respectively (entry 14 and 15).[4b]

For comparative purposes, we explored the use of $Fe_2(CO)_9$ as a catalyst. With 10 mol% of $Fe_2(CO)_9$ in toluene, the dehydrocoupling activity of $Ph_2PH{\cdot}BH_3$ was not significant at 60 or 110 °C (entries 18 and 19), but with 1.5 mol% of $Fe_2(CO)_9$ in the absence of solvent, 80% conversion to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2$ BH_3 was detected at 120 °C (entry 20). No dehydrocoupling activity was detected at 60 °C (entry 21). Interestingly, $Fe_2(CO)_9$ is a better catalyst than $Ru_3(CO)_{12}$ (entries 20 and 14, respectively).

Complex **1** is the first Fe complex that catalyzes the dehydrocoupling of phosphine–borane adducts. The observation that $Fe_2(CO)_9$ also catalyzes the dehydrocoupling reaction shows that compound **1** is not unique among Fe complexes in possessing the catalytic ability to promote the phosphine–borane dehydrocoupling reaction.

Conclusions

The iron phosphine–borane complex $CpFe(CO)_2(PPh_2{\cdot}BH_3)$ (**1**) and the ruthenium analogue $CpRu(CO)_2(PPh_2{\cdot}BH_3)$ (**4**) have been prepared. No stoichiometric P–B bond-formation chemistry was detected on treatment of these complexes with $Ph_2PH{\cdot}BH_3$ under mild conditions despite the observation that CO substitution with PMe_3 is facile. However, at 120 °C in the melt, complexes **1**, **4** and $Fe_2(CO)_9$ were shown to promote the *catalytic* dehydrocoupling of $Ph_2PH{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ Although no clear mechanistic conclusions can be been drawn from the results, complex **1** and $Fe_2(CO)_9$ represent the first Fe dehydrocoupling catalysts for phosphine–borane adducts.

Experimental

General considerations

All air-and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk, and cannula techniques or in an MBraun inert atmosphere drybox containing an atmosphere of Ar. All solvents were dried and distilled prior to use, or vacuum transferred directly from the appropriate drying agent except Et_2O and hexanes which were dried *via* the Grubbs′ method.[19] Deuterated solvents were purchased from Cambridge Isotope Laboratories and then degassed and vacuum-transferred from Na (C_6D_6) or CaH_2 ($CDCl_3$ and CD_2Cl_2) and stored over activated 4Å molecular sieves. $CpRu(CO)_2I$ was synthesized according to published procedures.[20] $CpFe(CO)_2I$, $Fe_2(CO)_9$, $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ and Ru/Al_2O_3 were purchased from Aldrich. $PPh_2H{\cdot}BH_3$ was prepared using a procedure analogous to that used for $PhPH_2{\cdot}BH_3$.[4b] Ph_2PH was purchased from Strem and PMe_3 was purchased from Alfa Aesar.

Photoirradiation experiments were carried out with Pyrex-glass filtered emission from a 125 W medium-pressure mercury lamp (Photochemical Reactors Ltd.). The emission lines of the mercury lamps were as follows: 577–579, 546, 436, 408–405, 366–365, 334, 313, 302, 297, 289, 280, 270, 265, 254 nm (Photochemical Reactors Ltd.).

NMR spectra were recorded at 20 °C on a Delta/GX 270, Eclipse 300/400 and Lambda300 MHz spectrometer unless otherwise indicated. Chemical shifts are reported relative to residual protonated solvent peaks (^1H and ^{13}C) or external $BF_3{\cdot}Et_2O$ (^{11}B) or H_3PO_4 (^{31}P) standards. NMR spectra were obtained at 300 MHz (^1H), 96 MHz (^{11}B) or 75 or 101 MHz (^{13}C). Infrared spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer using KBr windows. Elemental analysis was performed by the Laboratory for Microanalysis, University of Bristol. Mass spectrometry analyses (electron impact (EI) and chemical impact (CI), 70 eV) were carried out on a VG AutoSpec by the Mass Spectrometry service, University of Bristol.

The percentage conversion of $Ph_2PH{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was averaged from two or three trials.

