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18329Mapping boron catalysis onto a phosphorus
cluster platform†Benjamin L. L. Réant, ^a Bono van IJzendoorn, ^a George F. S. Whitehead ^b and
Meera Mehta ^{*,a}

Clusters of main group elements, such as phosphorus, arsenic, germanium, and tin – called Zintl clusters – have been known for more than a century. However, their application in main group catalysis is largely unknown. Here, we tether boranes to a seven-atom phosphorus cluster ((C₈H₁₄)BCH₂CH₂SiMe₂)₃P₇ (**2**) and we demonstrate Lewis acid catalysis as proof-of-principle that boron chemistry can be mapped onto clusters using this method. Catalyst **2** was employed to mediate key organic transformations, including the hydroboration of carbodiimides, isocyanates, ketones, alkenes, alkynes, and nitriles. To the best of our knowledge, this is the first application of Zintl-based clusters as an innocent platform in metal-free catalysis. By chaining boron, its treasure chest of chemistry can be unlocked at these clusters. Hence, beyond catalysis this method could find applications for main group clusters in neutron capture therapy, stimuli responsive materials, and cross-coupling, and frustrated Lewis pair and functional polymer chemistries.

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Introduction

Organoboranes, compounds that feature B–C bonds, are highly important in synthetic science, functional polymers, and neutron capture therapy.^{1–6} Within synthesis, boranes are crucial as stoichiometric reagents, for example in the reduction of carbonyls to alcohols and in cross-coupling reactions, and also as catalysts.^{7–10} Boron centered catalysts are particularly exciting because they are sustainable environment-friendly alternatives to expensive transition metal catalysts, based on their higher crustal abundance and lower costs.^{11–15}

Zintl clusters, clusters of main group elements, can be understood as molecular prototypes of heterogenous materials.¹⁶ Heptaphosphane ([P₇]) clusters are particularly interesting because they are structural fragments of red phosphorus.^{17–21} Red phosphorous is an inexpensive, highly available, and shelf-stable material, but it is also very insoluble in common laboratory solvents and thus can be difficult to study. In contrast, the heptaphosphane cluster, especially when functionalized, is soluble in many common laboratory solvents such as dimethylformamide, pyridine, tetrahydro-

furan, toluene, ether, and pentane. This solubility enables solution-state studies into its chemistry and may inform future applications of red phosphorus-based materials.

Although known for decades, the chemistry of hepta pnictogen ([Pn₇]; Pn = P or As) clusters towards small molecules is not well known. Historically, hepta pnictogen clusters have been protonated, functionalized with group 14 electrophiles, and coordinated to d- and f-block metals.^{17,18,22} In 2012 and 2014, the protonated heptapnictide cages [HPn₇]^{2–} (Pn = P, As) were reacted with carbodiimides and isocyanates in hydropniction reactions by the Goicoechea group.^{23–25} Goicoechea and co-workers also reacted the trianionic clusters [Pn₇]^{3–} (Pn = P, As) with alkynes to yield 1,2,3-tripnictolides by transfer of a [Pn₃][–] unit,^{26,27} while reaction of [P₇]^{3–} with carbon monoxide gave the [PCO][–] anion by P[–] transfer.²⁸ In 2021, we found that tris-silyl functionalized (R₃Si)₃P₇ clusters captured and exchanged heteroallenes between all three P–Si bonds on the cluster.²⁹

In 2021 Fässler prepared a boron functionalized [Ge₉] cluster.³⁰ Although the reactivity of the boron-[Ge₉] cluster itself has not yet been reported, the [Ge₉] cluster and chloroborane precursors were found to stoichiometrically ring open ethers and capture an acetonitrile.³¹ Further, group 14 clusters have been coordinated to transition metals and applied as spectator ligands in transition metal catalysis (Fig. 1).^{16,32,33} Very recently, we have reported on the first transition-metal free Zintl catalysis with a boron-functionalized [P₇] cluster, which was also found to be noninnocent in the transformation.³⁴

Here we tether boranes to a heptaphosphane cluster and use them in Lewis acid catalysis (Fig. 1). We mediate key

^aDepartment of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK. E-mail: meera.mehta@manchester.ac.uk

^bX-Ray Diffraction Facility, University of Manchester, Oxford Road, Manchester, M13 9PL, UK

