

Synthesis, characterization and thermolysis of phosphinite–borane adducts: investigation of an unusual thermally-induced phenol elimination reaction

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The synthesis, characterization and thermolytic behavior of a new class of phosphinite–borane adducts containing the bulky 2,4,6-*t*-Bu₃C₆H₂O (Mes*O) group is reported, including the description of the first example of a primary phosphinite–borane adduct isolable at room temperature (Mes*O)PH₂·BH₃ **1**. Adduct **1** and the phenylated derivative (Mes*O)PhPH·BH₃ **3** formed highly cross-linked solids, **7** and **8**, when heated to 100 and 140 °C, respectively. Characterization of these solids by solid state and solution NMR spectroscopy suggest that both dehydrocoupling (H₂ elimination) and Mes*OH elimination occur simultaneously to give the complex products [(Mes*O)_xRPH_y–BH_(2x+2y+z)]_n (R = H or Ph, x + y + z = 1). The tertiary adduct (Mes*O)Ph₂P·BH₃ **5** and the phosphite–borane (PhO)₃P·BH₃ **6** were found to decompose at high temperatures *via* P–B bond cleavage without formation of the corresponding phenol. These results suggest that the thermally-induced formation of Mes*OH from **1** and **3** occurs *via* α-elimination from a phosphorus center. Adducts **1**, **3**, **5** and **6** were also structurally characterized by single-crystal X-ray diffraction.

Introduction

The development of new bond-forming processes continues to be an important challenge in main group chemistry.¹ Significant advances in this area have recently occurred as a result of the discovery of various transition metal-catalyzed dehydrocoupling methodologies.¹ For example, catalytic formation of homonuclear Si–Si,² Ge–Ge,³ Sn–Sn⁴ and P–P bonds,⁵ and heteronuclear Sn–Te,⁶ Si–P,⁷ Si–N⁸ and Si–O⁹ bonds have been reported.

Recently, we discovered that a range of species with B–N and B–P skeletons are readily accessible by transition metal-mediated dehydrocoupling of appropriate amine– or phosphine–borane adducts. For example, alkyl-substituted secondary amine–boranes adducts, R₂NH·BH₃, dehydrocouple efficiently under mild conditions (< 45 °C) in the presence of Rh^I catalysts to give four-membered amino–borane rings [R₂N–BH₂]₂, whereas the primary amine–boranes RNH₂·BH₃ eliminate two equivalents of H₂ to form borazines [(RNH–BH)₃, R = H, Me, Ph].¹⁰ In addition, primary and secondary phosphine–borane adducts participate in dehydrocoupling chemistry, however higher temperatures are generally required (> 90 °C).¹¹ Secondary phosphine–boranes such as Ph₂PH·BH₃ dehydrocouple in the presence of Rh^I catalysts to give mixtures of six- and eight-membered cyclic phosphinoboranes [Ph₂P–BH₂]_x (x = 3 or 4) at high temperatures, and the unusual linear oligomer R₂PH–BH₂–PR₂–BH₃ when milder reaction conditions are employed. The less sterically congested primary phosphine–boranes dehydrocouple cleanly to give high molecular weight polyphosphinoboranes [RPH–BH₂]_n, an interesting class of stable inorganic polymers.^{11–15}

As part of our continuing research concerning the polymerization of phosphorus–boron precursors, we have now explored the chemistry of the related phosphinite–borane adducts, (RO)R'PH·BH₃, with the aim of synthesizing new rings, chains or macromolecules of the form [(RO)R'P–BH₂]_n using dehydrocoupling strategies. This paper reports our investigations in this area, and the discovery of a rare bond-forming process *via* the α-elimination of phenols.

Results and discussion

Before this work was initiated, to our knowledge, no examples of stable primary phosphinite–borane adducts, (RO)PH₂·BH₃, had been described. For example, Centofanti reported that the phosphonite–borane adduct, (MeO)₂PH·BH₃ is stable to 40 °C, while the primary phosphinite–borane adduct, (MeO)PH₂·BH₃, decomposed spontaneously at room temperature to give an insoluble yellow solid, H₂ and PH₃·BH₃.¹⁶ More recently, Roper and co-workers have shown that a variety of unstable alkyl phosphinites [*e.g.* (RO)PH₂, R = Me, Et] can be stabilized by forming coordination complexes with late transition metals.¹⁷ As a consequence, we decided to explore the synthesis and potential dehydrocoupling chemistry of a new class of bulky phosphinite–borane adducts containing the bulky 2,4,6-*t*-Bu₃C₆H₂O (Mes*O) group.

Synthesis and characterization of (Mes*O)PH₂·BH₃ **1**

The reaction of Mes*OPCl₂, synthesized from Mes*OLi·OEt₂ and PCl₃ in Et₂O,¹⁸ with 2 equivalents of Li[BH₄] in THF produced the novel primary phosphinite–borane adduct **1** (quantitative yield) as a white solid which is stable at room temperature.

The ³¹P{¹H} NMR spectrum of **1** consisted of a broad singlet at δ 78.9 which split into a 1 : 2 : 1 triplet in the proton-coupled spectrum (¹J_{PH} ≈ 390 Hz), which indicated the presence of two hydrogen atoms bound directly to a phosphorus center. Furthermore, the ¹H NMR spectrum of **1** showed a doublet of quartets (δ 6.73) assigned to coupling between the above mentioned PH₂ protons with a neighboring phosphorus atom (doublet, ¹J_{PH} = 399 Hz) and BH₃ protons (1 : 3 : 3 : 1 quartet, ³J_{HH} = 6.6 Hz). The observation of well-resolved coupling between P–H and B–H protons was somewhat surprising given the quadrupolar nature of the ¹¹B nucleus, however similar splitting patterns have been previously observed in the ¹H NMR spectra of PH₃·BH₃¹⁹ and the thermally unstable phosphinite–borane adduct, (MeO)PH₂·BH₃.¹⁶ Signals arising from the BH₃ group were also detected as a broad halo (δ 0.5–1.5) in the ¹H NMR spectrum, and as a broad singlet (δ –41.9) in the

Table 1 Selected bond lengths (Å) and angles (°) for adducts **1**, **3**, **5** and **6** with estimated standard deviations in parentheses

