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The Phosphinoboration Reaction**

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Abstract: *The synthesis of phosphinoboronate esters containing a single P–B bond is reported, together with preliminary reactivity studies towards a range of organic substrates. These compounds add readily to aldehydes, ketones, aldimines, and α,β-unsaturated enones to give primarily the corresponding 1,2-addition products containing a new P–C bond. The first examples of transition-metal-catalyzed phosphinoborations of C-C multiple bonds in which P–C and B–C bonds are formed in a single step are also disclosed; allenes react by a highly regioselective 1,2-addition whereas terminal alkynes undergo a formal 1,1-addition.*

Over the past decade, the transition-metal-catalyzed addition of boron–element bonds (E–B, where E = H,[1] B,[2] Sn,[3] Si,[4] S,[5] Se,[6]) to unsaturated compounds has received a considerable amount of attention. Hydroboration (E = H) is a remarkably powerful and useful reaction in organic synthesis, but generally leads to the functionalization of only one of the sites of unsaturation. Diboration (E = B) and borylation (replacing a H atom bound to an sp^2-hybridized C atom with a BR_2 group) are finding increasing use in organic synthesis,[7] but these reactions generally either functionalize the two sites equivocally or sacrifice one of the boryl (BR_2) groups. In pioneering studies, Morken and coworkers developed the catalytic asymmetric diboration of alkenes and allenes, and the differential reactivity of the B–C bonds in the resulting diboron intermediates has been used to develop tandem reaction sequences.[8] Reactions with heavier main-group elements (E = Se, Sn, Si, etc.) usually result in organodimetalloid compounds, which are highly versatile building blocks that are otherwise difficult to synthesize. Of these transformations, the silaboration of C–C multiple bonds is particularly promising as the resulting silyl and boryl groups can be independently transformed into different functional groups. Given the intensity of interest in the reactivity of E–B bonds it is somewhat surprising that relatively little is known about the analogous addition chemistry of compounds containing single E–B bonds where E is either nitrogen[9] or phosphorus. In this regard, a recent report of the regioselective and stereospecific aminoboration of styrenes actually involved a copper-catalyzed borylation with B_2pin_2 followed by an electrophilic amination with an *O*-benzoyl-*N*,*N*-dialkylhydroxylamine.[9a] The corresponding phosphinoboration would introduce a P–C bond and a reactive B–C bond, which could be further functionalized to provide access to a host of useful structural motifs and is also a worthy target as such. Even though there has been a tremendous amount of research on generating new phosphinoboron compounds in recent years because of their interesting structure,[10] potential applications in frustrated Lewis pair (FLP) chemistry,[11] and their use as ambiphilic ligands for transition metals,[12] there appears to be only a single report of phosphinoboration-type reactivity.[13] In a particularly elegant study, Lerner and coworkers recently demonstrated that a phosphinoborane derived from the salt elimination reaction between 9-bromo-9-borafulvalene and Li[P*t*Bu$_2$] reacted with 2,3-dimethylbutadiene to give the corresponding [4+2] Diels–Alder adduct in moderate yields and underwent 1,2-addition to benzophenone to afford the corresponding phosphinoborinic ester.[13] Using these lead studies and because of our interest in developing application-based phosphinoboration reactions as a synthetic method, we initiated a program to investigate the synthesis and reactivity of phosphinoboronate esters.

The phosphinoboronate esters R_2PBpin (**1** and **2**) required for this investigation were prepared in moderate to good yields (75 and 46%, respectively) by the addition of commercially available pinBO*i*Pr (pin = 1,2-pinacolato) to Li[PR_2]. Compound **1** displays a single broad peak in both the $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra at 34 and −63.5 ppm, respectively. Phosphinoboronate ester **1** was also characterized by a single-crystal X-ray diffraction study; its molecular structure is shown in Figure 1. The P–B bond length of 1.9274(14) Å suggests this is a single bond, and that there is a negligible π-dative interaction between the phosphorus lone pair and the empty orbital on the boron atom. For instance, the distances of 1.9882(17) Å[13] and 1.9512(2) Å[14] in a phosphaboradibenzofulvene-derived cycloadduct reported by Lerner and in 9,10-dihydro-9-phospha-10-boraphenanthrene, respectively, are both markedly similar to the P–B bond