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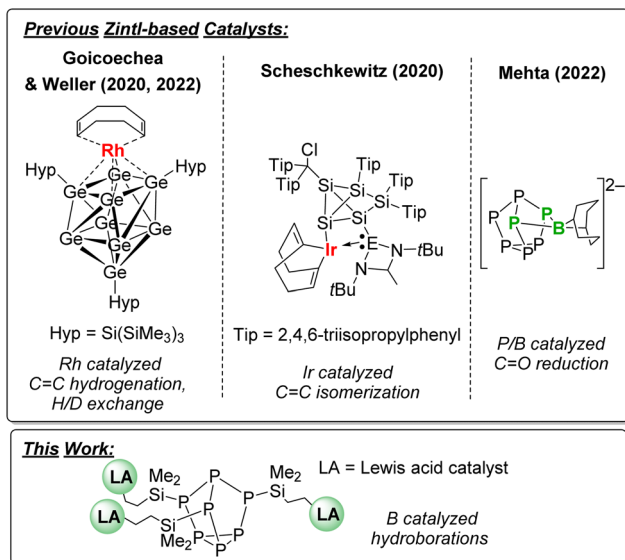


Fig. 1 Previous Zintl-based catalysts and this work.

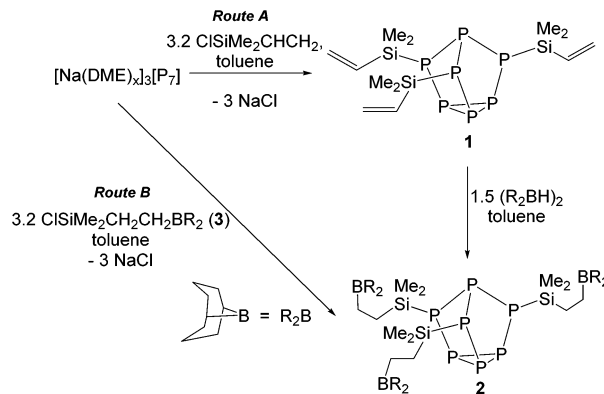
organic transformations, namely the hydroboration of heteroallenes (carbodiimides and isocyanates), ketones, alkenes, alkynes, and nitriles. To the best of our knowledge, this is the first application of Zintl-based clusters as an innocent platform in main group catalysis. Boron tethers on clusters offer the exciting possibility to translate the wealth of boron chemistry to less developed main group clusters.

Results and discussion

Synthesis of cluster catalysts

First, [Na(DME)_x]₃[P₇] (DME = dimethoxyethane) was prepared using a literature method.³⁵ Next, [Na(DME)_x]₃[P₇] was reacted with chlorodimethylvinylsilane in toluene. Nuclear magnetic resonance (NMR) spectroscopy investigations revealed 3 new multiplet resonances in the ³¹P NMR spectrum and complete consumption of starting material. The ²⁹Si NMR spectrum showed a doublet at −2.36 ppm with ¹J_{PSi} = 42.5 Hz consistent with installation of the silyl groups on the [P₇] cluster. Further, three doublets of doublets at 5.63 (³J_{HH} = 20.1 Hz, ²J_{HH} = 3.2 Hz), 5.83 (³J_{HH} = 14.4 Hz, ²J_{HH} = 3.2 Hz), and 6.18 (³J_{HH} = 20.1 Hz, 14.4 Hz) were observed in the ¹H NMR spectrum, confirming that the vinyl moiety is conserved. These NMR data are in line with the formation of (CH₂CHSiMe₂)₃P₇ (**1**) (Scheme 1). The solid-state structure of **1** was elucidated by single crystal X-ray diffraction (XRD) studies (Fig. 2). The XRD data of **1** further confirmed that the silyl groups are tethered to the bridging phosphorus atoms of the cluster (average P–Si bond lengths of 2.288 Å), and the preservation of the vinyl moiety (average C–C bond lengths of 1.304 Å, consistent with C=C double bonds).^{36,37} Compound **1** was isolated in 86% yield.

Next, **1** was reacted with 9-borabicyclo(3.3.1)nonane (9-BBN; R₂BH) dimer in toluene (Scheme 1, route A). ¹H NMR spec-



Scheme 1 Synthesis of boron tethered [P₇] cluster **2**.