The proton coupled ^{11}B spectra for compounds **1–5** are only partially resolved because they are not completely first-order. Higher temperatures of 35–60 °C showed no significant improvement, therefore, only approximate values of coupling constants are given. A representative spectrum is given in the ESI.‡

X-Ray structural characterization

Diffraction data were collected on a Bruker-Nonius Kappa-CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and were measured using a combination of ϕ scans and ω scans with κ offsets, to fill the Ewald sphere. The data were integrated and scaled using the Denzo-SMN package.[21] Absorption corrections were carried out using SORTAV.[22] The structures were solved and refined with the SHELXTL V6.13 software package.[23] Refinement was by full-matrix least squares on F^2 using all data (negative intensities included). Molecular structures are presented with thermal ellipsoids at a 30% probability level and most hydrogen atoms attached to carbon are omitted for clarity. In all structures, hydrogen atoms bonded to carbon were included in calculated positions and treated as riding atoms, whereas those attached to boron or nitrogen were located and refined with isotropic thermal parameters. Crystallographic data for the compounds is given in Table 2.

Synthesis of $CpFe(CO)_2(PPh_2{\cdot}BH_3)$ (1). The complex $CpFe(CO)_2I$ (1.000 g, 3.29 mmol) was dissolved in 30 mL THF in a round-bottom Schlenk flask and cooled to −30 °C. A similarly chilled (−30 °C) $LiPPh_2{\cdot}BH_3$ (23 mL, 0.149 M in THF) was added dropwise. The reaction temperature was maintained between −30 and −20 °C for 1.5 h, and then the volatile components of the reaction mixture were removed *in vacuo* to obtain burgundy oil. The product was chromatographed on silica (2 × 5 cm) supported on a medium porosity frit with diethyl ether (250 mL) to obtain a yellowish brown eluant. The solution volume was reduced to 50 mL *in vacuo* and the product crystallized at −40 °C for 2 days, affording amber yellow crystals (0.615 g, 50% yield) of **1**. In the case of having obtained only sticky brown crystals, these can be redissolved into Et_2O and chromatographed again on silica and recrystallized as described above to yield yellow crystals. Alternatively, the work-up can also be performed in toluene instead of Et_2O.

IR (Toluene): 2029 (s, CO), 1980 (s, CO) cm^{-1}.

IR (THF): 2028 (s, CO), 1978 (s, CO) cm^{-1}.

Table 2 Crystallographic data for **1**, **2**, **3** and **4**

	1	**2**	**3**	**4**
Empirical formula	$C_{19}H_{18}BFeO_2P$	$C_{21}H_{27}BFeOP_2$	$C_{23}H_{36}BFeP_3$	$C_{19}H_{18}BO_2PRu$
M_r	375.96	424.03	472.09	421.18
T/K	150(2)	150(2)	150(2)	150(1)
$\lambda/Å$	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	Cc	$P2_1/n$	$P2_1/n$
$a/Å$	13.1693(3)	15.5704(6)	9.6143(2)	13.4151(5)
$b/Å$	9.8830(4)	9.2138(4)	13.9049(2)	9.7058(3)
$c/Å$	13.8078(5)	15.2599(7)	18.1670(4)	14.0420(5)
$\beta/°$	102.900(2)	107.608(3)	90.5310(11)	101.7740(19)
$V Å^3$	1751.76(10)	2086.66(15)	2428.57(8)	1789.86(11)
Z	4	4	4	4
$D_c/g\ cm^{-3}$	1.426	1.350	1.291	1.563
μ/mm^{-1}	0.959	0.883	0.826	0.972
$F(000)$	776	888	1000	848
Crystal size/mm^3	0.30 × 0.26 × 0.18	0.10 × 0.09 × 0.08	0.28 × 0.26 × 0.24	0.30 × 0.30 × 0.14
θ Range for data collection/°	2.56–27.50	2.60–27.47	2.58–27.50	2.57–27.52
Index ranges, *hkl*	−17 to 17, −12 to 12, −17 to 17	−19 to 18, −11 to 11, −19 to 16	−12 to 12, −17 to 17, −16 to 23	−17 to 17, −11 to 12, −18 to 18
Reflections collected	12104	10243	13404	11118
Independent reflections	3982 ($R_{int} = 0.0538$)	3898 ($R_{int} = 0.0697$)	5489 ($R_{int} = 0.0369$)	4085 ($R_{int} = 0.0442$)
Completeness to $\theta = 27.50°$ (%)	99.1	99.5	99.1	99.1
Max., min. transmission	0.847, 0.644	0.935, 0.802	0.825, 0.735	0.874, 0.803
Data/restraints/parameters	3982/0/229	3898/12/250	5489/0/271	4085/0/230
Goodness-of-fit on F^2	1.044	1.042	1.039	1.086
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0377$, $wR2 = 0.0943$	$R1 = 0.0443$, $wR2 = 0.0774$	$R1 = 0.0375$, $wR2 = 0.0879$	$R1 = 0.0395$, $wR2 = 0.0889$
R Indices (all data)	$R1 = 0.0518$, $wR2 = 0.1033$	$R1 = 0.0733$, $wR2 = 0.0886$	$R1 = 0.0566$, $wR2 = 0.0983$	$R1 = 0.0638$, $wR2 = 0.1168$
Absolute structure parameter	—	−0.02(2)	—	0.0033(7)
$\Delta\rho/e\ Å^{-3}$	0.413, −0.574	0.706, −0.497	0.529, −0.367	1.730, −1.551