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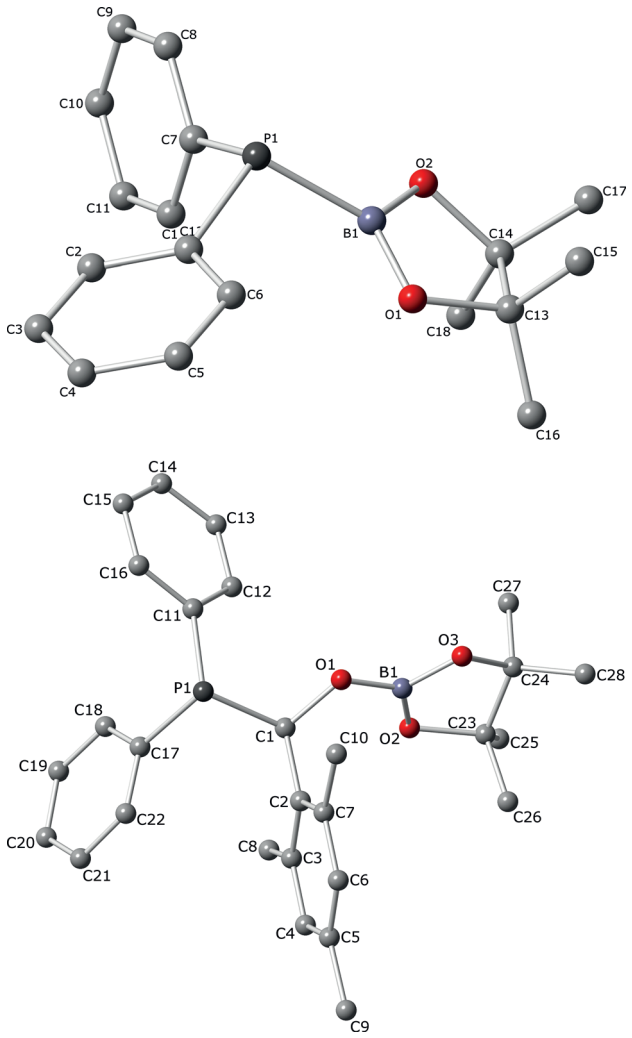
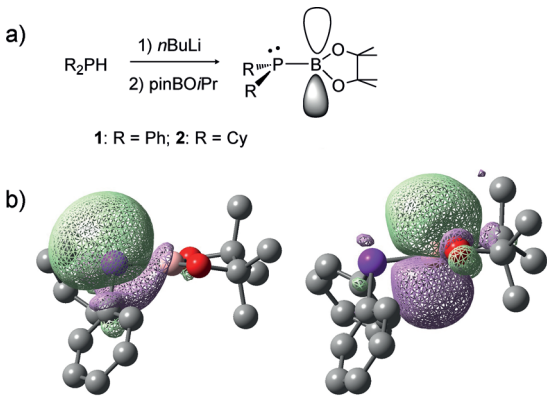


Figure 1. Molecular structures of **1** (top) and **5** (bottom) with hydrogen atoms omitted for clarity. Selected bond distances [Å] for **1**: P(1)–B(1) 1.9274(14), B(1)–O(1) 1.3612(16), B(1)–O(2) 1.3618(17); for **5**: P(1)–C(11) 1.8329(14), P(1)–C(17) 1.8455(14), P(1)–C(1) 1.8796(14), B(1)–O(1) 1.3583(19), B(1)–O(3) 1.3649(19), B(1)–O(2) 1.3719(19), C(1)–O(1) 1.4485(16).

length in **1**. Likewise, the P–B bond distances in a series of structurally related phosphines with N-heterocyclic boranyl substituents range from 1.923(2) to 1.953(2) Å; all of these compounds are considered to contain single P–B bonds.[15] The P–B bond in **1** has been investigated at the wb97xd/6-311 g(2d,p) level of theory, and the calculated structure ($\mathbf{1}_{calc}$) is an excellent match to that obtained by X-ray crystallography. In particular, the P–B bond length of 1.9274(14) Å in **1** is extremely close to the corresponding distance of 1.9269 Å in $\mathbf{1}_{calc}$. Natural bond orbital (NBO) analysis indicates that the phosphorus lone pair (HOMO-4) has $sp^{1.31}$ character with an occupancy of 1.87 electrons while the LUMO lies 12.3 eV higher in energy and is a vacant boron-based orbital of essentially pure p orbital character (Scheme 1). This finding is entirely consistent with the absence of any significant donor–acceptor interactions between the phosphorus and boron atoms as indicated by a Wiberg bond index of 1.028 for the P–B bond and a stabilization of only 8.1 kcal mol^{-1} for the