	1	3	5	6
P–B	1.882(6)	1.894(3)	1.917(5)	1.878(3)
P–O	1.597(3)	1.6117(15)	1.629(3)	1.5832(15) 1.5845(15) 1.5757(14)
P–C(phenyl)		1.799(2)	1.804(4) 1.807(3)	
P–H	1.33(4) 1.40(4)	1.391(10)		
B–H	1.05(4) 1.07(5) 1.12(4)	1.06(3) 1.17(4) 1.18(4)	1.10(4) 1.12(4) 1.27(4)	1.08(2) 1.10(2) 1.11(3)
O–P–B	110.5(2)	111.89(12)	115.2(2)	110.32(12) 117.56(11) 118.32(11)
H–P–H	100(2)			
H–P–C(phenyl)		95.5(9)		
H–P–B	114.0(14) 116.9(14)	100.0(9)		
H–P–O	106.5(13) 108.2(14)	122.0(9)		
C–P–B		116.81(13)	115.7(2) 111.5(2)	

¹¹B NMR spectrum. This ¹¹B NMR chemical shift is consistent with the presence of a phosphorus(III)–borane adduct as typical chemical shifts for these adducts are in the range of $\delta -40 \pm 5$.²⁰ All relevant signals associated with the pendant Mes*O group were located in both the ¹H and ¹³C{¹H} NMR spectra of **1**. Further characterization of **1** was provided by melting point determination, mass spectrometry and a single crystal X-ray diffraction study (discussed below).

Before this study, only a few reports of structurally characterized phosphinite–borane adducts could be found in the literature,²¹ and of these, none involved species with P–H bonds. In addition **1** represents, to our knowledge, the first primary phosphinite–borane adduct which is isolable as a stable compound at room temperature. To further characterize **1**, a single-crystal X-ray diffraction study was undertaken on small colorless crystals of **1** grown from toluene at -30 °C. Data collection and refinement parameters for **1** are summarized in Table 2 while relevant bond lengths and angles for **1** are listed in Table 1. The molecular structure of **1** is depicted in Fig. 1.

Despite some disorder in the para-*t*-Bu groups within the Mes*O moiety, the quality of the data permitted the location

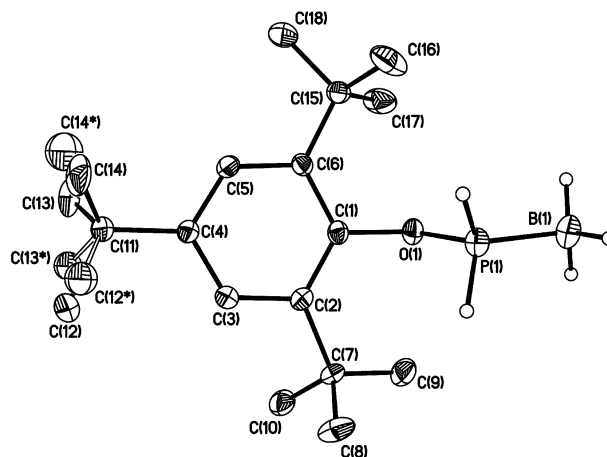


Fig. 1 Molecular structure of **1** with thermal ellipsoids at the 30% probability level (carbon bound hydrogen atoms omitted for clarity).

and refinement of the hydrogen atoms at phosphorus and boron. The geometry about the phosphorus and boron atoms in **1** can be described as distorted tetrahedral with bond angles ranging from the acute 100(2)° for the H–P–H angle to the wider H–P–B angle of 116.9(14)°. The B–P bond length in **1** was determined to be 1.882(6) Å and is significantly shorter than the B–P bonds observed in most structurally characterized phosphine–borane adducts [e.g. B–P bond length in PhPH₂·BH₃ is 1.924(4) Å¹²]. The P–H [1.37(6) Å avg.] and B–H [1.07(7) Å avg.] bond lengths are similar to those observed in other phosphorus–borane adducts. As both hydridic (B–H^{δ-}) and acidic (P–H^{δ+}) hydrogen atoms are present in **1**, there exists the possibility of intermolecular hydrogen bonding. In fact, such H–H interactions have been observed in PhPH₂·BH₃ with the shortest intermolecular H–H distance (2.38 Å) being similar to the sum of the van der Waals radii for P and B (2.4 Å).¹² By contrast, the closest intermolecular H–H contact in **1** was found to be > 3.2 Å, despite the more acidic nature of the P–H protons (*vide infra*) when compared to PhPH₂·BH₃. It is possible that the greater steric bulk in **1** hinders intermolecular H-bonding and thus only discrete monomers are observed in the solid state structure of **1**.

Synthesis and characterization of (Mes*O)PhPCl **2** and (Mes*O)PhPH·BH₃ **3**

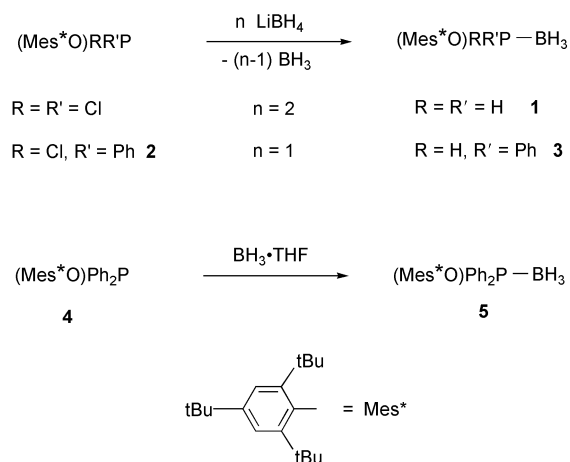
The previously reported synthesis of (Mes*O)PhPCl **2** by Pastor *et al.* involved the reaction of Mes*OH with PhPCl₂ in

Table 2 Crystal data, data and intensity collection parameters, and least squares parameters for **1**, **3**, **5** and **6**

	1	3	5	6
Empirical formula	C ₁₈ H ₃₄ BOP	C ₂₄ H ₃₈ BOP	C ₃₀ H ₄₂ BOP	C ₁₈ H ₁₈ BO ₃ P
Formula weight	308.23	384.32	460.42	324.10
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	P2 ₁ /c	P2 ₁ /c	Pca2 ₁	P $\bar{1}$
<i>a</i> /Å	9.9490(12)	18.0012(4)	18.2421(6)	9.4189(3)
<i>b</i> /Å	15.6210(19)	8.0595(2)	12.3496(6)	9.9295(4)
<i>c</i> /Å	12.7660(11)	18.4874(4)	12.3712(10)	9.9979(3)
<i>a</i> °	90	90	90	76.568(2)
<i>β</i> °	101.303(7)	98.7360(10)	90	84.550(2)
<i>γ</i> °	90	90	90	72.735(2)
<i>V</i> /Å ³	1945.5(4)	2651.05(11)	2787.0(3)	868.16(5)
<i>Z</i>	4	4	4	2
μ (Mo-K α)/mm ⁻¹	0.139	0.113	0.118	0.169
Temperature/K	150(1)	150(1)	150(1)	150(1)
θ Range/°	2.61 to 22.50	2.66 to 27.50	2.58 to 25.03	2.69 to 25.03
No. of reflections collected	13449	23956	14945	6801
No. of independent reflections/ <i>R</i> _{int}	2533/0.162	6062/0.067	4606/0.099	3054/0.039
No. of refined parameters	224	259	321	221
<i>R</i> (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0654	0.0620	0.0592	0.0410
<i>R</i> _w ^b	0.01548	0.01651	0.01035	0.0925

