A Zintl Cluster for Transition Metal-Free Catalysis: C═O Bond Reductions

Bono van IJzendoorn, Saad F. Albawardi, Inigo J. Vitorica-Yrezabal, George F. S. Whitehead, John E. McGrady,* and Meera Mehta*

ABSTRACT: The first fully characterized boron-functionalized heptaphosphide Zintl cluster, [(BBN)P$_7$]$_2$$^-$ ([I]$_2$$^-$), is synthesized by dehydrocoupling [HP$_3$]$_2$$^-$.

Dehydrocoupling is a previously unprecedented reaction pathway to functionalize Zintl clusters. [Na(18-c-6)]$_2$[I] was employed as a transition metal-free catalyst for the hydroboration of aldehydes and ketones. Moreover, the greenhouse gas carbon dioxide (CO$_2$) was efficiently and selectively reduced to methoxyborane. This work represents the first examples of Zintl catalysis where the transformation is transition metal-free and where the cluster is noninnocent.

INTRODUCTION

Methanol (CH$_3$OH) is a clean fuel and a highly important raw material for chemical industries.$^{1–3}$ Over half of the world’s methanol is upcycled into everyday products, including pharmaceuticals, adhesives, agrochemicals, and paints/coatings. Producing methanol from carbon dioxide (CO$_2$) has attracted global attention, because it converts a greenhouse gas into a resource that can re-enter the energy cycle. This approach is "two birds one stone" in contributing to global climate control and sustainable energy efforts.$^{13,15}$ On an industrial scale, the conversion of atmospheric CO$_2$ into methanol was first realized in 2012 by the George Olah Plant (Iceland), which produces up to 4500 m$^3$ of methanol per year.$^6$ The intrinsic stability of CO$_2$ means that catalysts are essential for efficient reduction, and these are often based on expensive metals. The large-scale development and utilization of CO$_2$ reduction necessarily requires any process to be sustainable and cost-effective, and so identifying less expensive and sustainable alternatives to these metals is an important target.

Heterogeneous phosphorus-containing materials represent one possible alternative to transition metals and are currently being explored for CO$_2$ reduction.$^{5,9}$ The synthesis of well-defined molecular analogues of these phosphorus materials offers the opportunity for mechanistic investigation, and molecular clusters offer an important middle ground between molecules and bulk solids. Zintl clusters, in particular, can be thought of as molecular mimics for heterogeneous materials;$^{10}$ for example, the structure of [P$_7$]$_3$$^-$ can be viewed as a fragment of red phosphorus,$^{11–14}$ which is an inexpensive and abundant material, albeit a challenging one to study because of its poor solubility. In contrast, [P$_7$]$_2$ cages, especially those that have been functionalized, are soluble in common laboratory solvents, offering a broader range of handles for in situ investigation. An improved understanding of reactivity patterns for [P$_7$]$_2$ could be extended to corresponding reactions with materials based on the many allotropes of phosphorus.

Only a small number of catalytic applications involving Zintl-derived clusters have been reported, where the cluster typically acts as a spectator ligand, supporting active rhodium or iridium centers.$^{10,15,16}$ (Figure 1) Catalysis of the reverse water–gas shift reaction by a Ru/Sn Zintl cluster, [Ru@Sn$_3$]$^6^-$, has been reported in the recent literature, although the degree to which the cluster remains intact when deposited on a CeO$_2$ surface remains to be established.$^{17}$

The reaction chemistry of clusters based on the [P$_7$]$_2$ framework is an emerging field.$^{11,12,18}$ But salt metathesis with group 14 electrophiles has already proven to be a powerful route to functionalizing the cluster. Further, in 2012, Goicoechea and co-workers reported the use of the protonated heptapnictide clusters [HPn$_n$]$_2^-$ (Pn = P, As) in hydropnictination reactions with carbodiimides and isocy-nates.$^{19–21}$ They also reported that the [Pn$_n$]$_3^-$ (Pn = P, As) cluster reacted with alkynes to afford 1,2,3-tripnictolides,$^{22,23}$ while reaction with carbon monoxide afforded the [PCO]$_2^-$
anion. In 2021, we reported that the trisilylated derivatives (R₃Si)₃P₂ (R = Me, Ph) captured 3 equiv of heteroallene and underwent subsequent small-molecule exchange reactions.

Herein we report that Zintl clusters based on the [P₂] architecture are catalytically competent for borohydride reductions. Specifically, we prepare the transition metal-free [Na(18-c-6)]⁺ salt metathesis reactions using BBNOTf (OTf = triflate), Cy₂Bi, or Cy₂BOTf with [P₂]³− did not result in functionalization of the cluster, but instead gave NMR spectra consistent with decomposition of the cluster. Nuclear magnetic resonance (NMR) spectroscopy studies of [M(18-c-6)]⁺[BBN]⁺ and [Na(18-c-6)]⁻ showed no evidence of reaction, and the starting materials were recovered. Thus, we again prepared [P₂]³− which was captured by 3 equiv of heteroallene to give [M(18-c-6)]²⁺.

Scheme 1. Synthesis of [M(18-c-6)]²⁺. These spectroscopic features are consistent with the [P₂] cage having a mirror plane and κ²-coordination of the BBN moiety to the cluster. Similar [¹³P NMR spectroscopic features were reported for the structurally related [(Ph₂In)P₂]³− cluster. Single-crystal X-ray diffraction (XRD) studies were performed on both sodium and potassium salts [Na(18-c-6)]²⁺ and [K(18-c-6)]²⁺ in both cases, consistent with the spectroscopic data, the BBN moiety in [¹³C] is coordinated to the [P₂] fragment in a κ²-coordination mode (Figure 2).