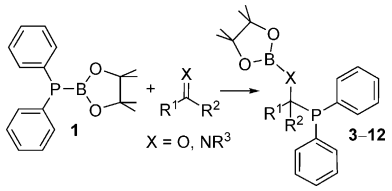
Scheme 1. a) Synthesis of phosphinoboronate esters. b) HOMO and LUMO of $\mathbf{1}_{calc}$ showing the phosphorus lone pair and the vacant p orbital on the boron atom.

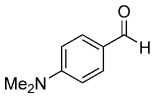
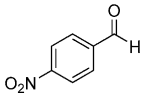
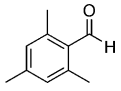
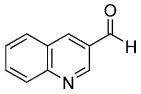
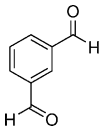
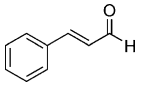
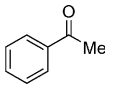
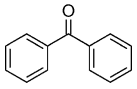
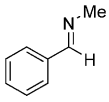
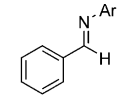
interaction between the phosphorus lone pair and the vacant boron-based p orbital (NBO deletion). Not surprisingly, **1** is stabilized by significant donor–acceptor interactions between the oxygen lone pairs and the vacant boron-based p orbitals; these were determined to each be worth 37 kcal mol^{-1}. In stark contrast, the corresponding computational study on $(t\mathrm{Bu})_2\mathrm{P}{-}\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_2$ revealed substantial P–B multiple bonding with a donor–acceptor interaction between the phosphorus lone pair and the vacant boron orbital providing 89.6 kcal mol^{-1} of stabilization.[16]

Preliminary reactivity studies revealed that **1** readily adds to an electronically and sterically diverse range of aldehydes at room temperature within several hours to afford the corresponding α-phosphinoboronate esters **3**–**8** in excellent yield (Table 1, entries 1–6). Whereas spectroscopic and analytical data for **3**–**8** are entirely consistent with 1,2-addition, the identity of **5** was unequivocally confirmed by a single-crystal X-ray diffraction study; its molecular structure is shown in Figure 1. The long C(1)–O(1) bond distance of 1.4485(16) Å illustrates that the double bond has been reduced. Interestingly, **1** also reacted with *trans*-cinnamaldehyde exclusively by 1,2-addition to afford **8** in high yield (entry 6). Whereas **1** reacted smoothly with ketones (entries 7 and 8) and aldimines (entries 9 and 10), markedly longer reaction times (18 h) were required to reach comparable conversions. A comparative study revealed that phosphinoboronate ester **2** reacted in the same manner to afford the corresponding dicyclohexane-based phosphine products in good yields after similar reaction times. In contrast, although catechol-derived Ph_2PBcat (**13**) also reacted similarly to give 1,2-addition products, minor amounts of degradation products were also observed, presumably arising from redistribution of the catecholato group.[1a]

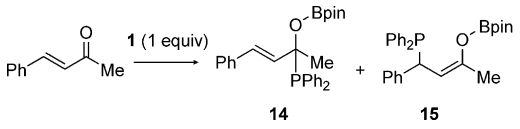
Encouraged by the efficacy and high selectivity of the addition to *trans*-cinnamaldehyde, the study was extended to include the addition of **1** to α,β-unsaturated ketones. The analogous E–B additions have been thoroughly studied, and a transition-metal catalyst or a strong base is typically required to affect these transformations.[17] We were therefore somewhat surprised to find that **1** readily added to *trans*-4-phenyl-3-buten-2-one at either ambient or even low temper-

Table 1: Phosphinoboration of aldehydes, ketones, and aldimines.