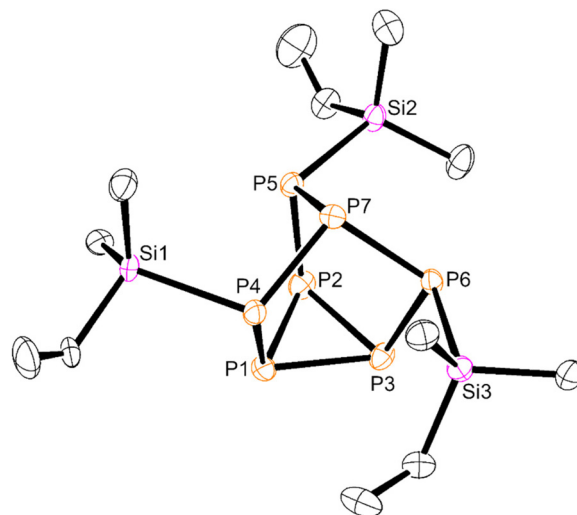


Fig. 2 Molecular structure of **1**. Anisotropic displacement ellipsoids pictured at 50% probability. Hydrogen atoms omitted for clarity. Phosphorus: orange; silicon: pink; carbon: black.

troscopy showed the disappearance of the vinyl moieties, consistent with hydroboration of all three vinyl groups to yield the boron tethered [P₇] cluster (R₂BCH₂CH₂SiMe₂)₃P₇ (**2**). The ¹¹B NMR spectrum revealed a broad signal at 86.5 ppm, consistent with three-coordinate boron. Despite multiple efforts, single crystals only of sufficient quality to verify the connectivity of **2** by XRD could be obtained (Fig. 3). Analysis of the crystal packing together with the downfield ¹¹B NMR resonance confirmed no self-assembly in the solution- or solid-state. Interestingly, it was found that cluster **2** could also be prepared by first hydroborating the chlorosilane to give ClSiMe₂CH₂CH₂BR₂ (**3**), then installing the silyl groups onto the cluster through salt metathesis (Scheme 1, route B). Regardless of the route taken, compound **2** was isolated in high yield (76–95%).

Lewis acidity tests

In order to quantify the Lewis acidity of the boron centres on **2**, the adapted Gutmann–Beckett test was performed and fluor-



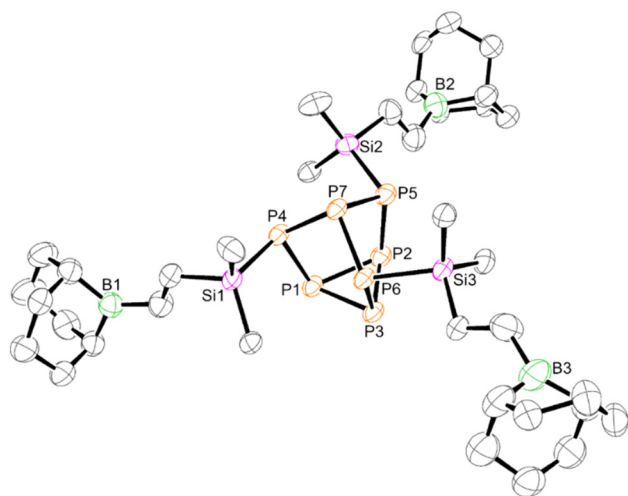


Fig. 3 Molecular structure of **2**. Anisotropic displacement ellipsoids pictured at 50% probability. Hydrogen atoms omitted for clarity. Phosphorus: orange; silicon: pink; carbon: black.

ide ion affinities (FIAs) computed (see ESI, Section 3†).^{38–42} The Gutmann–Beckett acceptor number was determined to be 46.7. Computationally, the FIA was found to be 350 kJ mol^{−1} upon addition of one fluoride, 220 kJ mol^{−1} for the second fluoride, and 113 kJ mol^{−1} for the third fluoride. The FIA values indicate that when one boron on **2** coordinates an anion, reactivity at the others decreases. This is thought to be because FIA computes anion coordination and not neutral bases, hence after the addition of the first fluoride the overall complex is anionic thus coulombic repulsion influences the 2nd and 3rd values. The Gutmann–Beckett acceptor number and first FIA for **2** are consistent with those of the untethered chlorosilane **3** (acceptor number = 46.6; FIA = 340 kJ mol^{−1}). These studies confirm that the Lewis acidity at the boron centres of **2** is not perturbed by tethering to the cluster, and thus their reactivity should be preserved.