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

the presence of KOH.²² A yield of 68% was reported, however little characterization (IR and melting point) was provided. We prepared pure **2** in an improved yield of 89% by reacting the lithium salt Mes*OLi·OEt₂ with PhPCl₂ in diethyl ether; a similar reaction between Mes*OLi·OEt₂ and PCl₃ was used by Power and co-workers to synthesize Mes*OPCl₂.¹⁸ In addition, compound **2** was further characterized by ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectroscopy, and high-resolution mass spectrometry (HR-MS) which were consistent with the assigned structure. Reaction of **2** with one equivalent of Li[BH₄] gave the phenyl substituted analogue of **1**, (Mes*O)PhPH·BH₃ **3**, in good yield (72%, Scheme 1) as a white solid that was character-



Scheme 1 Synthesis of adducts **1**, **3**, and **5**.

ized by NMR spectroscopy, mass spectrometry, melting point, elemental analysis and a single-crystal X-ray diffraction study.

The ³¹P{¹H} NMR spectrum of **3** gave a broad signal at δ 99.1 that split into a doublet (¹J_{PH} ≈ 410 Hz) in the proton-coupled spectrum, which confirmed the presence of a PH group. The associated doublet of quartets was observed in the ¹H NMR spectrum at δ 7.51 (¹J_{PH} = 403 Hz; ³J_{HH} = 5.4 Hz, coupling of PH to BH₃). This resonance was significantly downfield from the PH resonance in Ph₂PH·BH₃ (δ 5.51),²³ which suggests a greater acidity for the PH proton in **3** (due to the increased electronegativity of the neighboring aryloxy groups in comparison to their aryl counterparts). The ¹H and ¹³C{¹H} NMR spectra of **3** were similar to those observed for **1** except for the presence of added resonances due to the phenyl group; the ¹¹B{¹H} NMR spectrum of **3** consisted of a doublet at δ -40.7 (¹J_{BP} = 47 Hz).

Chiral (Mes*O)PhPH·BH₃ **3** crystallized from toluene (-30 °C) in the achiral space group P2₁c with both enantiomers of **3** present in the crystal lattice. Fig. 2 depicts the molecular structure of one of these enantiomers (*S*) while Table 2 contains relevant collection and refinement parameters for **3**; selected bond lengths and angles for **3** can be found in Table 1.

The geometry about the phosphorus and boron atoms in **3** is similar to that in **1** (distorted tetrahedral), however the O–P–B angle is somewhat wider [111.89(12)°] in **3** than in **1** [110.5(2)°]. The B–P bond length in **3** is similar [1.894(3) Å] to the B–P bond lengths in related substituted phosphinite–borane adducts.²¹ As with **1**, no significant intermolecular interactions could be observed in **3**. The pendant Mes*O and Ph groups in **3** showed no unusual features in the solved structure with typical C–C and C–O bond lengths and angles observed.

Synthesis and characterization of (Mes*O)Ph₂P **4** and (Mes*O)Ph₂P·BH₃ **5**

The diphenyl substituted phosphinite–borane adduct **5**, a colorless solid, was prepared in good yield (73%) by the reaction of the previously unknown (Mes*O)Ph₂P **4** (synthesized from Ph₂PCl and Mes*OLi·OEt₂) with a slight excess of BH₃·THF.

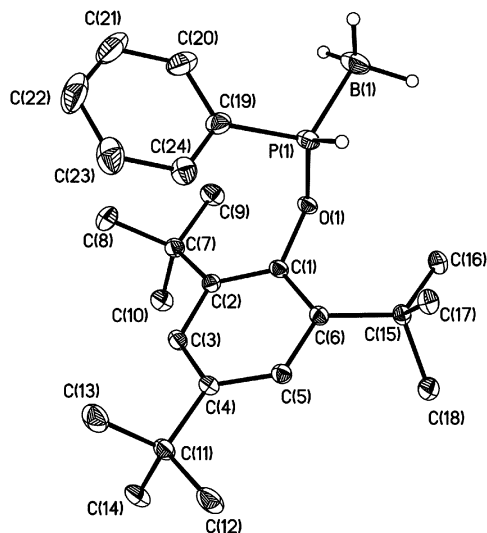


Fig. 2 Molecular structure of **3** with thermal ellipsoids at the 30% probability level (carbon bound hydrogen atoms omitted for clarity).

Compound **5** was characterized by NMR spectroscopy, mass spectrometry, melting point, elemental analysis and a single-crystal X-ray diffraction study.

The formation of **5** was monitored by ³¹P{¹H} NMR spectroscopy which showed the complete conversion of **4** (δ 127) to a new product with a chemical shift of 110 ppm. ¹H, ¹³C{¹H} and ¹¹B{¹H} NMR spectroscopy also confirmed the presence of **5**. To better understand how the B–P bonding in this class of phosphinite–borane adducts relies upon the steric bulk at phosphorus, we also examined the structure of this compound by single-crystal X-ray diffraction. The molecular structure of **5** can be found in Fig. 3, while relevant data collection and refinement parameters are found in Table 2. Table 1 contains selected bond lengths and angles for **5**.

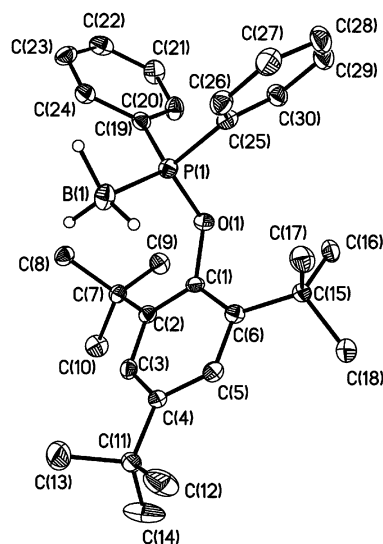


Fig. 3 Molecular structure of **5** with thermal ellipsoids at the 30% probability level (carbon bound hydrogen atoms omitted for clarity).