Figure 2. Molecular structure of [(BBN)P₂⁻(¹³C⁺)] in the [Na(18-c-6)]²⁺[BBN]⁺ salt. Anisotropic displacement ellipsoids pictured at 50% probability. Hydrogen atoms, THF solvent molecules, and countercations omitted for clarity. Phosphorus: orange; boron: green; carbon: white. Selected bond length [Å]: B1-P2 2.052(8), B1-P3 2.082(7), P1-P2 2.213(2), P1-P3 2.216(2), P1-P4 2.182(8), P2-P5 2.185(2), P4-P7 2.136(2), P5-P6 2.235(2), P5-P7 2.236(3), P6-P7 2.218(2); selected bond angles [deg]: P2-B1-P3 93.3(3).

average B−P bond length of 2.072 Å in[¹³C]²⁺ is somewhat longer than B−P bonds in typical borylphosphines (R₂P−BR₃, 1.889–1.953 Å) and considerably longer than those in typical phosphinoborones (R₂P=BR₃, 1.762–1.857 Å), where P=BR₃ π bonding is significant. The sum of the angles around phosphorus is 276°, also typical of borylphosphines (284–328°) rather than phosphinoborones (359.8–328.3°).

All efforts to react [Na(18-c-6)]²⁺[¹³C] with H₂ were unsuccessful. However, stoichiometric reactions of [Na(18-c-6)]⁺[¹³C] with carboxyls, including benzaldehyde and acetoephone, and heteroallenes such as phenyl isocyanate and CO₂, resulted in an immediate color change from orange to red. Unfortunately, and despite multiple efforts, XRD diffraction quality crystals could not be obtained from any of these
Hydroboration of Carbonyls

reactions, but in situ $^{31}$P and $^{11}$B NMR spectroscopy confirmed the disappearance of [Na(18-c-6)]$_2$[1], along with the formation of novel (asymmetric)$^{25}$ functionalized clusters that would be consistent with formation of a carbonyl or heteroallene adduct (see Supporting Information, Figures S126–S138). We note that others have previously isolated and crystallographically characterized adducts of carbonyls or heteroallenes with FLPs where the C–O bond bridges the B⋯P gap.$^{38–41}$ The clear color change and disappearance of [Na(18-c-6)]$_2$[1] in these carbonyl and heteroallene reactions but not with H$_2$ follows established reactivity patterns for borylphosphines$^{42}$ rather than phosphinoborenes.$^{42}$

**Catalytic Reduction of Carbonyls.** [M(18-c-6)]$_2$[1] salts (M = Na, K) were then explored for their potential as catalysts in the reduction of carbonyls, a transformation that is widely employed by the pharmaceutical, agrochemical, polymer, and fine chemical industries.$^{44}$ Initially the reduction of benzaldehyde and benzophenone was targeted (Table 1). In

Table 1. Reaction Condition Optimization for the Hydroboration of Carbonyls

| Catalyst (mol %) | $T$, °C | H–R | Solvent | 2b conv (%)$^a$ | 3b conv (%)$^a$ |
|------------------|---------|-----|---------|----------------|----------------|
| [Na(18-c-6)]$_2$[1] (5) | RT | HBpin | THF | 92 | 80 |
| [Na(18-c-6)]$_2$[1] (1) | RT | HBpin | THF | 76 | 48 |
| [Na(18-c-6)]$_2$[1] (1) | RT | HBpin | aDFB | >99(94) | >99(96) |
| [Na(18-c-6)]$_2$[1] (1) | 50 | Et$_3$SiH | aDFB | 0 | 0 |
| [Na(18-c-6)]$_2$[1] (1) | 50 | Ph$_2$SiH | aDFB | 0 | 0 |
| [K(18-c-6)]$_2$[1] (1) | RT | HBpin | THF | 75 | 52 |
| [K(18-c-6)]$_2$[1] (1) | RT | HBpin | aDFB | >99 | >99 |
| [Na(18-c-6)]$_2$[HP$_2$] (5)$^b$ | RT | HBpin | aDFB | 69 | 60 |
| K$_2$P$_2$ (5) | RT | HBpin | THF | 0 | 0 |
| [K(18-c-6)]$_2$[P$_2$] (5) | RT | HBpin | THF | 0 | 0 |

$^a$Determined by $^1$H NMR spectroscopy. Isolated yields are given in parentheses. $^b$Precatalyst.

tetrahydrofuran (THF) with 5 mol % [Na(18-c-6)]$_2$[1] catalyst loading and the mild reductant pinacolborane (HBpin), the hydroboration of benzaldehyde (2a) and benzophenone (3a) was quickly achieved at room temperature (RT) to give the benzylxoboranes 2b and 3b in high yields. Lowering the catalysts loading under the same conditions decreased the conversion, but it was found that a change of solvent to ortho-difluorobenzene (oDFB) improved the yield, giving near quantitative conversions even at 1 mol % catalyst loadings, under similar conditions. Hydroisolation of the carbonyls using triethylsilane and triphenylsilane was also tested, but no reactions were observed. Changing the counteranion from sodium to potassium did not affect catalyst performance. Control reactions confirmed that catalyst [M(18-c-6)]$_2$[1] was necessary and also that the unfunctionalized K$_2$P$_2$ salt was completely inactive in this hydroboration. The [Na(18-c-6)]$_2$[HP$_2$] salt was also tested as a precatalyst and displayed lower catalytic performance compared to [M(18-c-6)]$_2$[1].