Hydroboration catalysis

The Lewis acidity of boron has been widely exploited; one such area is in Lewis acid hydroboration catalysis.^{1,43} Previously, the 9-BBN dimer has been used as a catalyst to hydroborate carbodiimides at 25–60 °C.⁴⁴ To show that boron chemistry can be mapped onto Zintl-derived clusters *via* the silyl tethers, compound **2** was studied as a catalyst for the hydroboration of carbodiimides and isocyanates.

First, the stability of **2** in C₆D₆ was tested. No decomposition was observed by NMR spectroscopy after 72 hours at 25 °C, 120 hours at 50 °C, and 168 hours at 110 °C. Next, diisopropylcarbodiimide (**4a**) and phenyl isocyanate (**5a**) were reacted with pinacol borane, HB(pin), in the presence of 5 mol% **2** (Table 1). HB(pin) was selected as the boron reductant because the organic product is expected to display greater stability towards protodeboronation compared to the 9-BBN analogue.⁹ Boronic esters are also widely employed moieties for important organic transformations, such as Suzuki–

Table 1 Catalytic hydroboration of di-isopropylcarbodiimide (**4a**) and phenyl isocyanate (**5a**) with **2**

Solvent	Temp. (°C)	HB(pin) eq.	Time (h)	4b , % conv. ^a	Time (h)	5b : 5c : 5d , % conv. ^a
C ₆ D ₆	25	1	12	92	18	0
C ₆ D ₆	50	1	2	>99 (91)	72	43 : 0 : 0
C ₆ D ₆	50	2	24	>99	48	0 : 50 : 2
C ₆ D ₆	50	3	—	—	48	0 : 54 : 2
C ₆ D ₆	110	1	—	—	48	18 : 0 : 9
C ₆ D ₆	110	2	2	>99	48	0 : 0 : 21
C ₆ D ₆	110	3	—	—	48	0 : 0 : 53
THF	25	1	12	70	18	0
THF	50	1	2	95	72	18

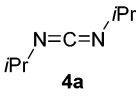
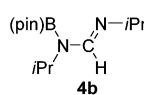

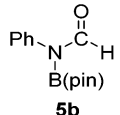

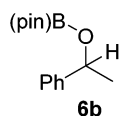

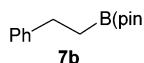

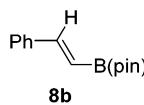

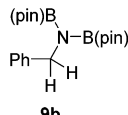
^a Determined by ¹H NMR spectroscopy. Isolated yields are given in parenthesis.

Miyaura couplings. In C₆D₆ at 50 °C after 2 hours complete hydroboration of **4a** to **4b** was observed by NMR spectroscopy. In contrast, **5a** required 72 hours under similar conditions to give 43% of the mono-hydroborated product **5b**. In the case of **5a**, increasing the equivalents of HB(pin) from 1 to 3 and increasing the reaction temperature from 50 to 110 °C gave mixtures of the mono-hydroborated (**5b**), bis-hydroborated (**5c**), and deoxygenated (**5d**) products, with higher temperatures favouring the deoxygenated product **5d**. For **4a**, even upon increasing the equivalents of HB(pin) and temperature no bis-hydroborated product was observed. Additionally, changing the solvent from C₆D₆ to tetrahydrofuran gave lower conversions, presumably because donor solvents will coordinate to the boron active site and quench some of its reactivity.

It is noteworthy that other s- and p-block catalysts have previously mediated these types of hydroborations.^{1,12,43,45–47} In fact, 9-BBN itself has also been employed to mediate the hydroboration of terminal alkynes and nitriles.^{48,49} To probe the generality of **2** as a hydroboration catalyst, we expanded our scope to other carbon-element multiple bonds, including a ketone, alkene, alkyne, and nitrile (Table 2). Acetophenone (**6a**) and styrene (**7a**) were converted to their hydroborated products **6b** and **7b** with 1 equivalent of HB(pin) and 5 mol% **2** in C₆D₆ at 110 °C after 15 h and 72 h respectively. In line with literature precedence,⁴⁹ only anti-Markovnikov hydroboration of **7a** was observed. Similarly, hydroboration of phenylacetylene (**8a**) exclusively gave the *syn*-addition to the *trans*-isomer **8b** in 79% conversion after 120 h at 50 °C. In contrast, when benzonitrile (**9a**) was reacted with 1 equivalent HB(pin) and 5 mol% **2** in C₆D₆ at 110 °C, 44% conversion to the bis-hydroborated product **9b** was observed after 120 h with no evidence of mono-hydroboration, thus 2 equivalent of HB(pin) was added to achieve conversion of **9a** to **9b** in 84% yield. Control reac-



