

Note

Synthetic, spectroscopic and structural studies of two novel phosphanyl(organyl)borane compounds

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Abstract

The titanium (II) complex, $\text{Cp}_2\text{Ti}(\text{HBcat})_2$, catalyzes the hydroboration of diphenylvinylphosphine by catecholborane and pinacolborane to afford exclusive anti-Markovnikov phosphanyl(organyl)boranes cleanly, rapidly and in good yields. Spectroscopic and X-ray studies of the phosphanyl(organyl)borane products show no evidence of boron–phosphorus interaction, indicating that the compounds preclude formation of Lewis pairs.

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1. Introduction

Phosphanyl(organyl)boranes (POBs) are molecules with phosphorus- and boron-containing termini bridged by a hydrocarbon group. The molecules have drawn interest because of their unique ambiphilic properties that are a consequence of their concurrent Lewis acidity and basicity [1–7]. Built-in geometric constraints [8,9] along with electronic [4] and steric [1,10] properties at either or both termini can be used to rationally design POB systems with an absence or presence of P–B Lewis coordination.

For example, compounds **A** [11] and **B** [12] demonstrate intermolecular and intramolecular adduct formation, respectively, whereas compounds **C** [8,9], **D** [1], **E** [4] and **F** [4] display neither (see Fig. 1). Compounds **A** and **B** combine a strongly Lewis acidic boron with a small, electron-rich phosphine and thus, unsurprisingly, form adducts. Compounds **C** and **D** preclude intra- and intermolecular adduct formation because of steric crowding at both phosphorus and boron. In compound **C** intramolecular coordination is rendered impossible by the molecule's

trans geometry. Electronic properties can also be utilized to prevent Lewis pairing as in compounds **E** and **F**. In these two cases, π -to- π donation from the heteroatom to boron diminishes the borane's acidity [3,4], making it impossible for the borane to attract the phosphine; neither intra- nor intermolecular adducts are detected.

The reactivity of POBs with other compounds depends on the POB's ability to preclude inter- and intramolecular Lewis acid–base adduct formation. For example, Stephan and co-workers recently demonstrated that a bulky and strongly Lewis acidic borane and a bulky electron-rich phosphine in the same molecule result in a “frustrated Lewis pair”. In this system, the phosphine and the borane are incapable of forming adducts with one another, but can instead heterolytically cleave H_2 in a reversible reaction [5].

Sufficient suppression of boron's Lewis acidity as in **E** and **F** results in POBs that are essentially phosphine in nature, and compounds **E** and **F** coordinate various transition metal centers via phosphorus alone [3,4]. POBs may also behave as bidentate ligands via simultaneous phosphorus coordination and non-classical metal–boron bonding similar to bonding modes observed in rare metal–boranes [2,13–15]. One recent example of such an interaction, is the Au (I) complex of **D** within which the rigid aromatic ring locks the

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POB ligand in the *cis* geometry resulting in chelation via boron and phosphorus [1]. Evidence of gold–boron interaction is provided by an upfield shift in the ligand's boron NMR signal, and an Au–B bond distance that is shorter than the sum of the individual atoms' van der Waals radii.

Current methods for POB synthesis include chloride displacement of chlorodialkylborane (A) or chlorodiaminoborane (F) substrates by secondary [11] or anionic phosphines [3,4], respectively; addition of secondary phosphines to vinylidioxaborolane substrates (E) [16]; addition of diboranes [20] and boranes (C) [8,9] to alkynylphosphines, vinylphosphines [7] or unsaturated phosphonic esters [17]; coupling of bromophosphines with chlorodialkylboranes (D) [1]; and addition of bulky P–B Lewis pairs to alkenes [18]. Several of these methods are high-yielding [1,17] and/or relatively fast [1,16], but only one of them is transition metal-catalyzed [20].

Our studies are directed at developing more catalytic routes to POBs, thereby extending the benefits of metal-catalyzed chemical transformations [19] to the synthesis of these molecules. We report a new catalytic hydroboration of vinylphosphines that yields phosphanyl(organyl)boranes stereoselectively, cleanly, and rapidly in one step. Spectroscopic and X-ray crystallographic data provide compelling evidence for the formation of a new class of phosphanyl(organyl)boranes that successfully preclude the formation of Lewis adducts.

2. Results and discussion

Metal-catalyzed hydroboration of alkenes and alkynes is a synthetic route to alkylboron and vinylboron compounds, and the literature is full of examples of this rich chemistry [21–27]. The advantage of utilizing metal-catalyzed hydroborations is that they enhance the chemo- [28], regio- [29–33], and stereoselectivity [30–32,34,35] of the uncatalyzed reaction [36].

