

Synthesis and novel reactivity of platinum phosphine–borane complexes *trans*-[PtH(PPhR·BH₃)(PEt₃)₂] (R = H, Ph)

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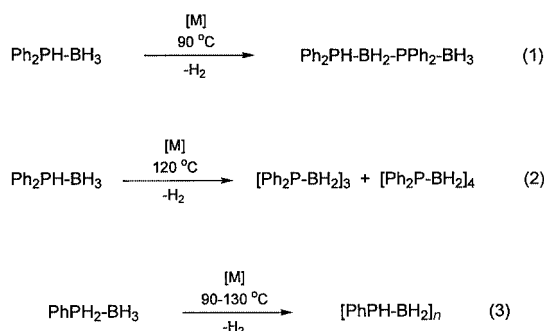
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The oxidative-addition reaction of Pt(PEt₃)₃ with the phosphine–borane adducts PhPH₂·BH₃ and Ph₂PH·BH₃ leads to regioselective insertion of the Pt(PEt₃)₂ fragment into the P–H bond to afford the hydride complexes *trans*-[PtH(PPhR·BH₃)(PEt₃)₂] (R = H **1**, R = Ph **2**); reaction of **2** with PhPH₂·BH₃ leads to an unusual ligand exchange reaction which generates **1** and Ph₂PH·BH₃.

The discovery of new synthetic methods for the formation of homonuclear or heteronuclear bonds between main group elements is of importance for the construction of inorganic polymer chains and also for the general development of p-block chemistry.^{1,2} Transition metal-catalyzed routes represent a particularly attractive approach to this problem.^{2,3} Recently we reported a novel metal-catalyzed route to linear and cyclic oligomeric and also high molecular weight poly(phosphinoboranes) which involved dehydrocoupling of phosphine–borane adducts in the presence of late transition metal complexes (Scheme 1).^{4,5} A plausible first step in these reactions involves insertion of the transition metal into either the P–H or B–H bond of the adduct. Subsequent steps may involve σ-bond metathesis and/or oxidative addition/reductive elimination processes. Significantly, no homodehydrocoupling products with P–P or B–B bonds have been detected from these reactions to date. It should be noted that the insertion of transition metals into the P–H bonds of secondary phosphines has ample precedent. For example, oxidative addition of P(III)–H bonds at Pt(0) or Pd(0) centers has been demonstrated and such processes are believed to be a key step in the catalytic hydrophosphination of alkenes and alkynes.⁶ On the other hand, a range of mono- and dinuclear boryl complexes have recently been reported as a result of the ambient temperature reactions of the B–H bonds in Me₃P·BH₃ or Me₃P·BH₂BH₂·PMe₃ at metal centers.^{7,8} In order to investigate potential pathways during the transition metal mediated P–B bond formation reactions we are studying the hitherto unexplored coordination chemistry of phosphine–borane adducts with both P–H and B–H bonds. Here, we report the oxidative-addition reactions of Ph₂PH·BH₃ and PhPH₂·BH₃

with the electron rich Pt(0) complex Pt(PEt₃)₃ and a preliminary reactivity study of the resulting phosphine–borane complexes.

Reaction of the primary phosphine–borane adduct PhPH₂·BH₃ with a stoichiometric amount of Pt(PEt₃)₃ in toluene at 60 °C and subsequent crystallization from hexanes resulted in the formation of a yellow solid **1** (23% isolated yield, quantitative by ¹¹B and ³¹P NMR before workup) which was characterized by multinuclear NMR spectroscopy in CDCl₃.[†] The spectroscopic data for the product was consistent with a structure **1** in which insertion of Pt into a P–H bond rather than the B–H bond had taken place. For example, the product displayed two distinct sets of signals in the ³¹P NMR spectrum: a doublet at δ 17.9 was assigned to the PEt₃ ligands attached to platinum, showing coupling to another phosphorus nucleus (*J*_{PP} 19.4 Hz) as well as ¹⁹⁵Pt satellite signals (*J*_{PPt} 2572 Hz). Furthermore, a broad doublet at δ ca. –48.7 indicated coupling to a quadrupolar boron nucleus and one hydrogen substituent (*J*_{PH} 299 Hz) and showed ¹⁹⁵Pt satellites with the magnitude *J*_{PPt} ca. 1440 Hz. This signal was assigned to the phosphorus of the fragment Pt–PPhH·BH₃. The ¹¹B NMR spectrum showed a single broad resonance at δ –33.2 which is in the region typical for BH₃ adducts of phosphines. The key ¹H NMR spectroscopic feature is the low-frequency hydride resonance at δ –5.74, which appears as a doublet of triplets with a larger coupling to one phosphorus atom (*J*_{HP} 124.6 Hz) and a smaller coupling to two phosphorus atoms (*J*_{HP} 15.4 Hz) as well as ¹⁹⁵Pt satellites (*J*_{HPt} 872 Hz). This suggested the presence of one *trans* substituent (PPhH·BH₃) and two *cis* substituents (PEt₃), with respect to the hydride ligand.