Using 1 mol % [Na(18-c-6)]$_2$[1] in oDFB, the scope of aldehyde hydroborations was expanded to include the substrates shown in Table 2. Similar to the hydroboration of benzaldehyde (2a), hydroboration of 2-formyl pyridine (4a) showed quantitative conversion to 4b after 30 min. In contrast, introducing electron-withdrawing groups in the 4-position of the benzaldehyde resulted in longer reaction times. In the case of (1,1′-biphenyl)-4-carbaldehyde (5a), 4-(pyridin-4-yl)-benzaldehyde (6a), 4-(trifluoromethyl)benzaldehyde (7a) and 4-bromobenzaldehyde (8a), complete conversion to the hydroborated products 5b–8b was obtained after 5–10 h. Electron-donating groups on the 2-position of the benzaldehyde (aldehydes 9a and 10a) also required longer reaction times to give complete conversion, presumably due to increased steric crowding. Unsaturated aliphatic substituted aldehydes 11a and 12a showed similar reaction times as the benzaldehydes. The hydroboration of acetylateddehyde (13a) was found to result in a mixture of paraldehyde and the desired hydroborated product 13b.

Next, the scope of ketone hydroborations was extended (Table 3). Substituting one phenyl group of benzophenone for a 2-pyridyl group (3a vs 14a) leads to a significantly longer reaction time (3 vs 18 h, respectively). In contrast, the hydroboration of di(pyridyl) ketone (15a) only required 30 min to give complete conversion to 15b. Coordination of the pyridyl group on the aldehyde to free HBpin could be a factor in determining the rate of these reactions; in support of this proposal, it was found that one of the pyridine nitrogens of 15b coordinates to the Bpin boron center in its crystal structure (Supporting Information, Figure S66). Similar to the hydroboration of benzophenone (3a), acetophenone (16a) and thiophene-2-carboxaldehyde (17a) gave complete conversion to 16b and 17b, respectively, after 30 min.

The incorporation of electron-withdrawing substituents resulted in longer reaction times, for example in the case of 1-(perfluorophenyl)ethan-1-one (18a) and acetylferrocene (19a), which required 72 h to give high conversions to 18b and 19b, respectively. The sterically bulky adamantone (20a) gave 20b after 18 h. The alkyl-substituted ketone cyclobutyl methyl ketone (21a) resulted in 21b after 2 h. Introduction of ethynyl and alkenyl groups on the ketone (22a and 23a) resulted in the formation of byproducts, decreasing the conversion to the desired hydroborated product.

To investigate the chemoselectivity of carbonyl hydroborations, a competition reaction was carried out between benzaldehyde, 2a, and acetophenone, 16a, with 1 equiv of HBpin (Scheme 2). Exclusive hydroboration of benzaldehyde was observed under these conditions, but addition of a second equivalent of HBpin resulted in hydroboration of the acetophenone as well. Neither 2b or 16b was found to undergo deoxygenation in the presence of an excess of HBpin. The selectivity of reduction toward aldehydes in the presence of ketones is consistent with literature precedent$^{45–47}$ and with the data in Table 1, which shows higher degrees of conversion for 2a compared to 3a.
Table 2. Catalytic Hydroboration of Aldehydes

| Aldehyde | Product | h   | Conv. (%) | a
|-----------|---------|-----|-----------|---
| (4a)      | pinB(a) | 0.5 | >99       | 85 |
| (5a)      | pinB(b) | 8   | >99       | 91 |
| (6a)      | pinB(b) | 5   | >99       | 91 |
| (7a)      | F C     | 10  | >99       | 89 |
| (8a)      | Br      | 10  | >99       | 93 |
| (9a)      | pinB(a) | 5   | >99       | 92 |
| (10a)     | pinB(b) | 10  | >99       | 90 |
| (11a)     | pinB(a) | 10  | 80 (67)   |    |
| (12a)     | pinB(b) | 10  | >99       | 91 |
| (13a)     | pinB(a) | 0.5 | 76 (6)    |    |

Table 3. Catalytic Hydroboration of Ketones

| Ketone | Product | Time (h) | Conv. (%) | a
|--------|---------|----------|-----------|---
| (14a)  | pinB(a) | 18       | >99 (95)  |    |
| (15a)  | pinB(a) | 0.5      | >99 (94)  |    |
| (16a)  | pinB(a) | 0.5      | >99 (96)  |    |
| (17a)  | pinB(a) | 0.5      | >99 (90)  |    |
| (18a)  | pinB(a) | 72       | 80 (69)   |    |
| (19a)  | Fe      | 72       | 85 (79)   |    |
| (20a)  | Fe      | 18       | >99 (92)  |    |
| (21a)  | Fe      | 2        | >99 (91)  |    |
| (22a)  | pinB(a) | 72       | 23        |    |
| (23a)  | pinB(a) | 72       | 33        |    |

Determined by \(^1^H\) NMR spectroscopy. Isolated yields are given in parentheses.