Titanocene bis-catecholborane, $\text{Cp}_2\text{Ti}(\text{HBcat})_2$, rapidly catalyzes hydroboration of alkenes by catecholborane with exclusive anti-Markovnikov selectivity in high yields and low catalyst loadings at room temperature [37]. We have extended these advantages to the synthesis of phosphanyl(organyl)boranes by using $\text{Cp}_2\text{Ti}(\text{HBcat})_2$ to catalyze anti-Markovnikov addition of catecholborane (HBcat) and pinacolborane (HBpin) to vinylphosphines. The use

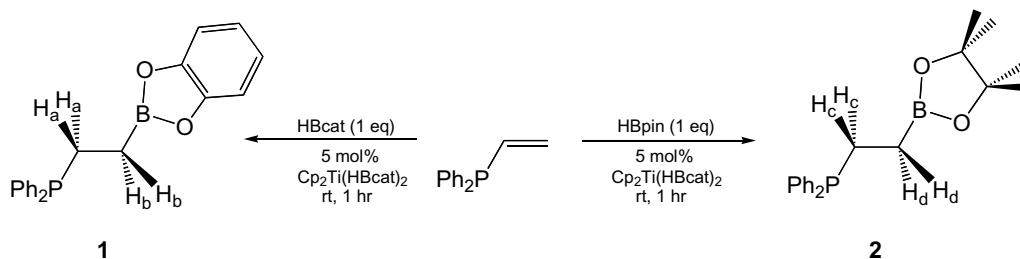
of these boronate esters as hydroboration agents is essential in obtaining POB products that preclude intra- and/or intermolecular Lewis pairing.

Addition of toluene solutions of borane and vinylphosphine, respectively, to cooled (-78°C) catalyst followed by warming to room temperature afforded phosphanyl(organyl)borane products in good yields (81% by NMR spectroscopy for compound 1) (Scheme 1). In a control experiment, addition of pinacolborane or catecholborane to toluene solutions of equimolar diphenylvinylphosphine showed no evidence vinylphosphine hydroboration within the time frame of the experiments by NMR spectroscopy.

Further, NMR spectroscopic studies showed that diphenylvinylphosphine did not appear to displace catecholborane from titanium, and thus did not poison the catalyst. This result is consistent with earlier studies showing that small alkyl phosphines (e.g., PMe_3) displaced catecholborane from titanocene and large aryl phosphines such as PPh_3 did not [38]. Thus, hydroboration of vinylphosphine was most likely catalyzed by $\text{Cp}_2\text{Ti}(\text{HBcat})_2$. To our knowledge, this reaction is the first application of transition metal-catalyzed hydroboration of vinylphosphines to the synthesis of phosphanyl(organyl)boranes.

Multinuclear NMR data revealed that phosphanyl(organyl)borane products were formed with exclusive anti-Markovnikov selectivity, and without Lewis adduct formation. The ^1H NMR spectra of compounds 1 and 2 displayed two signals in the methylene region integrating to two protons, each and in a 1:1 ratio (Scheme 1). The signals for the H_b and H_d protons were triplets, consistent with coupling to two neighboring Hs, H_a and H_c , respectively. The H_a and H_c resonances were themselves doublets of triplets, consistent with simultaneous coupling to two neighboring protons and one phosphorus atom. Further, H_a and H_c were upfield of H_b and H_d , respectively. These patterns are consistent with H_a and H_c being adjacent to the electron-releasing phosphorus atom, and H_b and H_d being adjacent to the electron-withdrawing boron atom. These peaks indicate the presence of a $-\text{CH}_2\text{CH}_2-$ bridge consistent with products of anti-Markovnikov hydroboration of the $\text{C}=\text{C}$ bond in diphenylvinylphosphine.

The ^{11}B NMR spectrum displayed resonances at δ 35.95 (1) and δ 34.24 (2), the region typical of alkylboronate esters [39]. Importantly, these signals were singlets, and not the doublets that would result from coordination of



Scheme 1.