Absorption correction: semi-empirical from equivalents; refinement method: full-matrix least-squares on F^2.

MS (CI, *m/z*): 375 (M^+, 13%), 347 ($M^+ - CO$, 10%), 79 (C_6H_7, 100%).

^1H NMR (300 MHz, $CDCl_3$): δ 7.69–7.75 (m, 4 H, Ph), 7.33–7.37 (m, 6H, Ph), 4.99 (s, 5H, Cp), 1.45 (br q, 3H, BH_3, $^1J_{HB}$ = *ca.* 100 Hz)

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 31.5 (br q, $^1J_{PB}$ = *ca.* 45 Hz, coupling is clearer at 60 °C)

$^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −30.4 (d, $^1J_{PB}$ = *ca.* 45 Hz).

^{11}B NMR (96 MHz, THF): δ−29.6 (br partially resolved q of d, at 50 °C, $^1J_{HB}$ = *ca.* 100 Hz, $^1J_{PB}$ = *ca.* 45 Hz).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 212.5 (d, CO, $^2J_{CP} = 18$ Hz), 139.01 (d, Ph, $J_{CP} = 29$ Hz), 132.6 (d, Ph, $J_{CP} = 8$ Hz), 129.1 (d, Ph, $J_{CP} = 2$ Hz), 128.0 (d, Ph, $J_{CP} = 9$ Hz), 86.8 (s, Cp).

Anal. Calc. for $C_{19}H_{18}O_2PBFe$: C, 60.71; H, 4.82. Found: C, 60.57; H, 4.72%.

Synthesis of $CpFe(CO)(PMe_3)(PPh_2BH_3)$ (2). Complex **1** (300 mg, 0.798 mmol) was dissolved in 1.8 mL THF in a round-bottom Schlenk flask. PMe_3 (82 µL, 0.798 mmol) was added to the solution which was stirred at 20 °C and monitored by ^{11}B and ^{31}P NMR. The pale yellow solution turned orange. After 2 days, the volatile components of the reaction mixture were removed *in vacuo* overnight. The product was chromatographed on silica (0.5 × 5 cm) with hexanes, Et_2O and then THF. The orange solutions were recrystallized at −40 °C for 15 days, affording orange crystals of **2** which were of X-ray quality. Only the crystals obtained from the THF eluant were pure with a yield of 41 mg (12% yield).

IR (THF): 1928 (s, CO) cm^{-1}.

HR-MS (CI): 423.0902 (M^+) − $1H^-$, 100%, calc. mass for $C_{21}H_{26}{}^{11}B^{56}FeO_1P_2$ 423.0901.

^1H NMR (300 MHz, $CDCl_3$): δ 7.17–8.03 (m, 10 H, Ph), 4.63 (m, 5H, Cp), 1.43 (q, 3H, BH_3, $^1J_{HB}$ = *ca.* 80 Hz), 1.13 (d, 9H, PMe_3, $^2J_{PH} = 9.0$ Hz).