[M] = transition metal catalyst

Scheme 1

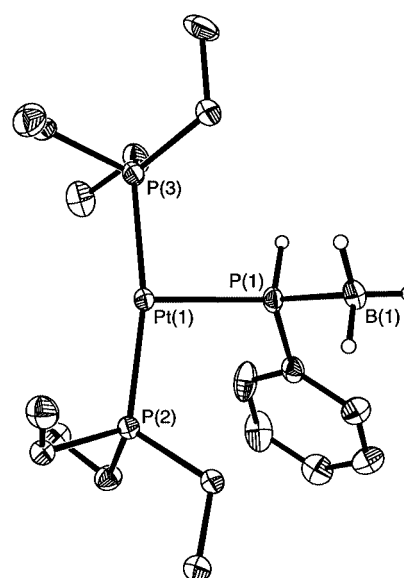
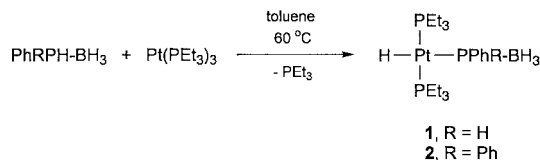


Fig. 1 Molecular structure of **1** (30% displacement ellipsoids). Hydrogen atoms attached to carbon are omitted. Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.3477(14), Pt(1)–P(2) 2.2863(13), Pt(1)–P(3) 2.2771(14), P(1)–B(1) 1.953(7), P(1)–H(1P) 1.32(6); P(3)–Pt(1)–P(2) 168.26(5), P(3)–Pt(1)–P(1) 92.83(5), P(2)–Pt(1)–P(1) 98.87(5), B(1)–P(1)–Pt(1) 119.8(2).



Scheme 2

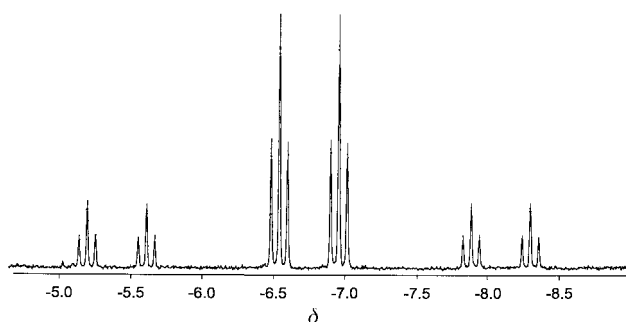


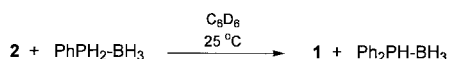
Fig. 2 ^1H NMR spectrum (300 MHz, C_6D_6) of the hydride region of **2** [$J_{\text{HP}}(\text{trans})$ 124.4 Hz, $J_{\text{HP}}(\text{cis})$ 16.9 Hz, J_{HPt} 805 Hz, PtH].

The molecular structure of compound **1** was confirmed by single crystal X-ray analysis[‡] and is consistent with the solution NMR data. A SHELXTL drawing is shown in Fig. 1. The geometry around the Pt(II) center is close to square-planar with *trans* PEt_3 ligands. Although the platinum hydride ligand was not observed in the X-ray study its presence is clearly indicated by the large P(3)–Pt(1)–P(2) angle of $168.26(5)^\circ$ and, as discussed, from the ^1H NMR spectroscopic data. The lengths of the bonds Pt(1)–P(2) [2.2863(13) Å] and Pt(1)–P(3) [2.2771(14) Å] are shorter than the Pt(1)–P(1) bond [2.3477(14) Å], presumably as a consequence of the *trans* influence of the hydride ligand. A similar observation was made in the hydride complex *cis*-[PtH(P(O)Ph₂)(PPh₂(OH))(PEt₃)].⁹

A similar reaction was observed between the secondary phosphine–borane adduct $\text{Ph}_2\text{PH-BH}_3$ and 1 equivalent of $\text{Pt}(\text{PEt}_3)_3$ (Scheme 2). The orange–yellow platinum complex **2** was isolated in 67% yield. For **2**, signals in the ^{31}P NMR spectrum are observed at δ 16.7 (PEt_3) and δ –3.7 ($\text{PPh}_2\text{-BH}_3$) and in the ^{11}B NMR spectrum at δ –31.4. Fig. 2 shows the hydride region of the ^1H NMR spectrum of **2** with the characteristic dt coupling pattern which is flanked by ^{195}Pt satellite signals (J_{HPt} 805 Hz).