Entry	Substrate[a]	Compound	*t* [h]	Yield[b] [%]
1		**3**	12	93
2		**4**	12	92
3		**5**	12	91
4		**6**	12	78
5		**7**	18	94
6		**8**	12	87
7		**9**	18	89
8		**10**	18	94
9		**11**	18	95
10	 Ar = 4-MeOC$_6$H$_4$	**12**	18	92

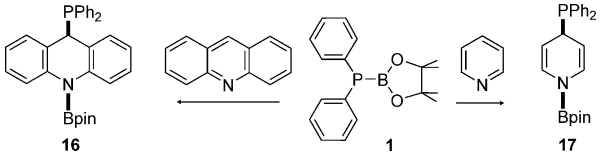
[a] Reactions were carried out in toluene at room temperature. [b] Yields of isolated products.



Scheme 2. Phosphinoboration of *trans*-4-phenyl-3-buten-2-one.

ature in the absence of any additive (Scheme 2). Interestingly, optimization studies revealed that both solvent and temperature had a profound influence on product distribution. For example, reactions in chloroform at room temperature favoured 1,4-addition to afford **15** whereas the same reaction conducted in chloroform at −30 °C resulted in a complete reversal in selectivity favoring 1,2-addition to give **14** as the major product. Reactions conducted in non-halogenated solvents gave **14** as the main product along with varying amounts of **15** (see the Supporting Information). Further studies are currently underway to develop a full understanding of this reaction with the aim of identifying optimal conditions and expanding the range of substrate combinations.

The addition of **1** to acridine also occurred with remarkable efficiency at room temperature to afford the unusual 1,4-addition product **16** as the only new phosphorus-containing species (Scheme 3). Compound **16** has a distinct signal at $\delta =$ 23 ppm in the ^{11}B NMR spectrum, which is diagnostic for an NBO_2 environment while the ^{1}H NMR spectrum contains a doublet at $\delta = 4.68$ ppm ($J_{HP} = 5$ Hz), which is characteristic of the saturated ring carbon atom bound to the PPh_2 group. The identity of **16** as the *syn* 1,4-addition adduct was confirmed by a single-crystal X-ray study; its molecular structure is shown in Figure 2. More remarkable, however, is the observation that **1** adds selectively to pyridine at room temperature and in the absence of a metal catalyst to give the 1,4-addition product **17**. The significance of reducing quinoline and pyridine derivatives has recently been documented,[18] and the generation of aminophosphines is of singular importance for their use as a privileged class of ligands in transition-metal catalysis.[19]



Scheme 3. Addition of **1** to acridine and pyridine.

Finally, we also examined the addition of phosphinoboronate ester **1** to unsaturated carbon–carbon bonds. Whereas no reaction was observed under conventional conditions in the absence of catalyst, the use of 5 mol% of either [RhCl(PPh$_3$)$_3$] or [Rh(η^6-catBcat)(dppp)][20] (dppp = 1,3-bis(diphenylphosphino)propane) enabled the addition of **1** to allenes and terminal alkynes within two hours at room temperature (Scheme 4). For instance, the rhodium-catalyzed reaction between **1** and cyclohexylallene resulted in regioselective 1,2-addition to afford **18** as the major product, with the boron atom attached to the terminal carbon atom. A similar 1,2-addition product was also observed in reactions of **1** with 3-(trimethylsilyl)-1,2-butadiene. Interestingly, reactions of **1** with phenylacetylene gave the unexpected product **19** as the major boron-containing species in solution as identified by a characteristic doublet at $\delta = 6.94$ ppm ($J_{HP} = 16.0$ Hz) in the ^{1}H NMR spectrum, which arises from coupling to the neighboring vicinal phosphorus atom. The regioselectivity in the formation of **19** was confirmed by an X-ray diffraction study, and a perspective view of the molecular structure is shown in Figure 2. The formation of **19** represents a unique example of the synthesis of a P–B compound that is analogous to the well known 1,1-carboboration reaction.[21]