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 31.2 (d, $^2J_{pp}$ = 43 Hz, PMe_3), 26.9 (br m, PPh_2BH_3)

$^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −31.5 (d, $^1J_{PB}$ = *ca.* 55 Hz).

^{11}B NMR (96 MHz, $CDCl_3$): δ −31.4 (br partially resolved q of d, at 60 °C, $^1J_{HB}$ = *ca.* 90 Hz, $^1J_{PB}$ = *ca.* 55 Hz).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 218.1 (dd, CO, $^2J_{CP}$ = 33, 20 Hz), 141.5 (m, *ipso*-C of Ph), 132.0 (m, Ph), 126.7 (m, Ph), 126.4 (m, Ph, J_{CP} = *ca.* 10 Hz), 83.9 (s, Cp), 19.3 (d, PMe_3, $^1J_{CP}$ = 30 Hz).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 219.9 (dd, CO, $^2J_{CP}$ = 33, 20 Hz), 143.5 (m, *ipso*-C of Ph), 133.7 (m, Ph), 128.3 (dd, Ph, J_{CP} = 11, 2 Hz), 127.9 (m, Ph, J_{CP} = 12, 8 Hz), 85.1 (s, Cp), 20.0 (d, PMe_3, $^1J_{CP}$ = 30 Hz).

Anal. Calc. for $C_{21}H_{27}OP_2BFe$: C, 59.48; H, 6.42. Found: C, 59.01; H, 5.99%.

Synthesis of $CpFe(PMe_3)_2(PPh_2BH_3)$ (3). Complex **1** (100 mg, 0.266 mmol) was dissolved in 1.8 mL THF in a round bottom Schlenk flask. PMe_3 (55 µL, 0.53 mmol) was added to the solution which was stirred at 20 °C and monitored by ^{11}B and ^{31}P NMR. The pale yellow solution turned orange. After 15 days, the volatile components of the reaction mixture were removed *in vacuo* overnight. The product was washed by filtering through Celite supported on glass wool with Et_2O to yield an orange solution.

The solution was recrystallized at −40 °C for 15 days, affording red needles of **3** and orange crystals of **2**.

Despite the fact that compound **3** crystallizes out in Et_2O along with **2** and that the red needles of **3** were hand-picked, on dissolution the red needles were still found to be contaminated with the residue of **2**, as detected by NMR spectroscopy. Other methods of purification such as silica chromatography and partial fraction crystallization failed to give pure **3**. Therefore, it was not possible to determine the yield. The NMR data were given by subtracting the signals from those of **2**. Compound **3** decomposes in $CDCl_3$ faster than compound **2**. Therefore, it was essential to run the $^{13}C\{^1H\}$ NMR in CD_2Cl_2 for the overnight scan.

MS (EI, m/z): 382 ($M^+ - BH_3 - PMe_3$, 10%), 306 ($M^+ - BH_3 - 2PMe_3$, 18%), 72 (THF, 100%).

^1H NMR (300 MHz, $CDCl_3$): δ 7.17–8.03 (m, 10 H, Ph), 4.01 (m, 5H, Cp), 1.43 (br q, 3H, BH_3), 1.43 (m, 18H, PMe_3).

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 24.1 (d, $^2J_{pp} = 40$ Hz, PMe_3) and 18.8 (br m, PPh_2BH_3)

$^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −28.4 (d, $^1J_{PB} = ca.$ 52 Hz)

^{11}B NMR (96 MHz, $CDCl_3$): δ −28.2 (br partially resolved q of d, at 60 °C, $^1J_{HB} = ca.$ 80 Hz, $^1J_{PB} = ca.$ 50 Hz).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 147.9 (dt, *ipso*-C of Ph, $J_{CP} = 18$ Hz, 2 Hz), 133.7 (m, Ph, $J_{CP} = 8$ Hz), 127.4 (d, Ph, $J_{CP} = 7$ Hz), 127.0 (d, Ph, $J_{CP} = 2$ Hz), 78.7 (s, Cp), 22.9 (m, PMe_3, $J_{CP} = 13$ Hz).