Scheme 2. Competition Reaction between Benzaldehyde (2a) and Acetophenone (16a)

\[ \text{\([Na(18-c-6)\]2[1]} \]

21216 https://doi.org/10.1021/jacs.2c08559
J. Am. Chem. Soc. 2022, 144, 21213–21223
Catalytic Reduction of Heteroallenes. Encouraged by the catalytic hydroboration of carbonyls, we next extended the scope to heteroallenes, including both carbodiimides and isocyanates (Table 4). Three equivalents of HBpin was used in these transformations to probe the potential for deoxygenation or denitrogenation. Hydroboration of carbodiimide (iPrN)2C (24a) gave exclusively the mono-hydroborated product iPr-N(Bpin)NCHN-iPr (24b), with no evidence for bis-hydroborated or denitrogenated products even over prolonged reaction times and at elevated temperatures (50 °C). The same reaction with (CyN)2C (25a) also gave the mono-hydroborated product, (Cy(N(Bpin))N)CHNCy (25b), whereas the hydroboration of isocyanates PhNCO (26a) and CyNCO (27a) gave detectable mixtures of the mono-hydroborated (26b and 27b), bis-hydroborated (26c and 27c), and deoxygenated (26d and 27d) products. Longer reaction times favored the deoxygenated products 26d and 27d, with 54−72% conversion obtained after 7 days.

Table 4. Hydroboration of Heteroallenes

| Heteroallene | Products | Days | Conv. (%) |
|--------------|----------|------|-----------|
| iPr | N=C=N-iPr | Bpin | E=CH | R’ |
| Cy | N=C=N-Cy | Bpin | N=CH | Cy |

Catalytic Reduction of CO2. Isocyanates (RN==C==O) are, of course, structurally related to the greenhouse gas CO2 (O==C==O), and so the successful deoxygenation of isocyanates to methyl amines motivated further investigations into the catalytic reduction of CO2. Molecular main group catalysts to convert CO2 to products such as formic acid (HCOOH), methanol (CH3OH), methane (CH4), and carbon monoxide (CO) have been previously reported, possibly the best known of which are the FLP catalysts used to hydroborate or hydrosilylate CO2.29,49

Triethylsilane and triphenylsilane were tested in the catalytic reduction of CO2 and gave no conversion (Table 5), confirming that, as was the case for the carbonyl compounds, silanes are not suitable reducing agents to drive the reduction of CO2 using [Na(18-c-6)]2[1] as a catalyst. Next, 3 equiv of HBpin with 3.33 mol % [Na(18-c-6)]2[1] was pressurized with 1 atm of CO2 at RT and found to give a mixture of products. In good agreement with literature reported chemical shifts, the formic acid (Table 5, b), acetal (Table 5, c), methanol (Table 5, d), and methane (Table 5, e) oxidation levels could be identified in the reaction mixture. Using 3.33 mol % [Na(18-c-6)]2[1], common borane reductants and solvents
were screened (see Supporting Information Section 5.1). Catecholborane (HBcat) and borane dimethylsulfide (BH$_2$SM$_2$) did not result in detectable amounts of product, but when the HBBN dimer, which has pinned back aliphatic groups and an accessible hydride, is used as the reductant, the conversion is 95% with a product distribution of 1:9 formylborane (28b):methoxyborane (28d). Control experiments confirmed that the naked [P$_3$]$_3$ clusters (as K or K(18-c-6) salts) or HBBN dimer as catalyst is not independently catalytically active (Table 5, entries 7–9). The tris-functionalized P$_3$ cluster (Me$_2$Si$_2$)$_3$P$_3$ was also prepared and found to be catalytically inactive (Table 5, entry 10). These controls confirm that the BBN moiety and P$_3$ cluster of [1]$_{12}$ cooperate to enable catalytic activity.

The effect of varying reaction conditions with the HBBN dimer as the reductant is summarized in Table 6. Reducing the catalyst loading from 3.33 mol % to 0.33 mol % increased the selectivity toward methoxyborane (MeOBBN, 28d) to >99%, while the introduction of toluene as a co-solvent improved solubility of (HBBN)$_2$ and thus increased the turnover frequency (TOF). Increasing the temperature from RT to 50 °C further increased the TOF to 300 while lowering the catalyst loading to 0.01 mol %, giving the maximum turnover number (TON) of 9800. Cluster decomposition is observed above 50 °C, limiting catalyst screening conditions at high temperatures. The maximum TON and TOF (Table 6, entries 3 and 5) are high compared to previously reported main group catalysts for this transformation (see Supporting Information Table S7).

Boron−phosphorus FLP systems reported by Fontaine and Stephan also show excellent activity with TONs between 2950 and 6556 and TOFs between 176 and 853 h$^{-1}$. However, these catalysts required more forcing conditions (higher temperature and/or pressure) than the ones reported here. Under the mild conditions described here TOFs in the range 2.6–50 h$^{-1}$ and TONs between 99 and 648 have been reported by Goicoechea, Datta and Mandal, Cantat, Song, and Ramos. Meaningful comparisons can be made between [Na(18-c-6)]$_2$[1] and Cantat’s P(MeNCH$_3$CH$_2$)$_3$N catalyst. Both show similar maximum TOFs ([Na(18-c-6)]$_2$[1]: 237 h$^{-1}$; P(MeNCH$_3$CH$_2$)$_3$N: 287 h$^{-1}$), but significantly higher maximum TONs can be achieved with catalyst [Na(18-c-6)]$_2$[1] (TON = 9800; P(MeNCH$_3$CH$_2$)$_3$N: 6043).

In addition to the excellent TON observed, catalyst [Na(18-c-6)]$_2$[1] was found to be surprisingly robust: after complete catalytic hydroboration of CO$_2$ to methoxyborane (28d) no decomposition of [Na(18-c-6)]$_2$[1] was detected by NMR spectroscopy. To investigate whether catalyst [Na(18-c-6)]$_2$[1] could be recycled, the reaction sample was reloaded with 3 equiv of HBBN and 1 atm of CO$_2$. Again, at RT, complete conversion to 28d was observed overnight. Catalyst [Na(18-c-6)]$_2$[1] was recycled a total of seven times with no loss of catalyst activity, consistent with living catalysis. After these cycles, water hydrolysis of methoxyborane gave methanol in complete conversion: 0.62 mmol of methanol was produced using 0.9 μmol of catalyst (a 689-fold excess of methanol).