The molecular structure of **5** revealed a highly crowded phosphorus center. A much wider O–P–B angle is present in **5** [115.2(2)°] and the P–O bond is significantly longer [1.629(3) Å] than in either adducts **1** [1.597(3) Å] or **3** [1.6117(15) Å]. The B–P bond length [1.917(5) Å] seems less influenced by steric effects and has a similar value to those in the previously mentioned phosphinite–borane adducts. Of note, the bond lengths and angles within **5** also compare closely to those within the phosphite–borane adduct (PhO)₃P·BH₃ **6** (see Fig. 4, Tables 1 and 2) which has a P–B bond length of 1.878(3) Å.

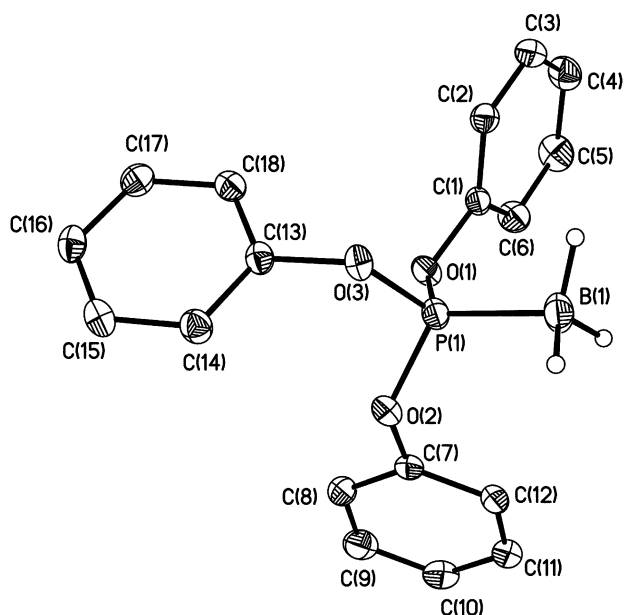


Fig. 4 Molecular structure of **6** with thermal ellipsoids at the 30% probability level (carbon bound hydrogen atoms omitted for clarity).

Attempted dehydrocoupling of (Mes*O)PH₂·BH₃ **1** and (Mes*O)PhPH·BH₃ **3**: discovery of an unusual thermally-induced phenol elimination reaction

In an attempt to evaluate the ability of **1** to participate in dehydrogenative B–P bond coupling, a sample was heated above its melting point (92–3 °C). Instead of the anticipated elimination of hydrogen, large white needles formed on the colder portion of the reaction vessel. ¹H NMR and mass spectral analysis surprisingly identified the pure product as the phenol, 2,4,6-*t*-Bu₃C₆H₂OH (*m/z* = 262). After **1** was heated under nitrogen for a further 3 d the production of the phenol ceased (~ 0.9 mole equivalents) and a yellow involatile solid remained. This residue (**7**) was found to be completely insoluble in common organic solvents (including polar solvents such as DMSO and DMF) therefore further characterization of this material was accomplished by solid state NMR and IR spectroscopy, and elemental analysis (C and H).

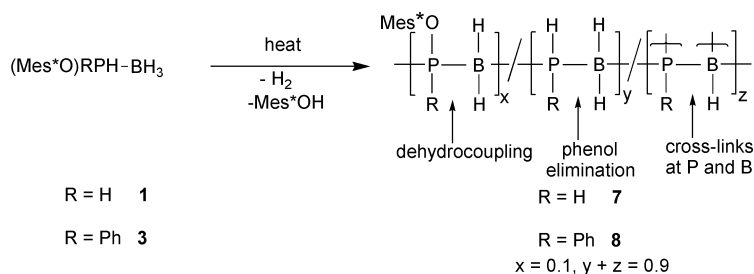
Based on the quantity of Mes*OH produced when **1** was heated, and the results from elemental analysis, we formulated the insoluble product **7** as [(Mes*O)_xRPH_y–BH_(2x+2y+z)]_n (*x* = 0.1, *y* + *z* = 0.9) (see Scheme 2). If Mes*OH elimination occurred exclusively (*x* = *z* = 0; *y* = 1) the resulting material [PH₂–BH₂]_n would be completely inorganic. However significant amounts of carbon and a deficiency of hydrogen was detected by elemental analysis, suggesting the formation of a more complex, cross-linked product resulting from simultaneous H₂ and Mes*OH elimination [Anal. Calc. for {(Mes*O)_xRPH_y–BH_(2x+2y+z)]_n, *x* = 0.085, *y* = 0, *z* = 0.915: C, 28.85, H, 7.21. Found: C, 28.75, H, 6.62%]. Moreover, IR spectroscopy confirmed the presence of carbon within **7** (in the form of Mes*O groups) as many bands were observed between 900 and 1200 cm⁻¹. The presence of B–H groups was also

detected by IR with B–H stretching modes detected at 2267 and 2384 cm⁻¹.

In order to further characterize **7**, solid state NMR spectroscopy was performed. The ¹³C CP-MAS NMR spectrum of **7** also supported the presence of Mes*O groups as the relevant aromatic and *t*-Bu resonances were observed. The ³¹P CP-MAS NMR spectrum of **7** was highly complex with a large number of signals between δ 100 and –200. The low field signals above δ 60 have similar chemical shift values as **1** (δ 80) and imply the presence of a similar chemical environment (namely a Mes*O group bonded to phosphorus). Resonances observed in the high field region of the spectrum, around δ –100, suggest the presence of B–PH₂–B environments (e.g. ³¹P chemical shift of [PhPH–BH₂]_n is –34.7 ppm).^{11,12} The signals which lie intermediate to the above mentioned resonances could represent P–P (or B–P) environments resulting from cross-linking reactions, however it is difficult to speculate further about the exact assignments of these signals as P–P bonded species exhibit widely varying chemical shifts^{24,25} [e.g. P₄, δ –549; (PhP)₅, δ –4]. The ¹¹B CP-MAS NMR spectrum of **7** was relatively straightforward with two clearly identifiable boron resonances at δ 3 and –42 respectively, consistent with four-coordinate boron environments. The signal at δ –42 is similar to previously reported ¹¹B NMR chemical shifts belonging to PBH₂P environments within polyphosphinoborane polymers ([PhPH–BH₂]_n, δ –34.0; [iBuPH–BH₂]_n, δ –36.3¹²), while the signal at δ 3 suggests the presence of an electro-negative atom such as oxygen at boron (possibly Mes*O–B).²⁰ Despite the complexity of **7**, the thermolysis of **1** remains significant as it represents an attempt to understand a potentially new inorganic bond-forming reaction involving the elimination of a phenol. All attempts to induce dehydrogenative coupling of **1** in toluene using Rh^I and Ir^I dehydrocoupling catalysts¹² only gave similar phenol elimination reactions as described above with equally complex and insoluble byproducts.