Synthesis of $CpRu(CO)_2(PPh_2{\cdot}BH_3)$ (4). The complex $CpRu(CO)_2I$ (250 mg, 0.716 mmol) was dissolved in 10 mL THF in a round-bottom Schlenk flask and cooled to −30 °C. Chilled (−30 °C) $LiPPh_2{\cdot}BH_3$ (4.5 mL, 0.18 M in THF) was added dropwise. The reaction temperature was maintained between −30 and −20 °C for 2 h, and then the volatile components of the reaction mixture were removed *in vacuo* in the cold bath to obtain yellow oil. The oily product was purified by chromatography with a column of celite (0.5 × 1.5 cm) supported on glass wool with hexanes and then with toluene to obtain an orange solution which was stored at −40 °C for 3 days, affording pale yellow crystals (190 mg, 63% yield) of **4**.

IR (Toluene): 2040 (s, CO), 1986 (s, CO) cm^{-1}.

IR (THF): 2039 (s, CO), 1985 (s, CO) cm^{-1}.

MS (EI, m/z): 421 (M^+, 44%), 408 ($M^+ - BH_3$, 60%), 352 ($M^+ - BH_3 - 2CO$, 100%).

^1H NMR (300 MHz, C_6D_6): δ 7.92–7.99 (m, 4 H, Ph), 7.00–7.19 (m, 6H, Ph), 4.54 (s, 5H, Cp), 2.39 (br q, 3H, BH_3, $^1J_{HB} = ca.$ 100 Hz)

$^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 18.7 (br q, at 60 °C, $^1J_{PB} = ca.$ 45 Hz)

$^{11}B\{^1H\}$ NMR (96 MHz, C_6D_6): δ −28.5 (br d, $^1J_{PB} = ca.$ 45 Hz).

^{11}B NMR (96 MHz, THF): δ −29.1 (br partially resolved q of d, at 50 °C, $^1J_{HB} = ca.$ 100 Hz, $^1J_{PB} = ca.$ 45 Hz).

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 199.3 (d, CO, $^2J_{CP} = 11$ Hz), 141.2 (d, Ph, $J_{CP} = 35$ Hz), 133.6 (d, Ph, $J_{CP} = 10$ Hz), 129.5 (d, Ph, $J_{CP} = 2$ Hz), 128.6 (d, Ph, $J_{CP} = 9$ Hz), 89.9 (s, Cp).

Anal. Calc. for $C_{19}H_{18}O_2PBRu$: C, 54.19; H, 4.31. Found: C, 54.49; H, 4.33%.

Synthesis of $CpRu(CO)(PMe_3)(PPh_2BH_3)$ (5). Complex **4** (110 mg, 0.261 mmol) was dissolved in 1.8 mL THF in a round-bottom Schlenk flask. PMe_3 (54 µL, 0.52 mmol) was added to the solution which was stirred at 20 °C and monitored by ^{11}B and ^{31}P NMR. The pale yellow solution slowly deposited a white precipitate. After 3 days, the volatile components of the reaction mixture were removed *in vacuo* overnight to yield a yellow powder. The product was washed by filtration through celite supported on glass wool with Et_2O–THF (5 : 1) solution to yield a yellow solution which was stored at −40 °C for 2 days. This afforded a white precipitate (20 mg, 16% yield) consisting of **5** which was not readily soluble in benzene. Even after silica chromatography and multiple recrystallizations for attempted further purification, this compound was isolated only *ca.* 97% pure with an unknown impurity indicated by the arrows in the ^1H and $^{13}C\{^1H\}$ NMR spectra in the ESI.‡ Therefore, accurate EA was not possible.

IR (THF): 1939 (s, CO) cm^{-1}.

MS (EI, m/z): 456 ($M^+ - CO$, 66%), 72 (THF, 100%).

^1H NMR (300 MHz, $CDCl_3$): δ 7.64–7.92 (m, 4 H, Ph), 7.14–7.35 (m, 6H, Ph), 5.09 (s, 5H, Cp), 1.43 (br q, 3H, BH_3, $^1J_{HB} = ca.$ 93 Hz), 1.23 (d, 9H, PMe_3, $^2J_{PH} = 9.0$ Hz)

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 13.5 (br m, PPh_2BH_3), 9.48 (d, $^1J_{pp} = 26$ Hz, PMe_3)

$^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −30.7 (br d, $^1J_{PB} = ca.$ 57 Hz).