The CO$_2$ hydroboration with HBBN dimer was monitored by $^1$H NMR spectroscopy with 0.33 mol % [Na(18-c-6)]$_2$[1] at room temperature and 50 °C (Table 6, entries 2, 3). In both cases, intermediate CH$_3$(OBBN)$_2$ (28c) quickly formed and then was consumed (Figure 3). Meanwhile 28d is formed gradually throughout the reaction. In line with literature reports, the intermediate formyl-BBN (28b) was not detected under these conditions and is presumed to be significantly more reactive toward hydroboration compared to CO$_2$, 28c, and 28d.

Stoichiometric reduction of CO$_2$ using equimolar [Na(18-c-6)]$_2$[1] and HBBN exclusively gave HC(O)OBNN (28b). Further, reaction of [Na(18-c-6)]$_2$[1] with 2 equiv of HBBN under a CO$_2$ atmosphere again exclusively gave 28b, indicating that CO$_2$ is not trapped and reduced to 28b then further reduced to 28c and 28d while intact on the catalyst. Rather, the evidence suggests that 28b is released after one addition of borane but then re-enters the catalytic cycle to form 28c and 28d.

![Figure 3](https://doi.org/10.1021/jacs.2c08559)

**Figure 3.** Tracked reaction: (a) reaction at RT; (b) reaction at 50 °C.

| Entry | [Na(18-c-6)]$_2$[1] (X mol %) | Time (h) | Temperature (°C) | 28d Conv (%) | TON | TOF (h$^{-1}$) |
|-------|-------------------------------|----------|------------------|--------------|-----|----------------|
| 1     | 0.33                          | 12       | RT               | >99          | 300 | 25             |
| 2     | 0.33                          | 10       | RT               | >99          | 300 | 30             |
| 3     | 0.33                          | 1        | 50               | >99          | 300 | 300            |
| 4     | 0.1                           | 32       | RT               | >99          | 1000| 31             |
| 5     | 0.01                          | 480      | 98               | >99          | 9800| 20             |
| 6     | 0.01                          | 40       | 50               | >99          | 9476| 237            |

*Relative to B−H bonds. Determined by $^1$H NMR spectroscopy, based on C−H bond formation. Alternative conditions: only oDFB as solvent.
Mimicking catalytic conditions, 28b could be independently prepared in situ by addition of an excess of HBBN to formic acid in DFB/toluene over 20 h. After generation of 28b, there is no further reaction with excess HBBN. However, when [1]2− was added to the reaction mixture, formation of 28c and 28d was observed. This observation is consistent with (1) the need for [1]2− in the reduction of 28b and (2) 28b being an intermediate in CO2 hydroboration and not a side product.

**Mechanistic Investigations.** In order to probe the mechanistic landscape for the reduction of C=O functional groups, we have performed DFT calculations on the simplest model substrate, formaldehyde (Figure 4). The optimized structure of [1]2− reproduces the crystallographic data with good accuracy: the optimized B−P bond lengths are 2.07 Å (vs 2.052(8) and 2.082(7) Å in Figure 2), while P1−P2 and P1−P3 are 2.21 Å vs crystallographic values of 2.213(2) and 2.216(2) Å, respectively. In its equilibrium structure, the boron center in [1]2− is saturated by two B−P bonds, but a wider survey of the potential energy surface reveals a second shallow local minimum only 15.1 kcal/mol above the equilibrium structure, where the BBN fragment is coordinated to only one of the two phosphorus centers (isomer [1']2−, Figure 4). In this case the single B−P bond length is 1.89 Å, precisely in the range for borylphosphines.

In the mechanistic scheme shown in Figure 4, a number of possible intermediates that are related by the addition of [B]H or formaldehyde or by the release of the product MeO[B] are identified. The changes in energy and zero-point-corrected free energy for the overall reaction H2CO + [B]H → MeO[B] are −50.5 and −34.8 kcal/mol, respectively, and the energies around each of the six triangles shown in Figure 4 sum to exactly these values. The cycle in the top left of the figure involves exothermic addition of H2CO to [1]2− to form I2, followed by marginally exothermic addition of H[B] to form the methoxy derivate, I3, where the OMe group bridges the two boron centers. Loss of the product to regenerate [1]2− is then moderately exothermic (−5.0 kcal/mol) but strongly favored on the free energy scale (−22.1 kcal/mol). The alternative pathway via initial activation of the borohydride (lower left triangle in Figure 4) proceeds via a marginally exothermic first step followed by a very exothermic binding and reduction of formaldehyde (∆E = −41.4 kcal/mol). Both cycles, [1]2− + CH2O + [B]H → I1 or I2 → I3 → [1]2− + MeO[B], therefore present a plausible cascade leading from reactants to products. We note, however, that only one of the two B−P bonds has been activated in I3, leaving open the possibility of a further series of reactions involving reaction of I3 with second equivalents of formaldehyde and borohydride to form I6 (via I4 or I5 depending on the order of addition) followed by release of MeO[B] to regenerate I3. The energies of the various steps in the cycle I3 + CH2O + [B]H → I4 or I5 → I6 → I3 + MeO[B] are strikingly similar to those for the original cycle ([1]2− + CH2O + [B]H → I1 or I2 → I3 → [1]2− + MeO[B]), other than a marginal decrease in exothermicity of the steps that involve binding of substrate and an increased exothermicity of the final release of product, both of which reflect the greater steric crowding as more molecules are assembled around the catalyst. Nevertheless, it is clear that the second B−P bond in I3 remains capable of binding further substrate molecules.