In light of the surprisingly facile phenol elimination reaction involving **1**, we also investigated the thermal stability of the analogous phenylated derivative, (Mes*O)PhPH·BH₃ **3**. We anticipated that if phenol elimination occurred in preference to H₂ elimination (dehydrocoupling), then the anticipated product, [PhPH₂–BH₂]_n, could be easily identified as this polymer has been characterized in detail by our group.^{11,12}

When a sample of **3** was heated to 140 °C (mp of **3**: 128–9 °C) in a sublimation apparatus, large white needles were observed on the water-cooled probe. As with **1**, these crystals were identified as Mes*OH by ¹H NMR spectroscopy and mass spectrometry. Prolonged heating (5 d) produced more phenol (~ 0.9 mole equivalents, *x* = 0.1 according to Scheme 2) along with an involatile glassy yellow solid, **8**, at the bottom of the sublimation apparatus. In this case, the glassy residue was found to be highly soluble in most organic solvents. Analysis of **8** by ³¹P{¹H} NMR spectroscopy was consistent with the presence of a highly complex material with a wide range of signals detected from δ 100 to –120. The ¹H NMR spectrum of **8** showed the presence of a broadened signal from δ 6 to 8 (phenyl groups), a series of broad resonances (δ 1.3–1.5) due to the *t*-Bu groups of the Mes*O moiety and a broad halo at δ 0.5–1.5 due to BH₂ protons. This product therefore seemed to be equally



Scheme 2 Thermolysis of **1** and **3**.

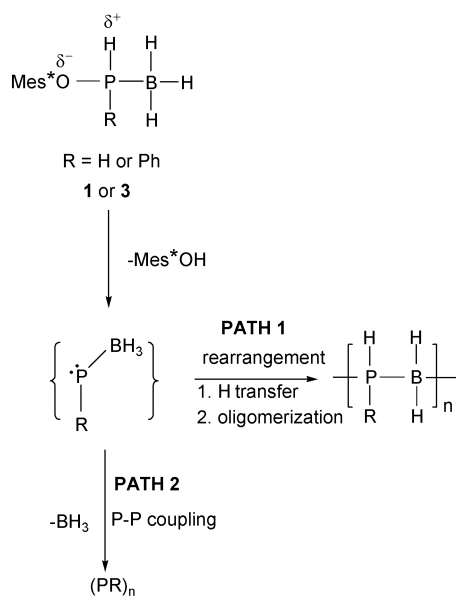
complex as **7**, and consequently further exploration of this reaction was not performed.

Thermolysis of (Mes*O)Ph₂P·BH₃ **5** and (PhO)₃P·BH₃ **6** at elevated temperatures

In the experiments described above, elimination of Mes*OH was found to be less facile for the more sterically encumbered phenyl-substituted derivative, **3**, (5 d at 140 °C, *ca.* 90% conversion) compared to the less sterically congested primary phosphinite–borane adduct **1** (3 d at 100 °C, *ca.* 90% conversion). To further examine whether phenol elimination was dependant on steric effects and to determine if the presence of a P–H bond was required, thermolysis experiments involving the sterically encumbered diphenyl-substituted phosphinite–borane adduct **5** and phosphite–borane **6** were also performed.

When a sample of **5** was heated to 110 °C (melting point of **5**: 103–4 °C) for one week, no change was detected by ¹H and ³¹P NMR spectroscopy. Increasing the temperature of the thermolysis to 160 °C led to the decomposition of **5**, however only P–B bond cleavage occurred to form the free phosphinite **4** (¹H and ³¹P NMR) and BH₃ (by inference), with no trace of Mes*OH detected by ¹H NMR. Again, as with the thermolysis of **1** and **3**, no catalytic effect was observed when **5** was heated in the presence of a rhodium catalyst, [Rh(μ-Cl)(1,5-cod)]₂.

We also investigated the thermolysis of **6** as Chopard and co-workers reported the production of one equivalent of phenol when a sample was heated in triglyme (130–140 °C).²⁶ However, our attempts to induce phenol elimination from **6** in tetraglyme (140 °C) gave exclusively P–B bond cleavage with no phenol formation. We subsequently heated a neat sample of **6** to 140 °C for eight days, and again only observed complete dissociation of the adduct to the free phosphite, (PhO)₃P, without formation of phenol. As there are previously reported examples of α-elimination of HX (where X = electronegative element/group) from halophosphine precursors, R(X)PH, to give cyclophosphanes (RP)_n,²⁷ it appears that such a mechanism could be responsible for the elimination of Mes*OH from **1** and **3** (Scheme 3). However in the case of **1** and **3**, many more



Scheme 3 Potential thermolysis pathways for **1** and **3**.

decomposition pathways are potentially available as the phosphorus–boron intermediate [RP·BH₃] could undergo rearrangement reactions to give polyphosphinoboranes (path 1) or simply decompose to form (RP)_n and free borane (path 2). By CP-MAS NMR, it appears that pathways 1 and 2 occur simultaneously to give insoluble (in the case of **7**), cross-linked products with a complex structure.²⁸

Conclusion

A new class of phosphinite–borane adducts containing the bulky 2,4,6-*t*-Bu₃C₆H₂O (Mes*O) group was prepared and we describe the structural characterization of the first primary phosphinite–borane adduct **1** which is stable at ambient temperature. Attempts to induce dehydrocoupling of **1** and the phenylated analogue **3**, resulted in an unexpected phenol elimination reaction to produce Mes*OH along with cross-linked materials with complex structures (**7** and **8**). These results indicate that dehydrocoupling of phosphinite–borane adducts does not proceed as cleanly as with phosphine–borane species. Attempts to initiate phenol elimination from the tertiary adducts **5** and **6** produced exclusively P–B bond cleavage. These results suggest that phenol formation occurs *via* an α-elimination pathway.