Table 2 Hydroboration of substrates **4a–9a** using **2**, **3** and (Me₃Si)₃P₇, and controls

Substrate	Catalyst	Temp. (°C)	Time (h)	% conv. ^a	Product
 4a	—	50	24	0	 4b
	2	50	2	>99 (91)	
	3	50	2	89	
	(Me ₃ Si) ₃ P ₇	50	2	0	
 5a	—	50	72	0	 5b
	2	50	72	43	
	3	50	72	31 ^b	
	(Me ₃ Si) ₃ P ₇	50	72	0	
 6a	—	110	48	0	 6b
	2	110	15	91	
	3	110	15	96	
	(Me ₃ Si) ₃ P ₇	110	15	0	
 7a	—	110	48	0	 7b
	2	110	72	80	
	3	110	72	68	
	(Me ₃ Si) ₃ P ₇	110	72	0	
 8a	—	50	120	0	 8b
	2	50	120	79	
	3	50	120	68	
	(Me ₃ Si) ₃ P ₇	50	120	0	
 9a	—	110	120	0	 9b
	2	110	120	84	
	3	110	120	70	
	(Me ₃ Si) ₃ P ₇	110	120	0	

^a Determined by ¹H NMR spectroscopy. ^b Additional 8% **5c** and 3% **5d** detected. Isolated yields are given in parenthesis.

tions further confirmed that in the absence of **2** no hydroboration of **4a–9a** was observed. Further, no deoxygenation of acetophenone (**6a**) or bis-hydroborations of phenylacetylene (**8a**) was observed with an excess of HB(pin) and 5 mol% **2**.

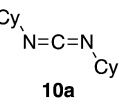
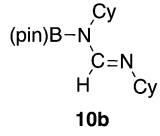
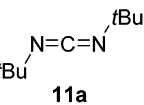
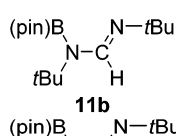
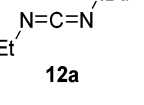
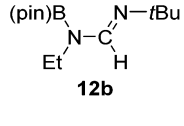
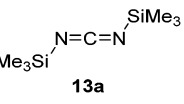
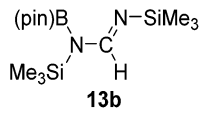
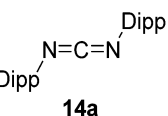
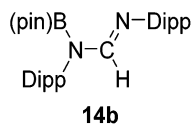
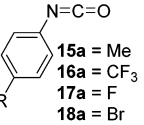
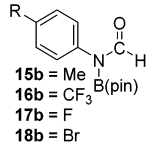
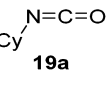
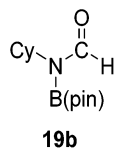
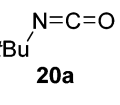
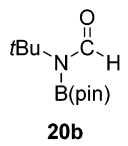
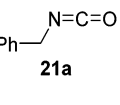
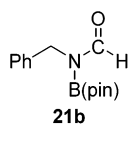
In order to probe the role of the cluster in catalysis, 15 mol% of the untethered chlorosilane **3** was investigated as a hydroboration catalyst (Table 2, see ESI, Section 5.3†). It was found that under the established reaction conditions for each substrate, when 15 mol% **3** was employed in lieu of 5 mol% **2** conversions to the respective hydroborated products **4b–9b** were nearly the same. With a minor increase in conversion between 10–14% observed for catalyst **2**, except for in the case of acetophenone (**6a**) hydroboration. It is also noteworthy that no degradation of the Cl–Si bond could be observed in any of the reaction mixtures by ²⁹Si NMR spectroscopy. Further, in the case of phenyl isocyanate (**5b**) hydroboration with **3** minor amounts of **5c** and **5d** were also observed by ¹H NMR spectroscopy, showing that the transformation is less selective than when the boranes are tethered. Next, (Me₃Si)₃P₇ was prepared, using a literature method,³⁵ and tested in place of catalyst **2** at 5 mol% catalyst loading where it showed no catalytic activity. These findings demonstrate that the [P₇] cluster acts as a

mostly innocent platform and the catalysis originates at the B-tethered arms.