Some support for the presence of I4 in solution comes from monitoring of the hydroboration of 5a, 7a, 11a, 11a, and 7a (see Supporting Information, Section 6.4).1H NMR studies on the hydroboration of 5a, 7a, and 11a reveal the presence of a second-order AB spin system with similar chemical shifts and coupling as the hydroborated products (selected spectra, Figure 5a). The AB spin system is consistent with the presence of a pair of enantiotopic protons displaying a 10−12 Hz...
geminal coupling, an assertion that is further supported by $^1$H correlated NMR spectroscopy (COSY) studies (Supporting Information, Figure S142). $^1$H diffusion-ordered NMR spectroscopy (DOSY) studies on the hydroboration of 7a (Supporting Information, Figure S143) confirmed that the species giving rise to the AB spin system has the lowest diffusion coefficient, indicating that it is the largest species present in the reaction mixture, in line with the proposed structure for I4 given in Figure 4. In contrast, the analogues of I4 detected from the hydroboration of the ketones 14a and 17a, where only a single proton is present, display similar resonances but without further geminal coupling (selected spectra, Figure 5b). The characteristic resonances for I4 are observed only during the reaction and disappear when the reaction is complete. Moreover, addition of 500 equiv of HBpin confirmed (Scheme 3) compound 16b to be the major product, but its BBN analogue 16b$'$ was also detected as a minor product in a 95:5 ratio. One possible source of the minor isomer is the methoxy-bridged intermediate, I3 in Figure 4, where the oxygen is almost symmetrically bonded to both boron centers (B−O = 1.59 and 1.60 Å to the BBN and [B] groups, respectively). Cleavage of the two almost equivalent B−O bonds could then lead to either 16b or 16b$'$. At the wb97XD/def2-TZVP level, decomposition to give 16b$'$ ([B]=P$_2$) was found to be less favorable by 15.1 kcal/mol ($\Delta G = -16.2$ kcal/mol) than to 16b ([B]=$^1$P$_2$), qualitatively consistent with the observed product distribution. The formation of 16b$'$ in the experiment does, however, indicate a 5% degradation of the catalyst under these conditions. Of course, a cluster functionalized with Bpin ([[Bpin]P$_2$]) could also be catalytically active, following equivalent pathways to those shown in Figure 4, and a catalytic role for [[Bpin]P$_2$]=$^1$P$_2$ would be consistent with our description of the [Na(18-c-6)]$^+$(HP$_2$) salt as a precatalyst in Table 1. We

Figure 5. $^1$H NMR spectroscopic monitoring of hydroboration of (a) 7a and (b) 17a.

Scheme 3. Stoichiometric Hydroboration of Acetophenone
have not, however, been able to isolate or independently synthesize this species and test its catalytic performance, despite multiple attempts to do so. It is noteworthy that catalyst degradation via this route is not an issue when the HBBN dimer is used as a reducing agent, as it is in our experiments on CO₂ hydroboration, simply because the analogue of I₃ is then symmetric.

The mechanism of the CO₂ and heteroallene reduction reactions will be the subject of a further study, but it seems likely that, in their initial stages, at least, they will share many common features with the formaldehyde reaction shown in Figure 4. The geometries of the analogues of I₂ with CO₂, HNCNH, and HC≡CCHO shown in Supporting Information, Figure S170, certainly show no significant differences in the binding mode of the substrate to [I]₂⁻.

■ CONCLUSION

In conclusion, a boron-functionalized group 15 Zintl cluster, [(BBN)P₂]⁺⁻ [(I)₂⁻], is prepared and found to be competent in the catalytic hydroboration of C=O bonds. Aldehydes, ketones, carbodiimides, isocyanates, and CO₂ are all reduced, and, in the case of CO₂ hydroboration, based on catalyst performance alone, [Na(18-c-6)]⁻[I] is competitive with other main group catalysts. Further, high selectivity to methoxyborane under mild conditions and catalyst recycling is established. This work represents the first application of a Zintl cluster in transition metal-free catalysis and establishes clearly that the cluster itself can play an active role in the catalytic cycle beyond that of a spectator ligand.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c08559.

The general information, experimental procedures, characterization data, and computational details (PDF)

Accession Codes
CCDC 2195882–2195885 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors
Meera Mehta — Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.; orcid.org/0000-0002-6833-5574; Email: meera.mehta@manchester.ac.uk
John E. McGrady — Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3QR, U.K.; orcid.org/0000-0002-8991-1921; Email: john.mcgrady@chem.ox.ac.uk

Authors
Bono van IJzendoorn — Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.; orcid.org/0000-0003-1010-4834
Saad F. Albawardi — Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3QR, U.K.; orcid.org/0000-0001-5957-5106

Inigo J. Vitorica-Yrezabal — X-ray Diffraction Facility, University of Manchester, Manchester M13 9PL, U.K.
George F. S. Whitehead — X-ray Diffraction Facility, University of Manchester, Manchester M13 9PL, U.K.; orcid.org/0000-0003-1949-4250

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/jacs.2c08559

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the EPSRC for funding (EP/V012061/1) and supporting a DTA studentship (B.v.I.). We thank the Royal Society (RGS/R1/211101) for supporting a consumables budget. We are also grateful to the UK Materials and Molecular Modelling Hub for computational resources, which is partially funded by EPSRC (EP/P020194/1 and EP/T022213/1). We also thank Gareth Smith for mass spectrometric analyses, Anne Davies and Martin Jennings for elemental analyses, and Ralph Adams for NMR spectroscopic enquiries. S.F.A. acknowledges the Saudi government for a postgraduate scholarship.