Experimental

General procedures

All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen (Matheson) using either Schlenk techniques or an inert atmosphere glove box (Innovative Technology). All solvents were dried and distilled using standard methods prior to use. Solution ¹H NMR spectra were obtained on a Varian Gemini 300 spectrometer (300.1 MHz) and referenced to protio impurities in the solvent. Solution ³¹P, ¹³C{¹H} and ¹¹B NMR spectra were also obtained using a Gemini 300 spectrometer (122.1, 75.5 and 96.6 MHz) and referenced externally to 85% H₃PO₄, SiMe₄ (TMS) and BF₃·OEt₂ respectively in either CDCl₃ or D₂O (insert). Solid-state CP-MAS NMR spectra were obtained on a Bruker DSX-400 (¹³C at 100.6 MHz) or Bruker DSX-200 (¹¹B at 64.2 MHz, ³¹P at 81.0 MHz) spectrometers and referenced to adamantane (¹³C, δ 38.4 *vs.* TMS), 85% H₃PO₄ (³¹P) or NaBH₄ (¹¹B, δ –42.0 *vs.* BF₃·OEt₂).²⁹ Solid-state ¹¹B NMR spectra of **7** were also run as 90°-τ–180° spin-echo experiments, where τ is one rotor period. Mass spectra were obtained with the use of a VG 70–250S mass spectrometer using a 70 eV electron impact ionization source. Melting points (uncorrected) were obtained under a nitrogen atmosphere in flame sealed capillaries (0.5 mm o.d.). Infrared spectra were obtained as Nujol mulls between KBr plates with a Nicolet Magna-IR 550 spectrometer. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. PhPCl₂ (Aldrich) was vacuum distilled prior to use. Ph₂PCl, BH₃ (1.0 M solution in THF), (PhO)₃P and [Ir(1,5-cod)]₂[OTf] (1,5-cod = cycloocta-1,5-diene) were obtained from Aldrich and used as received. 2,4,6-*t*-Bu₃C₆H₂OLi·OEt₂ (Mes*OLi·OEt₂),³⁰ Mes*OPCl₂,¹⁸ (PhO)₃P·BH₃,³¹ and [Rh(μ-Cl)(1,5-cod)]₂³² were prepared according to literature methods.

Preparation of (Mes*O)PH₂·BH₃ **1.** A pale yellow solution of Mes*OPCl₂ (5.01 g, 13.8 mmol) in THF (25 mL) was added dropwise to a suspension of Li[BH₄] (0.61 g, 28 mmol) in 100 mL of THF at 0 °C. The reaction was warmed to room temperature and stirred for 16 h giving a clear, colorless solution. The volatiles were removed under reduced pressure and the residue was extracted with hexanes (100 mL) and filtered through Celite. Removal of the hexanes afforded a white solid when vacuum dried (4.24 g, 100%). Dissolution of the product in a minimum amount of toluene (*ca.* 0.2 g mL⁻¹) and cooling to –30 °C for 3 weeks produced small, colorless crystals (blocks) suitable for a single crystal X-ray diffraction study. ¹H NMR (CDCl₃): δ 0.5–1.5 (br, BH₃, 3H), 1.36 (s, *para* *t*-Bu, 9H), 1.50 (s, *ortho* *t*-Bu, 18H), 6.73 (d of q, PH₂, ¹J_{PH} = 399 Hz, ³J_{HH} = 6.6 Hz, 2H) and 7.33 (s, Ar–H, 2H). ³¹P NMR (CDCl₃): δ 78.9 (t, PH₂, ¹J_{PH} = 389 Hz). ¹¹B{¹H} NMR (CDCl₃): δ –41.9 (br). ¹³C{¹H} NMR (CDCl₃): δ 31.6 (s), 31.8 (s), 32.7 (s), 36.4 (s), 124.8 (d, *J* = 2 Hz), 140.5 (d, *J* = 4 Hz), 147.0 (d, *J* = 1 Hz) and 151.7 (d, *J* = 23 Hz). MS 70 eV, EI (*m/z*, %): 294

($M^+ - BH_3$, 26), 279 ($M^+ - BH_3 - Me$, 40), 57 ($t-Bu^+$, 100). mp 92–3 °C (dec).

Preparation of (Mes*O)PhPCl₂ 2. A clear solution of PhPCl₂ (5.0 g, 28 mmol) in diethyl ether (10 mL) was added dropwise to a cooled (0 °C) pale yellow suspension of Mes*OLi·OEt₂ (9.00 g, 26.3 mmol) in 125 mL of diethyl ether. The reaction mixture was warmed to room temperature and stirred for 16 h to give a clear yellow solution over a white precipitate. The volatiles were removed, and the resulting residue was extracted with hexanes (100 mL) and filtered through Celite. Removal of the hexanes afforded **2** as a pure white solid when vacuum dried (9.52 g, 89%). ¹H NMR (CDCl₃): δ 1.38 (s, *para* t-Bu, 9H), 1.50 (s, *ortho* t-Bu, 18 H), 7.35 (s, Ar–H, 2H), 7.5–7.9 (m, Ph–H, 5H). ³¹P{¹H} NMR (CDCl₃): δ 177.1 (s). ¹³C{¹H} NMR (CDCl₃): δ 31.8 (s), 33.9 (d, *J* = 5 Hz), 34.7 (s), 36.7 (s), 124.9 (d, *J* = 2.0 Hz), 128.9 (d, *J* = 6.0 Hz), 130.1 (d, *J* = 26 Hz), 131.4 (s), 141.5 (d, *J* = 4 Hz), 141.8 (s), 142.3 (s), and 145.4 (d, *J* = 2 Hz). MS 70 eV, EI (*m/z*, %): 404 (M^+ , 49), 347 ($M^+ - t-Bu$, 10), 57 ($t-Bu^+$). HR-MS: Calc.: 404.2044. Found: 404.2036.