^{11}B NMR (96 MHz, $CDCl_3$): δ −30.7 (br partially resolved q of d, at 60 °C, $^1J_{HB} = ca.$ 92 Hz, $^1J_{PB} = ca.$ 57 Hz).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 204.6 (dd, CO, $^2J_{CP} = 20$, 11 Hz), 143.0 (dd, *ipso*-C of Ph, $^2J_{CP} = 63.9$, 31 Hz), 133.4 (dd, Ph, $J_{CP} = 61$, 8 Hz), 127.9 (dd, Ph, $J_{CP} = 16$, 2 Hz), 127.5 (dd, Ph, $J_{CP} = 16$, 9 Hz), 87.9 (s, Cp), 21.3 (d, $^2J_{CP} = 33$ Hz).

Thermal dehydrocoupling of $Ph_2PH{\cdot}BH_3$. The adduct $Ph_2PH{\cdot}BH_3$ (40 mg, 0.20 mmol) in toluene (1.8 mL) was stirred at 110 °C. After 16 h, 10% conversion to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was observed by $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR. A new unidentified peak was detected by $^{11}B\{^1H\}$ NMR at δ 17 ppm (10%). After 40 h, 16% conversion was detected. PPh_2H was also observed at δ −40.1 by $^{31}P\{^1H\}$ NMR.

Thermal reaction of complex 1. Complex **1** (50 mg, 0.13 mmol) in toluene (1.8 mL) was stirred at 110 °C for 19 h.

$^{31}P\{^1H\}$ (toluene) δ 194 (s, 17%), 187 (1%), 57 (d, $J = 40$ Hz, 20%), 34 (br d) and 33 (br., **1**, 51%), 12 (br s, 10%).

$^{11}B\{^1H\}$ (toluene) δ −16 (s, 4%), −29 (d, 96%, **1**)

Thermal dehydrocoupling of $PPh_2H{\cdot}BH_3$ in the presence of 1. (a) Complex **1** (56 mg, 0.15 mmol, 100 mol%) was added to a toluene (0.9 mL) solution of $PPh_2H{\cdot}BH_3$ (30 mg, 0.15 mmol) and the solution was stirred at 110 °C. After 15 h, 75% conversion of $PPh_2H{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was observed by $^{11}B\{^1H\}$ NMR.

$^{31}P\{^1H\}$ (toluene) δ 194.7 (s), 56.1 (d, $J_{PP} = 21$ Hz), 32 (**1**), 30 (br. s), 2.0 (d, $Ph_2PH{\cdot}BH_3$), −3 (br. s, $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$), −16 (br. s, $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$).

$^{11}B\{^1H\}$ (toluene) δ −30.9 (s, 52%), −34.4 and −38.6 (s, 34%. $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$), −41.4 (d, $^1J_{PB} = 35$ Hz, 14%, $PPh_2H{\cdot}BH_3$).

(b) Complex **1** (28 mg, 0.074 mmol, 25 mol%) was added to a toluene (1.8 mL) solution of $PPh_2H{\cdot}BH_3$ (60 mg, 0.300 mmol) and the solution was stirred at 110 °C. After 15 h, 50% conversion of $PPh_2H{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was observed by $^{11}B\{^1H\}$ NMR. The same reaction with complex **1** (11 mg, 0.029 mmol, 10 mol%) yielded 20% conversion of $PPh_2H{\cdot}BH_3$

to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$, observed by $^{11}B\{^1H\}$ NMR. The same reaction heated at 60 °C for 15 h yielded 0% conversion.

(c) Complex **1** (2 mg, 0.005 mmol, 1.5 mol%) was added to $PPh_2H{\cdot}BH_3$ (60 mg, 0.300 mmol) and the neat mixture was heated at 120 °C. After 15 h, 65% conversion of $PPh_2H{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was observed by $^{11}B\{^1H\}$ NMR. When the same reaction was performed at 60 °C, 5% conversion was noted and there was no conversion at 20 °C with 1.8 mL of toluene.

Attempted UV induced dehydrocoupling of $PPh_2H{\cdot}BH_3$. (a) The complex $CpFe(CO)_2PPh_2BH_3$ (**1**) (6 mg, 10 mol%) was added to a toluene (0.9 mL) solution of $PPh_2H{\cdot}BH_3$ (30 mg, 0.15 mmol) and stirred under UV lamp at 5 °C. After 15 h, 0% conversion of $PPh_2H{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was observed by $^{11}B\{^1H\}$ NMR.