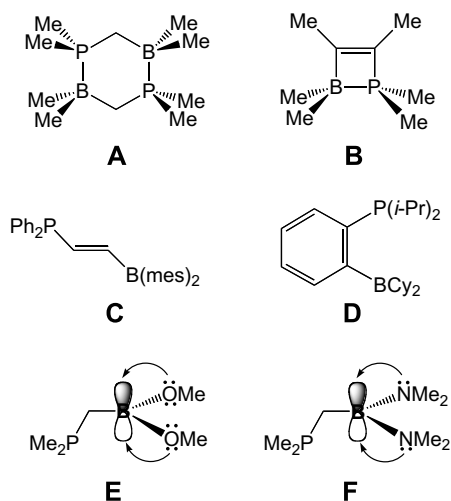


Fig. 1. Examples of phosphanyl(organyl)boranes.

phosphorus ($I = 1/2$) to boron in the Lewis adduct. The ^{31}P $\{^1\text{H}\}$ NMR spectrum showed a single resonance at -9.83 ppm (**1**) and -9.73 ppm (**2**). These signals were also singlets, and not the broad quartets that would be expected from coordination of phosphorus to the quadrupolar boron nucleus ($I = 3/2$) [40]. The NMR data strongly correlate with the formation of non-adduct forming, anti-Markovnikov products of vinylphosphine hydroboration.

The absence of boron–phosphorus interaction was further confirmed by an X-ray crystallographic study of compound **2**. An ORTEP drawing of **2** is provided in Fig. 2. Acquisition parameters and selected bond distances are provided in Tables 1 and 2, respectively. The phosphorus–boron bond distance was $4.231(2)$ Å. This distance is longer than the sum of the phosphorus and boron atoms' van der Waals' radii of 3.8 Å [41]. It is also well outside the range of a typical phosphorus–boron Lewis bond such as that of $\text{Br}_3\text{PBBBr}_3$ (2.01 Å) [42]. Furthermore, the sum of the three angles around boron is 360° indicating trigonal

Table 1
Acquisition parameters for compound **2**

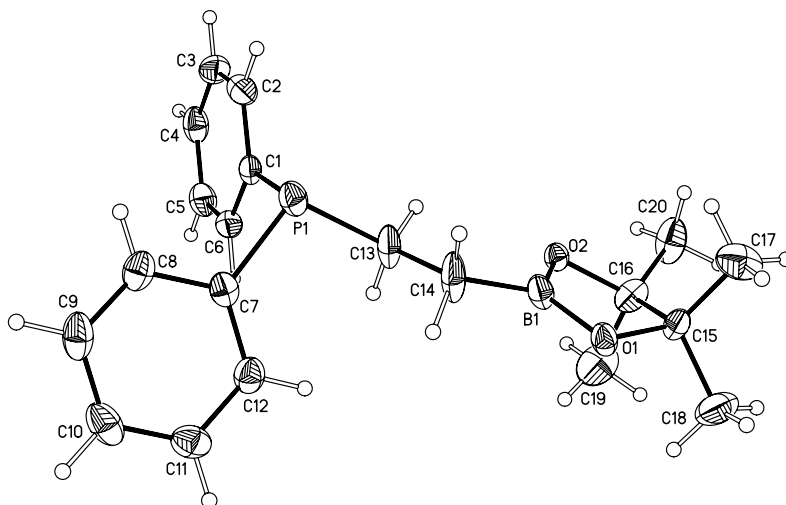
Empirical formula	$\text{C}_{20}\text{H}_{26}\text{BO}_2\text{P}$
Formula weight	340.19
Temperature (K)	110
Color of crystal	Colorless
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
<i>Unit cell dimensions</i>	
A (Å)	5.9969(2)
B (Å)	12.3137(3)
C (Å)	25.9356(6)
α ($^\circ$)	90
β ($^\circ$)	90
γ ($^\circ$)	90
Cell volume (Å ³)	1915.19
Calculated density (g/cm ³)	1.180
Z value	4
Theta range ($^\circ$)	3.86–28.58
Goodness-of-fit on F^2	1.072
Final R indices	$R_1 = 0.0420$, $wR_2 = 0.1045$
Absorption correction	Analytical
Reflections collected/unique [R_{int}]	15450/4865 [0.0312]

Table 2
Selected bond distances (Å) and angles ($^\circ$) in compound **2**

Atom	Atom	Atom	Angle ($^\circ$)	Bond	Distance (Å)
C1	P	C7	100.37 (8)	P–C1	1.8381 (17)
C1	P	C13	98.58 (9)	P–C7	1.8349 (19)
C7	P	C13	104.15 (10)	P–C13	1.842 (2)
P	C13	C14	114.05 (16)	C13–C14	1.541 (3)
C13	C14	B	112.53 (17)	B–C14–B	1.561 (3)
C14	B	O1	122.9 (2)	B–O1	1.353 (5)
C14	B	O2	120.8 (2)	B–O2	1.347 (4)
O1	B	O2	116.3 (3)		

planarity at the central boron atom; boron is clearly not tetrahedral as would be required for adduct formation. These data are consistent with an absence of phosphorus–boron interaction.