Having demonstrated the generality of **2** as a hydroboration catalyst, the substrate scope was expanded (Tables 3–5). First, carbodiimides and isocyanates were investigated with 1 equivalent of HB(pin) and 5 mol% **2** in C₆D₆ at 50 °C (Table 3). Similar to the reactivity of di-isopropylcarbodiimide (**4a**), dicyclohexylcarbodiimide (**10a**) gave the hydroborated product **10b** after 6 h in high yield. The bulkier carbodiimides di-*tert*-butylcarbodiimide (**11a**) and 1-*tert*-butyl-3-ethylcarbodiimide (**12a**) required longer reaction times to give the hydroborated products **11b** and **12b**, respectively. Carbodiimide **13a**, which features the electron-withdrawing trimethylsilyl group only gave 19% **13b** after 72 h, whereas the aromatic functionalized carbodiimide bis(2,6-di-isopropylphenyl)carbodiimide (**14a**) afforded product **14b** in 88% conversion after 36 h. Similar to the reactivity of phenyl isocyanate (**5a**), *para*-phenyl functionalized isocyanates **15a–18a** all gave moderate conversions, between 32–42%, to the mono-hydroborated products **15b–18b**. Those with the electron withdrawing trifluoromethyl- (**16a**) and fluoro- (**17a**) groups required longer reaction times. Meanwhile, cyclohexyl isocyanate (**19a**) yielded **19b** in 60%



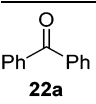
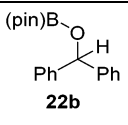
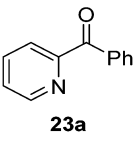
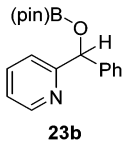
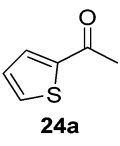
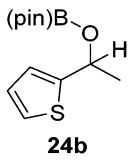
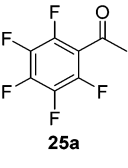
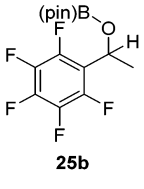
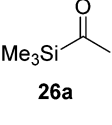
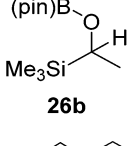
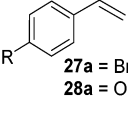
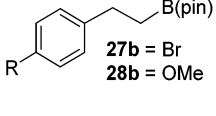
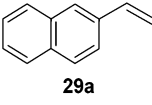
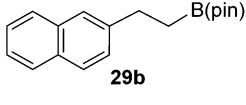
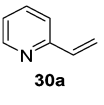
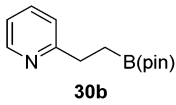
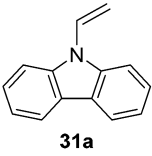
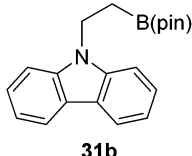
Table 3 Catalytic hydroboration of carbodiimides and isocyanates with **2**

$\text{R}-\text{N}=\text{C}=\text{E} \xrightarrow[\text{C}_6\text{D}_6, 50^\circ\text{C}]{\text{HB(pin)}, 5 \text{ mol\% } \mathbf{2}} (\text{pin})\text{B}-\text{N}(\text{R})-\text{C}(\text{H})(\text{E})$ $\text{E} = \text{NR}, \text{O}$			
Substrate	Time (h)	% conv. ^a	Product
 10a	6	82	 10b
 11a	24	>99 (88)	 11b
 12a	72	56	 12b
 13a	72	19	 13b
 14a	36	88	 14b
 15a = Me 16a = CF ₃ 17a = F 18a = Br	72 15b 120 16b 120 17b 72 18b	42 15b 34 16b 32 17b 36 18b	 15b = Me 16b = CF ₃ 17b = F 18b = Br
 19a	72	60	 19b
 20a	90	49	 20b
 21a	120	41	 21b

^a Determined by ¹H NMR spectroscopy. Isolated yield given in parenthesis.

conversion after 72 h. The bulkier *tert*-butyl isocyanate (**20a**) required 90 h to afford 49% **20b**, and benzyl isocyanate (**21a**) required 120 h to give 41% of the hydroborated product **21b**.