Compound **1** represents the first example of a metal complex of a primary phosphine–borane adduct and only two other examples of transition metal complexes of secondary phosphine–borane adducts analogous to **2** are known; a tetrahedral iron complex, $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{PPh}_2\text{-BH}_3)]$,¹⁰ and a square-planar palladium complex, $[\text{Pd}(\text{dppp})\text{-(C}_6\text{F}_5)(\text{PPh}_2\text{-BH}_3)]$ [dppp = 1,3-bis(diphenylphosphino)propane], a proposed intermediate in the Pd-catalyzed coupling of secondary phosphine–boranes with aryl halides.¹¹ However, the synthesis of the latter compounds involved nucleophilic substitution steps rather than insertion of the transition metal fragment.

The isolation of novel complexes **1** and **2** via oxidative addition suggests that P–H bond activation may be the key initial step in the late transition metal-catalyzed formation of P–B bonds. In order to explore the reactivity of the complexes, a solution of **2** in C_6D_6 was treated with another equivalent of $\text{PhPH}_2\text{-BH}_3$. After 8 h at room temperature the solution had changed from orange to yellow, however, no P–B coupling reaction was observed by ^{31}P NMR spectroscopy. Surprisingly, a complete exchange of the phosphine–borane ligand had occurred to form exclusively complex **1** together with $\text{Ph}_2\text{PH-BH}_3$ (Scheme 3).



Scheme 3

The demonstration of a novel phosphine–borane ligand exchange reaction at the Pt center indicates that relatively complex reaction chemistry may need to be unravelled if a full mechanistic understanding of late transition metal-catalyzed P–B bond formation reactions is to take place. Detailed studies of the reactivity of novel complexes such as **1** and **2** and analogs directed towards this goal are in progress.

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Notes and references

[†] Selected spectroscopic data: for **1**: ^1H NMR (300 MHz, CDCl_3) δ 7.76–7.70 (m, Ar), 7.26–7.19 (m, Ar), 4.39 (d, J_{HP} 299 Hz, PH), 2.0–0.9 (br q, BH_3), 1.80 (m, CH_2), 1.03 (m, CH_3), –5.74 [dt, $J_{\text{HP}}(\text{trans})$ = 124.6 Hz, $J_{\text{HP}}(\text{cis})$ 15.4 Hz, J_{HPt} 872 Hz, PtH]; $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3) δ –33.2 (br); ^{31}P NMR (121 MHz, CDCl_3) δ 17.9 (d, J_{PP} 19.4 Hz, J_{PPt} 2572 Hz, PEt_3), –48.7 (br d, J_{PH} 299 Hz, J_{PPt} 1440 Hz, PPH); IR (Nujol) 2350 (ν_{BH}), 2022 (ν_{PH}) cm^{-1} ; EIMS m/z (%): 541 (1) [$\text{M}^+ - \text{BH}_3$], 118 (100) [PEt_3]. For **2**: ^1H NMR (300 MHz, C_6D_6) δ 8.26–8.14 (m, Ar), 7.26–7.00 (m, Ar), 3.0–1.9 (br q, BH_3), 1.48 (m, CH_2), 0.93 (m, CH_3), –6.75 [dt, $J_{\text{HP}}(\text{trans})$ 124.4 Hz, $J_{\text{HP}}(\text{cis})$ 16.9 Hz, J_{HPt} 805 Hz, PtH]; $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, C_6D_6) δ –31.4 (br); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6) δ 16.7 (d, J_{PP} 17.4 Hz, J_{PPt} 2648 Hz, PEt_3), –3.7 (br, J_{PPt} 1575 Hz, PPh₂); IR (Nujol) 2341 (ν_{BH}), 2009 (ν_{PH}) cm^{-1} ; EIMS m/z (%): 617 (21) [$\text{M}^+ - \text{BH}_3$], 62 (100) [H_2PEt].

[‡] Crystal data for **1**: $\text{C}_{18}\text{H}_{30}\text{BP}_3\text{Pt}$, M = 554.30, monoclinic, space group $\text{C}2/c$, a = 27.1904(13), b = 9.8355(7), c = 19.0955(11) Å, β = $110.777(3)^\circ$, U = 4774.6(5) Å³, Z = 8, D_c = 1.542 g cm^{-3} , μ = 6.077 mm^{-1} , $F(000)$ 2200, T = 150(1) K, crystal size $0.15 \times 0.15 \times 0.10$ mm, 1576 independent reflections, 51791 collected. Goodness-of-fit on F^2 = 1.042, final R indices [$I > 2\sigma(I)$], R_1 = 0.0387, wR_2 = 0.0969. The structures were solved and refined with the SHELXTL-PC V5.1 software package.¹² Refinement was by full-matrix least squares on F^2 using all data (negative intensities included). Hydrogens bonded to carbon atoms were included in calculated positions and treated as riding atoms, hydrogens attached to P(1) and B(1) were refined with isotropic thermal parameters. CCDC 182/1620. See <http://www.rsc.org/suppdata/cc/b0/b002615h/> for crystallographic files in .cif format.

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