In summary, we have demonstrated that titanium-catalyzed hydroboration of vinylphosphines exclusively affords

Fig. 2. ORTEP drawing of compound **2**.

anti-Markovnikov phosphanyl(organyl)boranes. This one-pot procedure is rapid, clean, and stereoselective, and eliminates the need for multiple steps, harsh reagents and long reaction times. The diminished Lewis acidity at boron precludes formation of Lewis pairs in POB products. Thus, the compounds are likely to behave as classic phosphines, and future investigations will be directed at generating transition metal complexes with these systems.

3. Experimental

3.1. General considerations

All manipulations were conducted using standard Schlenk techniques or in a VAC system 37897 inert atmosphere glovebox. All protiated solvents were refluxed and distilled from purple solutions containing sodium benzo-phenone. Deuterated solvents were dried similarly, but were collected by vacuum transfer. The following reagents were obtained from commercial suppliers and used without further purification: HBcat, HBpin, and Ph₂P(H)CCH₂. The catalyst Cp₂Ti(HBcat)₂ was prepared using the literature procedures [43]. All NMR data were collected on a 400 MHz Bruker Avance Spectrometer. ³¹P and ¹¹B NMR chemical shifts are reported relative to 85% H₃PO₄ and BH₃ · Et₂O, respectively, as external standards.

3.2. Synthesis of Ph₂P(CH₂)₂Bcat (1)

A sidearm flask was charged with Cp₂Ti(HBcat)₂ (1.64 mmol, 0.686 g) and sealed with a rubber septum. The flask was cooled to –78 °C and 25 mL of toluene was slowly added to the flask via syringe. To the resultant pale yellow slurry was added drop wise via syringe first catecholborane (16.4 mmol, 1.75 mL) then vinylphosphine (16.4 mmol, 3.26 mL). The reaction mixture was left at –78 °C for 10 min, and then allowed to slowly warm to room temperature where it was permitted to stir for 1 h. The solvent was removed in vacuo to yield an olive-green solid. This solid was dissolved in the minimal amount of toluene (5–6 mL), and transferred to a vial. The vial was carefully layered with 2–3 mL of pentane and stored in a –30 °C freezer overnight. A white precipitate was formed after this time period, and was collected by vacuum filtration and washed three times with 2 mL aliquots of cold pentane. The solid was dried under reduced pressure. Yield: 17% (109 mg). ¹H NMR (C₇D₈, rt): δ 1.25 (dt, J_{Ha-Hb} = 8.4 Hz, J_{Ha-P} = 12.0 Hz, 2H), 2.18 (t, J_{Ha-Hb} = 8.4 Hz, 2H), 6.79 (m, 2H), 6.97 (m, 2H), 7.05 (m, 6H), 7.37 (m, 4H). ¹¹B {¹H} NMR (C₇D₈, rt): δ 35.95. ³¹P {¹H} NMR (C₇D₈, rt): δ –9.83.

3.3. Synthesis of Ph₂P(CH₂)₂Bpin (2)

A sidearm flask was charged with Cp₂Ti(HBcat)₂ (0.345 mmol, 0.144 g) and sealed with a rubber septum. The flask was cooled to –78 °C and 15 mL of toluene

was slowly added to the flask via syringe. To the resultant pale yellow slurry was added dropwise via syringe first pinacolborane (6.89 mmol, 1.0 mL) then vinylphosphine (6.89 mmol, 1.37 mL). The reaction mixture was left at –78 °C for 10 min, and then allowed to slowly warm to room temperature where it was permitted to stir for 1 h. The solvent was removed in vacuo to yield an olive-green paste-like solid. This solid was dissolved in the minimal amount of toluene (3–4 mL), and transferred to a vial. The vial was carefully layered with 0.5–1 mL of pentane and stored in a –30 °C freezer overnight. A pale-yellow precipitate was formed after this time period, and was collected by vacuum filtration and washed three times with 2 mL aliquots of cold pentane. The solid was dried under reduced pressure. Yield: 48% (1.13 g). ¹H NMR (C₇D₈, rt): δ 1.05 (s, 12H), 1.03 (dt, J_{Hc-Hd} = 8.4 Hz, J_{Hc-P} = 12.8 Hz, 2H), 2.19 (t, J_{Hc-Hd} = 8.4 Hz, 2H), 7.05 (m, 6H), 7.38 (m, 4H). ¹¹B {¹H} NMR (C₇D₈, rt): δ 34.24. ³¹P {¹H} NMR (C₇D₈, rt): δ –9.73.

Acknowledgements

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Appendix A. Supplementary material

CCDC 665874 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.11.030](https://doi.org/10.1016/j.jorganchem.2007.11.030).

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