Table 4 Catalytic hydroboration of ketones and alkenes with **2**

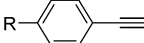
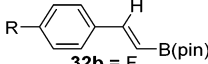
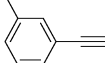
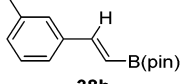
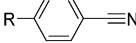
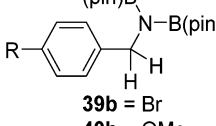

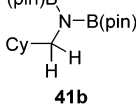
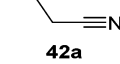
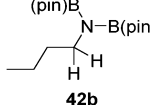
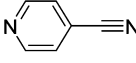
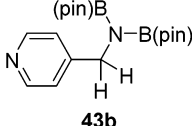
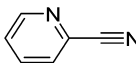
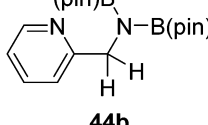
$\text{R}-\text{C}(=\text{E})-\text{R} \xrightarrow[\text{C}_6\text{D}_6, 110^\circ\text{C}]{\text{HB(pin)}, 5 \text{ mol\% } \mathbf{2}} (\text{pin})\text{B}-\text{C}(\text{R})_2-\text{H}$ $\text{E} = \text{O}, \text{CH}_2$			
Substrate	Time (h)	% conv. ^a	Product
 22a	72	42	 22b
 23a	36	86	 23b
 24a	36	82	 24b
 25a	72	69	 25b
 26a	18	>99	 26b
 27a = Br 28a = OMe	72	78 27a 79 28a	 27b = Br 28b = OMe
 29a	72	76	 29b
 30a	72	49	 30b
 31a	72	54	 31b

^a Determined by ¹H NMR spectroscopy.

Then, the scope of carbonyls and alkenes was expanded at 110 °C with 5 mol% **2** (Table 4). Benzophenone (**22a**) was hydroborated to **22b** after 72 h in 42% conversion. Pyridine



Table 5 Catalytic hydroboration of alkynes and nitriles with 2

$\text{R}-\text{C}\equiv\text{C} + 1\text{eq HB(pin)} \xrightarrow[50\text{ }^\circ\text{C}]{5\text{ mol\% X, C}_6\text{D}_6, 120\text{ h}} \text{R}-\text{CH}=\text{CH}-\text{B(pin)}$		
$\text{R}-\text{C}\equiv\text{N} + 2\text{eq HB(pin)} \xrightarrow{110\text{ }^\circ\text{C}} \text{R}-\text{CH}_2-\text{CH}_2-\text{N}(\text{B(pin)})_2$		
Substrate	% conv. ^a	Product
 32a = F 33a = Cl 34a = Br 35a = CF ₃ 36a = OMe 37a = Me	80 32b 81 33b 80 34b 76 35b 87 36b 90 37b	 32b = F 33b = Cl 34b = Br 35b = CF ₃ 36b = OMe 37b = Me
 38a	86	 38b
 39a = Br 40a = OMe	68 39b 66 40b	 39b = Br 40b = OMe
 41a	74	 41b
 42a	95	 42b
 43a	16	 43b
 44a	10	 44b

^a Determined by ¹H NMR spectroscopy.

(23a) and thiophene (24a) functionalized ketones were hydroborated to **23b** and **24b**, correspondingly, in high yield but required 36 h, presumably because the pyridine and thiophene groups compete with substrate coordination. The pentafluorophenyl functionalized ketone **25a** required longer reaction times, 72 hours, to give moderate conversion to **25b**. While the silyl functionalized ketone **26a** was converted to **26b** in quanti-

tative yield in 19 hours. For alkenes, 4-bromostyrene (**27a**), 4-vinylanisole (**28a**), and 2-vinylnaphthalene (**29a**) hydroborated to give **27b**, **28b**, and **29b**, respectively, in similar conversions (between 76–78%). 4-Vinylpyridine (**30a**) and 9-vinyl-9H-carbazole (**31a**) were hydroborated to **30b** and **31b**, respectively, in moderate conversions.

Finally, the scope of terminal alkynes and nitriles was expanded (Table 5). Phenylacetylene derivatives were investigated with 1 equivalent of HB(pin) and 5 mol% **2** in C₆D₆ at 50 °C. 4-Fluorophenylacetylene (**32a**), 4-chlorophenylacetylene (**33a**), 4-bromophenylacetylene (**34a**), 4-trifluoromethylphenylacetylene (**35a**), 4-methoxyphenylacetylene (**36a**), 4-methylphenylacetylene (**37a**), and 3-methylphenylacetylene (**38a**) all gave the corresponding hydroborated products **32b**–**38b** with similarly high conversions (between 76–90%). Next, nitriles were investigated with 2 equivalent of HB(pin) in a similar fashion. 4-Bromobenzonitrile (**39a**), 4-methoxybenzonitrile (**40a**), cyclohexanecarbonitrile (**41a**), and butyronitrile (**42a**) were all bis-hydroborated to the **39b**–**42b** products in moderate to high yield. While, similar to the ketone and alkene hydroborations, the pyridine functionalized nitriles **43a** and **44a** could only be bis-hydroborated to **43b** and **44b**, respectively, in low conversions.

