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Sterically Unprotected Nucleophilic Boron Cluster Reagents

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Abstract: A cornerstone of modern synthetic chemistry rests on the ability to manipulate the reactivity of a carbon center by rendering it either electrophilic or nucleophilic. However, accessing a similar reactivity spectrum with boron-based reagents has been significantly more challenging. While classical nucleophilic carbon-based reagents normally do not require steric protection, readily accessible, unprotected boron-based nucleophiles have not yet been realized. Herein, we demonstrate that the bench stable *closo*-hexaborate cluster anion can engage in a nucleophilic substitution reaction with a wide array of organic and main group electrophiles. The resulting molecules containing B–C bonds can be further converted to tricoordinate boron species widely used in organic synthesis.

Electronic polarization at an atom (*e.g.* carbon) generally dictates its reactivity profile and determines whether it can undergo electrophilic or nucleophilic substitution chemistry[1]. Since the seminal work by Grignard, researchers have been able to generate a variety of useful synthetic reagents featuring an electropositive element interacting with a carbon, rendering the carbon center nucleophilic[2]. Given the prevalence of organoboron compounds used in synthesis[3,4], researchers recently have been interested in applying a similar concept of polarity switching commonly used for carbon reagents to boron congeners (Fig. 1a)[5]. This strategy can potentially diversify the reactivity repertoire beyond the classical electrophilic nature of boron-based reagents[6]. However, access to synthetically practical nucleophilic boron compounds remains a significant fundamental challenge. In 2006, Segawa and co-workers reported the first synthesis and isolation of a well-defined anionic boryllithium **1** (Fig. 1b), which undergoes several reactions with carbon-based electrophiles[7]. This discovery was enabled by the use of a sterically encumbering ligand platform that stabilizes the highly reactive nucleophilic boron site, termed as "boryl"[8]. Inspired by the idea of using steric protection, others have targeted the synthesis of nucleophilic boron compounds, generally leveraging electron-donating and sterically bulky ligands to tame the reactivity of the nucleophilic boron species **2 – 5** (Fig. 1b)[9-12]. Recently, several ligand frameworks were also developed to constrain boron-based centers in a non-traditional electronic environment rendering some of the species (*e.g.*, **6**) nucleophilic[13,14]. While significant progress has been made in stabilizing nucleophilic boron centers, synthetically

demanding protocols and lack of overall benchtop stability have hindered the widespread use of nucleophilic boron reagents in synthetic methodology.

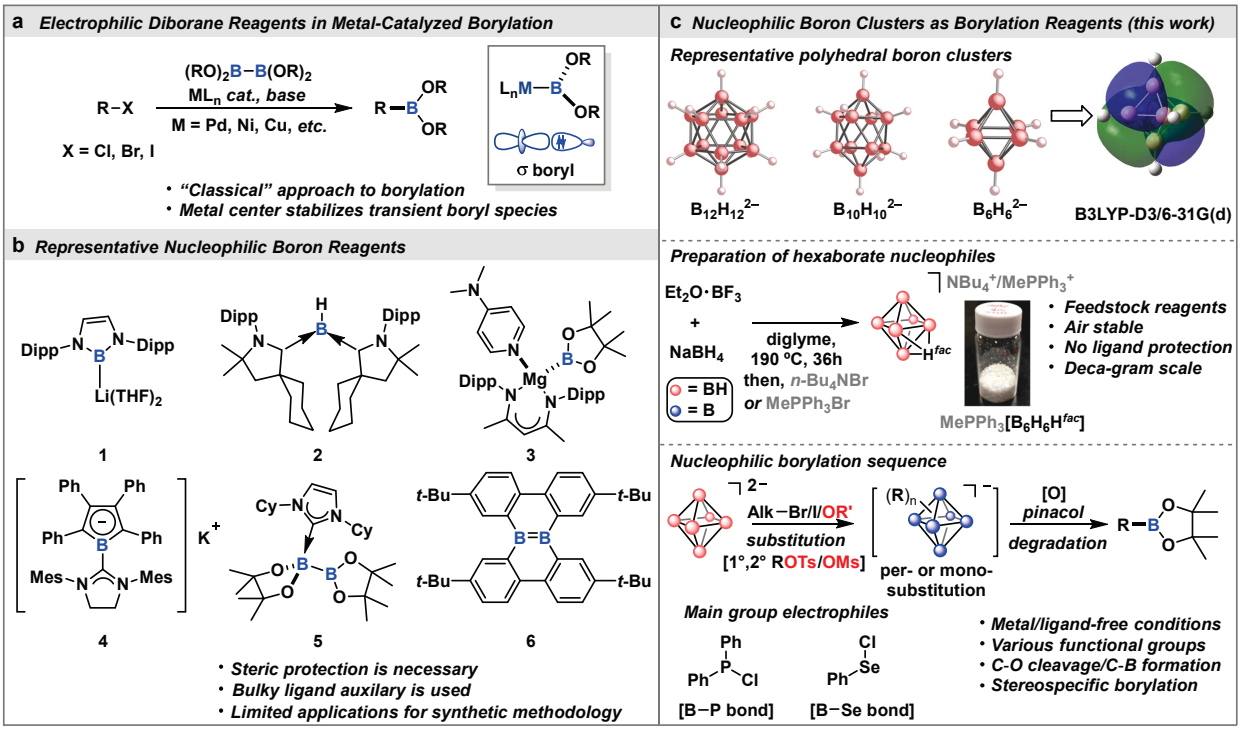

Fig. 1 Development of sterically unprotected cluster-based borylation reagents. **a**, General scheme for metal-catalyzed borylation using tricoordinate diborane reagents. **b**, Representative nucleophilic boron reagents developed previously. **c**, One of three triply degenerate HOMO representations of $B_6H_6^{2-}$, synthesis of the $B_6H_7^{1-}$ anion, and a general borylation strategy using sterically unprotected cluster-based nucleophiles developed in this work.