Preparation of (Mes*O)PhPH·BH₃ 3. A clear yellow solution of **2** (6.13 g, 15.1 mmol) in THF (20 mL) was added dropwise to a cold (0 °C) suspension of Li[BH₄] (0.33 g, 15 mmol) in 100 mL of THF. The reaction mixture was warmed to room temperature and stirred for 16 h to give a clear colorless solution. The volatiles were removed, and the resulting residue was extracted with hexanes (75 mL) and filtered through Celite. Removal of the hexanes afforded a white solid when vacuum dried (4.16 g, 72%). Crystals of **3** (large colorless plates) suitable for a single-crystal X-ray diffraction study were obtained by cooling a solution in toluene (0.3 g mL⁻¹) to –30 °C for one week. ¹H NMR (CDCl₃): δ 1.31 (s, *ortho* t-Bu, 18H), 1.34 (s, *para* t-Bu, 9H), 7.22 (s, Ar–H, 2H), 7.51 (d of q, PH, ¹*J*_{PH} = 403 Hz, ³*J*_{HH} = 5.4 Hz, 1H), 7.3–7.5 (m, PhH, 5H). ³¹P NMR (CDCl₃): δ 99.1 (d, PH, ¹*J*_{PH} = 413 Hz). ¹¹B{¹H} NMR (CDCl₃): δ –40.7 (d, BH₃, ¹*J*_{BP} = 47 Hz). ¹³C{¹H} NMR (CDCl₃): δ 31.8 (s), 32.7 (s), 34.8 (s), 36.3 (s), 124.4 (d, *J* = 2 Hz), 128.6 (d, *J* = 10 Hz), 133.4 (d, *J* = 1 Hz), 134.1 (d, *J* = 31 Hz), 141.3 (d, *J* = 3 Hz), 146.5 (d, *J* = 1 Hz), 148.5 (s), and 148.7 (s). MS 70 eV, EI (*m/z*, %): 370 ($M^+ - BH_3$, 7), 355 ($M^+ - Me - BH_3$, 5), 299 ($M^+ - BH_3 - Me - t-Bu$, 22), 257 ($M^+ - Me - 2 t-Bu$, 38), 57 ($t-Bu^+$, 100). mp 128–9 °C (dec). Anal. Calc. for C₂₄H₃₈BOP (384.3): C, 75.00. H, 9.97. Found: C, 74.85. H, 9.88%.

Preparation of (Mes*O)Ph₂P 4. In a similar procedure as for **2**, a pale yellow solution of Ph₂PCl (8.1 mL, 45 mmol) in 25 mL of Et₂O was added dropwise to a suspension (0 °C) of Mes*OLi·OEt₂ (15.35 g, 44.8 mmol) in 150 mL of Et₂O. Work-up of the reaction mixture after 16 h gave a colorless solid in high yield (18.23 g, 91%). ¹H NMR (CDCl₃): δ 1.25 (s, *ortho* t-Bu, 18H), 1.36 (s, *para* t-Bu, 9H), 7.21 (s, Ar–H, 2H), 7.35 (m, Ph–H, 10H). ³¹P{¹H} NMR (CDCl₃): δ 127.3 (s). ¹³C{¹H} NMR (CDCl₃): δ 31.8 (s), 33.0 (d, *J* = 5 Hz), 34.6 (s), 38.4 (s), 123.9 (s), 128.2 (d, *J* = 6 Hz), 129.8 (s), 132.5 (d, *J* = 22 Hz), 139.3 (d, *J* = 27 Hz), 141.6 (d, *J* = 4 Hz), 143.7 (d, *J* = 2 Hz), 150.8 (d, *J* = 8 Hz). MS 70 eV, EI (*m/z*, %): 446 (M^+ , 35), 431 ($M^+ - Me$, 4), 389 ($M^+ - t-Bu$, 85), 355 ($M^+ - C_7H_7$, 40), 185 (Ph₂P⁺, 100). mp 95–7 °C. HR-MS: Calc.: 446.2739. Found: 446.2732.

Preparation of (Mes*O)Ph₂P·BH₃ 5. BH₃ (19.0 mL, 1.0 M solution in THF, 19.0 mmol) was added dropwise to a cold (0 °C), pale yellow solution of **4** (8.34 g, 18.7 mmol) in 100 mL of THF. The reaction was warmed to room temperature and stirred for 24 h. The resulting clear and colorless solution was concentrated to 20 mL and cooled to –30 °C for 6 d affording large colorless blocks suitable for a single-crystal X-ray structure determination (6.27 g, 73%). ¹H NMR (CDCl₃): δ 1.15 (s, *ortho* t-Bu, 18H), 1.34 (s, *para* t-Bu, 9H), 7.19 (s, Ar–H, 2H), 7.45 and 7.78 (m, Ph–H, 10H). No BH₃ protons were detected

in the ¹H NMR spectrum. ³¹P{¹H} NMR (CDCl₃): δ 111.0 (s). ¹¹B{¹H} NMR (CDCl₃): δ –38.6 (br). ¹³C{¹H} NMR (CDCl₃): δ 31.8 (s), 33.0 (s), 34.6 (s), 36.7 (s), 124.0 (d, *J* = 2 Hz), 128.5 (d, *J* = 11 Hz), 132.0 (d, *J* = 2 Hz), 132.9 (d, *J* = 11 Hz), 142.4 (d, *J* = 4 Hz), and 145.7 (d, *J* = 2 Hz); *Ispo* C were not detected. MS 70 eV, EI (*m/z*, %): 446 ($M^+ - BH_3$, 37), 389 ($M^+ - BH_3 - t-Bu$, 90), 431 ($M^+ - BH_3 - Me$, 5), 355 ($M^+ - BH_3 - C_7H_7$, 40), 185 (Ph₂P⁺, 100). mp 103–4 °C. Anal. Calc. for C₃₀H₄₂BOP (460.4): C, 78.26. H, 9.19. Found: C, 78.35. H, 8.88%.

Preparation of (PhO)₃P·BH₃ 6. The adduct was prepared in quantitative yields by a similar manner as described by Pelter *et al.*³¹ Crystals (colorless plates) suitable for a single-crystal X-ray diffraction study were grown from a concentrated solution of the adduct in THF (1 g mL⁻¹) at –30 °C (2 d). ¹H NMR (CDCl₃): δ 0.3–1.2 (q, BH₃, ¹*J*_{BH} = ~ 100 Hz, 3H), 7.2–7.4 (m, Ph–H, 15 H). ³¹P{¹H} NMR (CDCl₃): δ 108.0 (pseudo-quartet, ¹*J*_{PB} = 90 Hz). ¹¹B{¹H} NMR (CDCl₃): δ –42.7 (d, ¹*J*_{BP} = 82 Hz). ¹³C{¹H} NMR (CDCl₃): δ 121.1 (d, *J* = 8 Hz), 126.1 (s) and 130.1 (s); *Ispo* C not detected. MS 70 eV, EI (*m/z*, %): 310 ($M^+ - BH_3$, 37), 217 ($M^+ - BH_3 - PhOH$, 100), 94 (PhOH, 7).