Mechanistically, compound **2** is expected to operate in line with previously well-established p- and s-block Lewis acid mediated hydroboration and hydrosilylation reactions.^{13,50–52} Catalyst **2** is expected to activate the H–B bond of HB(pin) which then can undergo attack by the substrate to transfer the B(pin) followed by hydride transfer from the catalyst. However, when compound **2** was reacted with 3 equivalents of HB(pin) no coordination could be observed by NMR spectroscopy, at room temperature and –70 °C. It must be noted that even undetected small amounts of adduct formation between **2** and HB(pin) could still promote catalysis. And in fact, would be consistent with the mild catalyst performance of **2**. Additionally, 1 : 3 reactions of **2** with phenyl isocyanate (**5a**), acetophenone (**18a**), and phenylacetylene (**30a**) also showed no evidence of substrate coordination by NMR spectroscopy. In contrast, 1 : 3 reactions of **2** with di-isopropylphenylcarbodiimide (**4a**) and benzonitrile (**38a**) both showed a small upfield shift in the ¹¹B NMR spectra, consistent with substrate coordination. However, no noticeable changes were observed in the ³¹P NMR spectra, consistent with the cluster being innocent towards substrate activation (see ESI, Section 8†). Because no decomposition or retro-hydroboration of **2** has been observed, secondary borane catalyst mechanisms that invoke initial catalyst hydroboration at the substrate are not expected to be possible.^{44,53,54} Further, Thomas and co-workers have previously reported the ‘hidden role’ that BH₃ and borohydrides can play in hydroboration catalysis.⁴³ In order to test for hidden BH₃ and borohydride generation, 5 mol% of **2** was heated with HBpin and benzonitrile (**9a**) for 5 days at 110 °C, the most pushing conditions employed for catalyst **2**. Next an excess of tetramethylethylenediamine (TMEDA) was added to capture borohydrides and allow for their detection by NMR spectroscopy. No evidence of TMEDA captured



BH₃ or borohydride could be detected by ¹¹B and ¹H NMR spectroscopy (see ESI, Section 9†).⁵⁵

It is also noteworthy that no catalyst decomposition was observed after any of the catalytic transformations. This stability opens the door to catalyst recycling. In the case of di-isopropylcarbodiimide (**4a**) hydroboration, after complete conversion the reaction was reloaded with substrates and the catalyst recycled 8 additional times with no loss in catalytic performance. We believe that the catalyst could have been reused >8 times, but detection of this living catalyst was not possible by ³¹P NMR spectroscopy after cycle 9 (see ESI, Section 10†).

Conclusions

In conclusion we find that boron catalysts can be tethered onto a heptaphosphane cluster (**2**). We show that once tethered, the reactivity of the borane is fully retained. As proof-of-principle, compound **2** was applied as a catalyst for the hydroboration of carbon-element multiple bonds, including carbodiimides, isocyanates, ketones, alkenes, alkynes, and nitriles. This work shows the diverse chemistry possible with boron can be chained onto main group clusters. This work represents the first application of Zintl-based clusters as an innocent platform in main group catalysis. At its heart this is not a study of highly active boron catalysis, but in fact a method that could be applied to unlock the vault of boron chemistry at main group clusters. Applications with Zintl-derived clusters is in its infancy. Beyond catalysis, boron tethers on clusters could be used to find applications for main group clusters in neutron capture therapy, cross-coupling reactions to build polymers, and frustrated Lewis pair (FLP) chemistry. This work reminds us of boron functionalized polymers, interest in which has since exploded with the development of them as components in stimuli-responsive, optical, self-healing, and sensor materials.^{56,57} Thus, a similar trajectory could be imagined.

Author contributions

B. L. L. R. and B. v. I. performed the synthesis of compounds **1**–**3**. B. L. L. R. performed the catalysis. G. F. S. W. collected and solved the XRD data. B. v. I. performed the DFT calculations. B. L. L. R. constructed the ESI.† M. M. wrote and edited the manuscript with contributions from all authors.

Conflicts of interest

There are no conflicts to declare.

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metric analyses. We also thank Anne Davies and Martin Jennings for elemental analyses.

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