■ ABBREVIATIONS

THF; tetrahydrofuran; RT; room temperature; HBpin; pinacolborane; HBBN; 9-borabicyclo(3.3.1)nonane; eDBF; ortho-difluorobenzene; XRD; X-ray diffraction; NMR; nuclear magnetic resonance; OTf; triflate; DFT; density functional theory; FLP; frustrated Lewis pair; COSY; correlation spectroscopy; DOSY; diffusion-ordered spectroscopy

■ REFERENCES

(1) Müller, L. J.; Kätelhön, A.; Bringezu, S.; McCoy, S.; Suh, S.; Edwards, R.; Sick, V.; Kaiser, S.; Cuéllar-Franca, R.; El Khamlichi, A.; Lee, J. H.; von der Assen, N.; Bardow, A. The Carbon Footprint of the Carbon Feedstock CO₂. Energy Environ. Sci. 2020, 13 (9), 2979–2992.
(2) Zhang, X.; Zhang, G.; Song, C.; Guo, X. Catalytic Conversion of Carbon Dioxide to Methanol: Current Status and Future Perspective. Front. Energy Res. 2021, 8, 62119.
(3) Roede-Gutzmer, Q. J.; Kaiser, D.; Bertau, M. Renewable Methanol Synthesis. ChemBioEng. Reviews 2019, 6 (6), 209–236.
(4) Iwarewe, S. A.; Ramjugernath, D. In Carbon Dioxide to Energy: Killing Two Birds with One Stone; Raghavan, K. V.; Ghosh, P., Eds.; Springer Singapore: Singapore, 2017; pp 93–103.
(5) Roy, S.; Cherevotan, A.; Peter, S. C. Thermochromic CO₂ Hydrogenation to Single Carbon Products: Scientific and Technological Challenges. ACS Energy Lett. 2018, 3 (8), 1938–1966.
(6) Goeppter, A.; Czaun, M.; Jones, J-P.; Surya Prakash, G. K.; Olah, G. A. Recycling of Carbon Dioxide to Methanol and Derived Products — Closing the Loop. Chem. Soc. Rev. 2014, 43 (23), 7995–8048.
(7) Navarro-Jaén, S.; Virginie, M.; Bonin, J.; Robert, M.; Wojcieszak, R.; Khodakov, A. Y. Highlights and Challenges in the Selective Reduction of Carbon Dioxide to Methanol. Nat. Rev. Chem. 2021, 5, 564–579.
(8) Zhao, G.-Q.; Hu, J.; Long, X.; Zou, J.; Yu, J.-G.; Jiao, F.-P. A Critical Review on Black Phosphorus-Based Photocatalytic CO₂ Reduction Application. Small 2021, 17 (49), 2102155.
(9) Fung, C.-M.; Er, C.-C.; Tan, L.-L.; Mohamed, A. R.; Chai, S.-P. Red Phosphorus: An Up-and-Coming Photocatalyst on the Horizon for Sustainable Energy Development and Environmental Remediation. Chem. Rev. 2022, 122 (3), 3879–3965.
(10) Townrow, O. P. E.; Chung, C.; Macgregor, S. A.; Weller, A. S.; Goicoechea, J. M. A Neutral Heteroatomic Zintl Cluster for the Catalytic Hydrogenation of Cyclic Alkenes. J. Am. Chem. Soc. 2020, 142 (43), 18330–18335.

(11) Turberville, R. S. P.; Goicoechea, J. M. From Clusters to Unorthodox Pnicogen Sources: Solution-Phase Reactivity of [E]3− (E = P–Sb) Anions. Chem. Rev. 2014, 114 (21), 10807–10828.

(12) van Ijzendoorn, B.; Mehta, M. Frontiers in the Solution-Phase Chemistry of Heteroatomic Group 15 Zintl Clusters. Dalton Trans. 2020, 49 (42), 14758–14765.

(13) Dragulescu-Andrasi, A.; Miller, L. Z.; Chen, B.; McQuade, D. T.; Shatruck, M. Facile Conversion of Red Phosphorus into Soluble Polyphosphide Anions by Reaction with Potassium Ethoxide. Angew. Chem. Int. Ed. 2016, 55 (12), 3904–3908.

(14) Jo, M.; Dragulescu-Andrasi, A.; Miller, L. Z.; Pak, C.; Shatruck, M. Nucleophilic Activation of Red Phosphorus for Controlled Synthesis of Polyphosphides. Inorg. Chem. 2020, 59 (8), 5483–5489.

(15) Poitiers, N. E.; Giarrana, L.; Huch, V.; Zimmer, M.; Scheschkewitz, D. Exohedral Functionalization vs. Core Expansion of Siliconoids with Group 9 Metals: Catalytic Activity in Alkene Isomerization. Chem. Sci. 2020, 11 (30), 7782–7788.

(16) Townrow, O. P. E.; Duckett, S. B.; Weller, A. S.; Goicoechea, J. M. Zintl Cluster Supported Low Coordinate Rh(i) Centers for Isomerization. Scheschkewitz, D. Exohedral Functionalization vs. Core Expansion (E = P–Sb) Anions. Chem. Rev. 2014, 114 (21), 10807–10828.