Thermolysis of 1: elimination of Mes*OH. Compound **1** (5.05 g, 16.4 mmol) was heated to 100 °C (under N₂) in a sublimation apparatus. Within minutes of heating, white needles of Mes*OH could be seen on the water-cooled cold finger. A white liquid was seen at the bottom of the sublimation apparatus, which slowly became yellow and solidified upon prolonged heating. After 24 h at 100 °C, the apparatus was cooled and the yellow residue was ground in a mortar and heated again at 100 °C for a further 2 d. This produced a further crop of Mes*OH. The yellow material which remained was placed in a Soxlet apparatus (under nitrogen) and extracted continuously with hexanes (250 mL) for 3 d to give a pale yellow insoluble powder, **7**, (0.73 g, 54% yield based on amount of Mes*OH produced) along with more Mes*OH as part of the soluble fraction (total amount of Mes*OH recovered = 3.7 g; *ca.* 0.9 mole equivalents, identified by ¹H and ¹³C{¹H} NMR spectroscopy and mass spectrometry). The insoluble product (**7**) was characterized by solid-state CP-MAS NMR, IR and elemental analysis (C and H).

Data for **7**: Solid-state ³¹P CP-MAS (200 MHz, 8.5 KHz spin rate): δ –183, –119, –82, 0.7, 67 and 91. Solid-state ¹¹B CP-MAS NMR (200 MHz, 8.5 KHz spin rate): δ –42 and 3 (four-coordinate boron environments). Solid-state ¹³C CP-MAS NMR 400 MHz, 6.5 KHz spin rate): δ 31, 34 and 36 (*t-Bu*, Mes*O), 124, 128, 141, 146 and 150 (aromatic, Mes*O). IR (*v*_{max}, cm⁻¹): 3209s, 2384m (*v* B–H), 2267w (*v* B–H), 1262w, 1102m, 1025w, 967vw, 917w, 881w, 797s, 788s, 729m, 696w, 677w, 649m, 550w. Anal. Calc. for [(Mes*O)_xRPH_y–BH_z]_{(2x + 2y + z)_n, *x* = 0.085, *y* = 0, *z* = 0.915]: C, 28.85. H, 7.21. Found: C, 28.75. H, 6.62%.}

Data for Mes*OH: ¹H NMR (CDCl₃): δ 1.38 (s, *para* t-Bu, 9H), 1.49 (s, *ortho* t-Bu, 18H), 5.09 (s, OH, 1H), 7.26 (Ar–H, 2H). ¹³C{¹H} NMR (CDCl₃): δ 30.7 (s), 32.0 (s), 34.8 (s), 34.7 (s), 122.1 (s), 135.2 (s), 141.7 (s) and 151.6 (s). MS 70 eV, EI (*m/z*, %): 262 (M^+ , 100).

Attempts to induce dehydrocoupling of **1** (150–200 mg) were also conducted in toluene (100 °C, 2–3 mL) in the presence of *ca.* 5 mol% [{Rh(μ-Cl)(1,5-cod)}₂], *ca.* 5 mol% [Ir(1,5-cod)₂][OTf] and in the absence of transition metal complexes. In all cases, **1** eliminated Mes*OH (0.8–0.9 equivalents) to give insoluble yellow or brown (in the presence of catalyst) solids with no evidence of clean dehydrocoupling.

Thermolysis of 3: elimination of Mes*OH. Compound **3** (4.95 g, 12.9 mmol) was heated to 140 °C for 5 d (under N₂) in a sublimation apparatus. Upon heating the adduct melted to give a colorless liquid and white needles of Mes*OH could be seen on the cold finger (water-cooled). As heating was continued, the

colorless liquid gradually became pale yellow and eventually solidified to give a glassy residue **8** (1.52 g, 79% yield based on the amount of Mes*OH isolated). Mes*OH (3.03 g, ~ 0.9 mole equivalents) was also recovered and characterized by ¹H NMR spectroscopy. Compound **8** was found to be highly soluble in chlorinated solvents, THF, toluene and sparingly soluble in hexanes. ¹H NMR (CDCl₃): δ 0.5–1.5 (br, BH₂), 1.32, 1.34 and 1.48 (t-Bu, Mes*O), 6.8–7.6 (br, Ph). ³¹P{¹H} NMR (CDCl₃): many signals from δ –120 to 100. ¹¹B{¹H} NMR (CDCl₃): δ –30 (very broad). ¹³C{¹H} NMR (CDCl₃): δ 30.9, 32.0, 32.2, 33.0, 35.0 and 36.5 (t-Bu, Mes*O), 122.0, 124.2, 127.5–129 (many signals), 133.1, 133.8, 134.0 and 135.0 (aromatic, Mes*O).

Thermolysis of 5 and 6: P–B bond cleavage without phenol formation. Adducts **5** and **6** were heated for extended periods of time under nitrogen, and the reaction progress was followed by ³¹P{¹H} NMR. Representative examples are described below.

A sample of **5** was heated to 160 °C for 7 d. Analysis of the remaining solid indicated complete dissociation of **5** [³¹P{¹H} NMR: δ 111 (s)] into the free phosphinite **4** [³¹P{¹H} NMR: δ 127 (s)] and volatile diborane (by inference). The ¹H NMR spectrum consisted exclusively of resonances attributed to the formation of **4**. Similar results were obtained when the experiment was repeated in the presence of *ca.* 5 mol% [{Rh(μ-Cl)-(1,5-cod)}₂].

A sample of **6** was heated to 140 °C for 8 d. Analysis of the remaining pale beige oil indicated complete dissociation of **6** [³¹P{¹H} NMR: δ 108 (pseudo-quartet)] into the free phosphite, (PhO)₃P [³¹P{¹H} NMR: δ 129 (s)], and presumably volatile diborane. The ¹H NMR spectrum consisted exclusively of resonances attributed to the formation of (PhO)₃P. Thermolysis experiments in tetraglyme (140 °C) and in the presence of *ca.* 5 mol% [{Rh(μ-Cl)(1,5-cod)}₂] yielded similar results after 5 d.

Single-crystal X-ray structural determination of 1, 3, 5 and 6. Diffraction data were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). A combination of 1° φ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.³³ The structures were solved and refined with the SHELXTL-PC v5.1 software package.³⁴ Refinement was by full-matrix least squares on F² using all data (including negative intensities). In all structures, hydrogen atoms bonded to carbon atoms were included in calculated positions and treated as riding atoms. The disorder within the *para* t-Bu-groups in **1** were modeled with an 87/13 occupancy. Data collection and refinement parameters are summarized in Table 2.

CCDC reference numbers 181265–181268.

See <http://www.rsc.org/suppdata/dt/b2/b202361j/> for crystallographic data in CIF or other electronic format.

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