(b) The complex $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ (1 mg, 0.8 mol% Rh) was added to a THF (1.8 mL) solution of $PPh_2H{\cdot}BH_3$ (100 mg, 0.500 mmol) and stirred under UV lamp at 5 °C. After 15 h, 0% conversion of $PPh_2H{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was observed by $^{11}B\{^1H\}$ NMR.

(c) A toluene (0.9 mL) solution of $PPh_2H{\cdot}BH_3$ (50 mg, 0.25 mmol) was stirred under UV lamp at 5 °C. After 15 h, 0% conversion of $PPh_2H{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was observed by $^{11}B\{^1H\}$ NMR and a new peak, δ 18.6 (s), was detected by $^{31}P\{^1H\}$ NMR.

Reaction of $PPh_2H{\cdot}BH_3$ with 4. (a) Complex **4** (68 mg, 0.16 mmol, 100 mol%) was added to a toluene (1.8 mL) solution of $PPh_2H{\cdot}BH_3$ (33 mg, 0.16 mmol) and stirred at 110 °C. After 4 days, $PPh_2H{\cdot}BH_3$ was completely consumed.

$^{31}P\{^1H\}$ (toluene) δ 38.0 (d, $J = 26$ Hz), 20.0 (br s), 17.4 (s), −40.1 (s, PPh_2H).

$^{11}B\{^1H\}$ (toluene) δ −29.1 (s).

(b) Complex **4** (2 mg, 5 μmol, 1.5 mol%) was added $PPh_2H{\cdot}BH_3$ (60 mg, 0.30 mmol) and stirred at 120 °C. After 15 h, 60% conversion of $PPh_2H{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was observed by $^{11}B\{^1H\}$ NMR.

Reaction of $Ph_2PH{\cdot}BH_3$ with Ru/Al_2O_3. Ru/Al_2O_3 (9 mg, 1.5 mol%) was added $PPh_2H{\cdot}BH_3$ (60 mg, 0.30 mmol) and stirred at 120 °C. After 15 h, 5% conversion of $PPh_2H{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was observed by $^{11}B\{^1H\}$ NMR.

Reaction of $Ph_2PH{\cdot}BH_3$ with $Fe_2(CO)_9$. (a) Complex $Fe_2(CO)_9$ (5 mg, 0.027 mmol, 10 mol% Fe) was added to a toluene (1.8 mL) solution of $PPh_2H{\cdot}BH_3$ (60 mg, 0.300 mmol) and the solution was stirred at 110 °C. After 15 h, 10% conversion of $PPh_2H{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was observed by $^{11}B\{^1H\}$ NMR. The same reaction mixture heated at 60 °C for 15 h yielded 0% conversion.

(b) Complex $Fe_2(CO)_9$ (1 mg, 0.005 mmol, 1.5 mol% Fe) was added to $PPh_2H{\cdot}BH_3$ (60 mg, 0.300 mmol) and the neat mixture was heated at 120 °C. After 15 h, 80% conversion of $PPh_2H{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was observed by $^{11}B\{^1H\}$ NMR. When the same experiment was done at 60 °C, 0% conversion was detected.

Experiments of entries 9, 13, 15 and 20 in Table 1. In these experiments the conversion is an upper-limit estimate due to sublimation of mostly $PPh_2H{\cdot}BH_3$ and a small amount of $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ during the reaction onto the top of the reaction flask. The following experiment was conducted to assess the effect of the sublimation.

(a) Complex $Fe_2(CO)_9$ (1 mg, 0.005 mmol, 1.5 mol% Fe) was added to $PPh_2H{\cdot}BH_3$ (60 mg, 0.300 mmol) and the neat mixture was heated at 120 °C. The reaction was stopped every 2–3 h to return the sublimed $PPh_2H{\cdot}BH_3$ back into the reaction mixture. After 15 h, 70% conversion of $PPh_2H{\cdot}BH_3$ to $Ph_2PH{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$ was observed by $^{11}B\{^1H\}$ NMR. This is 10% less than entry 20 in Table 1, suggesting an error of *ca.* 10%.

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