(17) Wang, Y.; Zhang, C.; Wang, X.; Guo, J.; Sun, Z.-M.; Zhang, H. Site-Selective CO2 Reduction over Highly Dispersed Ru–SnOx Sites Derived from a [Ru@Sn36]-Zintl Cluster. ACS Catal. 2020, 10 (14), 7808–7819.

(18) Wilson, R. J.; Weizert, B.; Dehnen, S. Recent Developments in Zintl Cluster Chemistry. Dalton Trans 2018, 47 (42), 14861–14869.

(19) Turberville, R. S. P.; Goicoechea, J. M. Studies on the Reactivity of Group 15 Zintl ions with Carbodiimides: Synthesis and Characterization of a Heptaphosphaguanidine Dianion. Chem. Commun. 2012, 48 (10), 1470–1472.

(20) Turberville, R. S. P.; Goicoechea, J. M. Hydrophinctination Reactions of Carbodiimides and Isocyanates with Protonated Heptaphosphide and Heptaarsenide Zintl Ions. Eur. J. Inorg. Chem. 2014, 2014 (10), 1660–1668.

(21) Turberville, R. S. P.; Goicoechea, J. M. Hydrophosphinilation of Carbodiimides Using Protic Heptaphosphide Cages: A Unique Effect of the Bimodal Activity of Protonated Group 15 Zintl Ions. Organometallics 2012, 31 (6), 2452–2462.

(22) Turberville, R. S. P.; Goicoechea, J. M. An Asymmetrically Derived 1,2,3-Triphospholide: Synthesis and Reactivity of the 4-(2′-Pyridy1)-1,2,3-triphospholide Anion. Inorg. Chem. 2013, 52 (9), 5527–5534.

(23) Turberville, R. S. P.; Jupp, A. R.; McCullough, P. S. B.; Ergöçmen, D.; Goicoechea, J. M. Synthesis and Characterization of Free and Coordinated 1,2,3-Triphosphinolide Anions. Organometallics 2013, 32 (7), 2234–2244.

(24) Jupp, A. R.; Goicoechea, J. M. The 2-Phosphaethynolate Anion: A Convenient Synthesis and [2 + 2] Cycloaddition Chemistry. Angew. Chem. Int. Ed. 2013, 52 (38), 10064–10067.

(25) van Ijzendoorn, B.; Vitorica-Treval, I.; Whitehead, G.; Mehta, M. Heteroallene Capture and Exchange at Functionalised Hepta phosphane Clusters. Chem.—Eur. J. 2022, 28 (6), No. e202103737.

(26) Stephen, D. W. The Broadening Reach of Frustrated Lewis Pair Chemistry. Science 2016, 354 (6317), No. aa7229.

(27) Stephen, D. W. Catalysis, FLPs, and Beyond. Chem. 2020, 6 (7), 1520–1526.

(28) Lam, J.; Szkop, K. M.; Mosafari, E.; Stephen, D. W. FLP Catalysis: Main Group Hydrogenations of Organic Unsaturated Substrates. Chem. Soc. Rev. 2019, 48 (13), 3592–3612.

(29) Ashley, A. E. O. H. D. FLP-Mediated Activations and Reductions of CO2 and CO. Springer: Berlin, 2012; Vol. 334.

(30) Stephen, D. W.; Erker, G. Frustrated Lewis Pair Chemistry: Development and Perspectives. Angew. Chem. Int. Ed 2015, 54 (22), 6400–6441.
(53) Liu, L.; Lo, S.-K.; Smith, C.; Goicoechea, J. M. Pincer-Supported Gallium Complexes for the Catalytic Hydroboration of Aldehydes, Ketones and Carbon Dioxide. *Chem.—Eur. J.* 2021, 27 (69), 17379–17385.

(54) Sau, S. C.; Bhattacharjee, R.; Vardhanapu, P. K.; Vijaykumar, G.; Datta, A.; Mandal, S. K. Metal-Free Reduction of CO₂ to Methoxyborane Under Ambient Conditions Through Borondiformate Formation. *Angew. Chem. Int. Ed* 2016, 55 (48), 15147–15151.

(55) Das Neves Gomes, C.; Blondiaux, E.; Thuéry, P.; Cantat, T. Metal-Free Reduction of CO₂ with Hydroboranes: Two Efficient Pathways at Play for the Reduction of CO₂ to Methanol. *Chem.—Eur. J.* 2014, 20 (23), 7098–7106.

(56) Yang, Y.; Xu, M.; Song, D. Organocatalysts with Carbon-Centered Activity for CO₂ Reduction with Boranes. *Chem. Commun.* 2015, 51 (56), 11293–11296.

(57) Ramos, A.; Antínolo, A.; Carrillo-Hermosilla, F.; Fernández-Galán, R. Ph,PCH₂CH₂B(C₈H₁₄) and Its Formaldehyde Adduct as Catalysts for the Reduction of CO₂ with Hydroboranes. *Inorg. Chem.* 2020, 59 (14), 9998–10012.

(58) Blondiaux, E.; Pouessel, J.; Cantat, T. Carbon Dioxide Reduction to Methylamines Under Metal-Free Conditions. *Angew. Chem. Int. Ed* 2014, 53 (45), 12186–12190.

(59) Lim, C.-H.; Holder, A. M.; Hynes, J. T.; Musgrave, C. B. Roles of the Lewis Acid and Base in the Chemical Reduction of CO₂ Catalyzed by Frustrated Lewis Pairs. *Inorg. Chem.* 2013, 52 (17), 10062–10066.