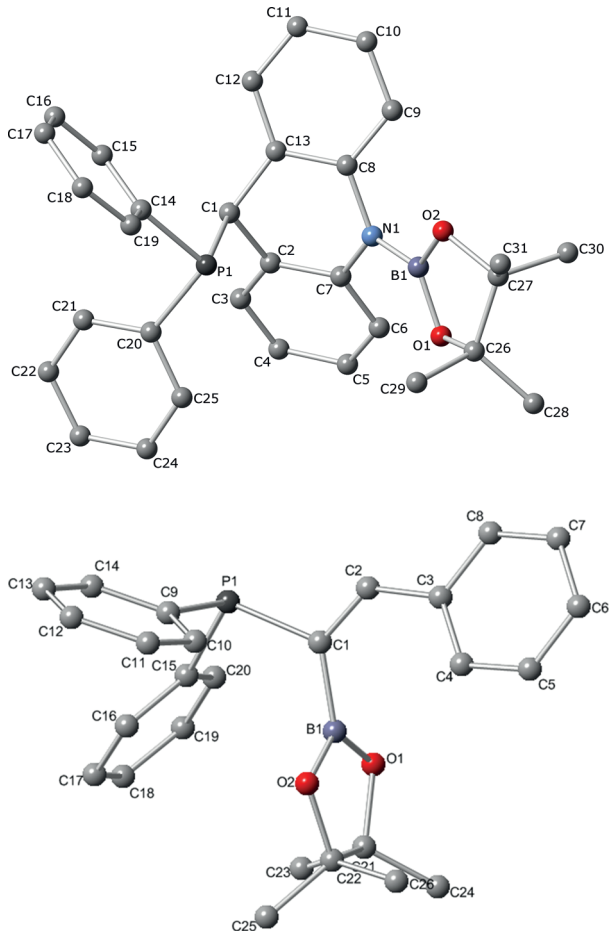
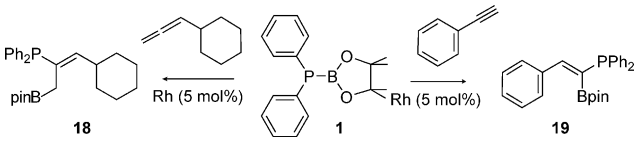


Figure 2. Molecular structures of **16** (top) and **19** (bottom) with hydrogen atoms omitted for clarity. Selected bond distances [Å] for **16**: P(1)–C(14) 1.8295(13), P(1)–C(20) 1.8344(13), P(1)–C(1) 1.9018(13), B(1)–O(2) 1.3715(17), B(1)–O(1) 1.3724(17), B(1)–N(1) 1.4331(18); for **19**: P(1)–C(15) 1.830(2), P(1)–C(1) 1.833(2), P(1)–C(9) 1.837(2), B(1)–O(1) 1.353(3), B(1)–O(2) 1.357(3), B(1)–C(1) 1.567(3), C(1)–C(2) 1.345(3).



Scheme 4. Rhodium-catalyzed phosphinoboration of allenes and terminal alkynes.

Likewise, related PC=CB systems have been reported previously by Marder and co-workers.[22] Although we are presently investigating the mechanism of this unique metal-catalyzed reaction to give **19**, it is quite likely that a vinylidene pathway is involved, similar to that observed by Miyaura[5] and Leitner[23] in related hydroboration studies. Unfortunately, reactions of **1** with diphenylacetylene, 1-octene, styrene, or isoprene in the presence of a catalytic amount of rhodium all failed to give any significant amounts of the addition products.

In conclusion, we have prepared novel phosphinoboronate esters and demonstrated that the single P–B bond in these species is highly reactive and readily undergoes addition across the C=E bond in aldehydes, ketones, aldimines, and α,β-unsaturated ketones to give a wide variety of phosphines. Unlike reactions involving bonds between boron and other main-group atoms, a catalyst or strong base is not required to facilitate additions of the P–B bond. Reduction of pyridine and acridine proceeds selectively at room temperature to give the corresponding 1,4-addition products. To the best of our knowledge, we have also reported the first examples of transition-metal-catalyzed phosphinoborations of C–C multiple bonds. We are presently investigating the bonding and reactivity of these phosphinoboronate esters using a combination of computational methods and kinetic studies to understand the mechanism of this unique reaction, expand the substrate scope, identify an optimum catalyst and conditions, and develop an asymmetric variant; these results will be reported in due course.

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Keywords: addition · boron · catalysis · phosphines · phosphinoboration

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