In this work, we demonstrate a conceptually different approach to stabilize a reactive boron nucleophile, predicated on three-dimensional electron delocalization instead of steric protection enforced by a ligand auxiliary (Fig. 1c). In order to engender the necessary delocalization, we identified a system in which boron atoms are bonded in a cluster-based environment. Specifically, we evaluated polyhedral boranes ($B_nH_n^{2-}$, n = 6, 10, 12) (Fig. 1c, top), which are some of the simplest clusters containing catenated boron atoms known to date. In these clusters, electron delocalization across cage boron vertices reduces the otherwise extreme reactivity of atom-centered boryl anions[15]. A manifestation of this delocalization can be seen in the example of $B_{12}H_{12}^{2-}$, which has a nucleophilicity as low as that of benzene; neither of these molecules readily react with carbon-based electrophiles[16]. On the other hand, smaller boron clusters have been previously suggested to be less inert and could potentially exhibit an increased nucleophilic character compared to $B_{12}H_{12}^{2-}$ [17]. For example, DFT analysis of $B_6H_6^{2-}$ at the B3LYP-D3/6-31G(d) level of theory suggests that the triply degenerate highest occupied molecular orbitals (HOMO) are delocalized across eight faces of octahedron and that the corresponding energy is 3eV higher than the HOMO of $B_{12}H_{12}^{2-}$ (see SI). Ultimately, this begged the question of whether $B_6H_6^{2-}$ can be considered as a competent nucleophile in the context of nucleophilic borylation chemistry to produce substrates that can be efficiently transformed into tricoordinate boron compounds commonly used in synthesis (Fig. 1c, bottom).

Monoanionic hexaborate compound **7** (Fig. 2a) can be synthesized on a multi-gram scale in one step from cheap and commercially available $NaBH_4$ and $BF_3 \cdot Et_2O$. Crude **7** can be directly converted into **8** and **9** from a salt metathesis reaction in water, producing singly-protonated, air-stable hexaborate species soluble in organic solvents. The protonation state of **8** and **9** imply that the Brønsted-basic character of $B_6H_6^{2-}$ is readily accessible and could be applied to other electrophiles beyond H^+.

To probe whether this cluster could engage in nucleophilic substitution towards organic electrophiles, we conducted reactions between **8** and a series of benzyl bromides in acetonitrile (Fig. 2a; see also Table S1). Using K_3PO_4 as a base, persubstituted B_6-based clusters **10** and **11** can be formed quantitatively as judged by ^{11}B NMR spectroscopy (see supporting information for all spectroscopic data). During our investigations into the purification of **10** and **11**, we noticed that subjecting these compounds to a slurry of silica gel in dichloroethane at 50 °C results in the formation of a new cluster-based species as evidenced by a diagnostic change in ^{11}B NMR spectra of the corresponding products (Fig. 2b). From the reaction mixture initially containing **11**, we were able to isolate a crystalline solid and subject this material to a series of structural characterization techniques. ^1H NMR spectroscopy suggested the formation of new bridging hydrides and implied a loss of one "B–CH_2Ar" vertex from starting **11**. Both X-ray photoelectron spectroscopy (XPS) and ^{11}B NMR spectroscopy suggest desymmetrization of the cluster precursor and the appearance of two unique boron sites with distinct electronic environments. Single crystals of the material grown from a concentrated toluene solution were subjected to X-ray diffraction studies and identified the solid as a neutral pentaborane cluster **13** with one benzyl-attached boron vertex removed from parent cluster **11** (Fig. 2b). This unprecedented partial cage deconstruction suggests that unlike large *closo*-borane clusters (*e.g.*, $B_{12}H_{12}^{2-}$)[18], peralkylated B_6-based clusters can be oxidatively unstable towards B–B bond rupture and that this instability could be leveraged to selectively generate tricoordinate boron reagents through substituted hexaborate cage deconstruction.

To further probe this hypothesis, we investigated the deconstruction of **11** with a range of model oxidants (Table S2). Upon employing 7,7,8,8-tetracyanoquinodimethane (TCNQ) as single electron oxidant, significant quantities of the corresponding benzyl boronate products (**14** and **15**) were observed suggesting a successful cage deconstruction under these conditions. While these results are conceptually promising and suggest that one can employ monoanionic **8** or **9** as a nucleophilic boron source to synthesize organic boronates through a substitution/cage deconstruction sequence, several challenges revealed themselves during the course of our investigation that necessitated a modified strategy. Specifically, when cyclic voltammetry (CV) data was compared for **10**, **11** and **12**, significant variability in oxidation potentials, ranging from +0.48 V to 0.03 V (vs. Fc^+/Fc), was observed for these compounds (Fig. 2c). This suggests that the nature of the organic substituents dramatically affects the oxidative stability of the perfunctionalized intermediates potentially limiting the synthetic generality of the cage substitution/deconstruction protocol.

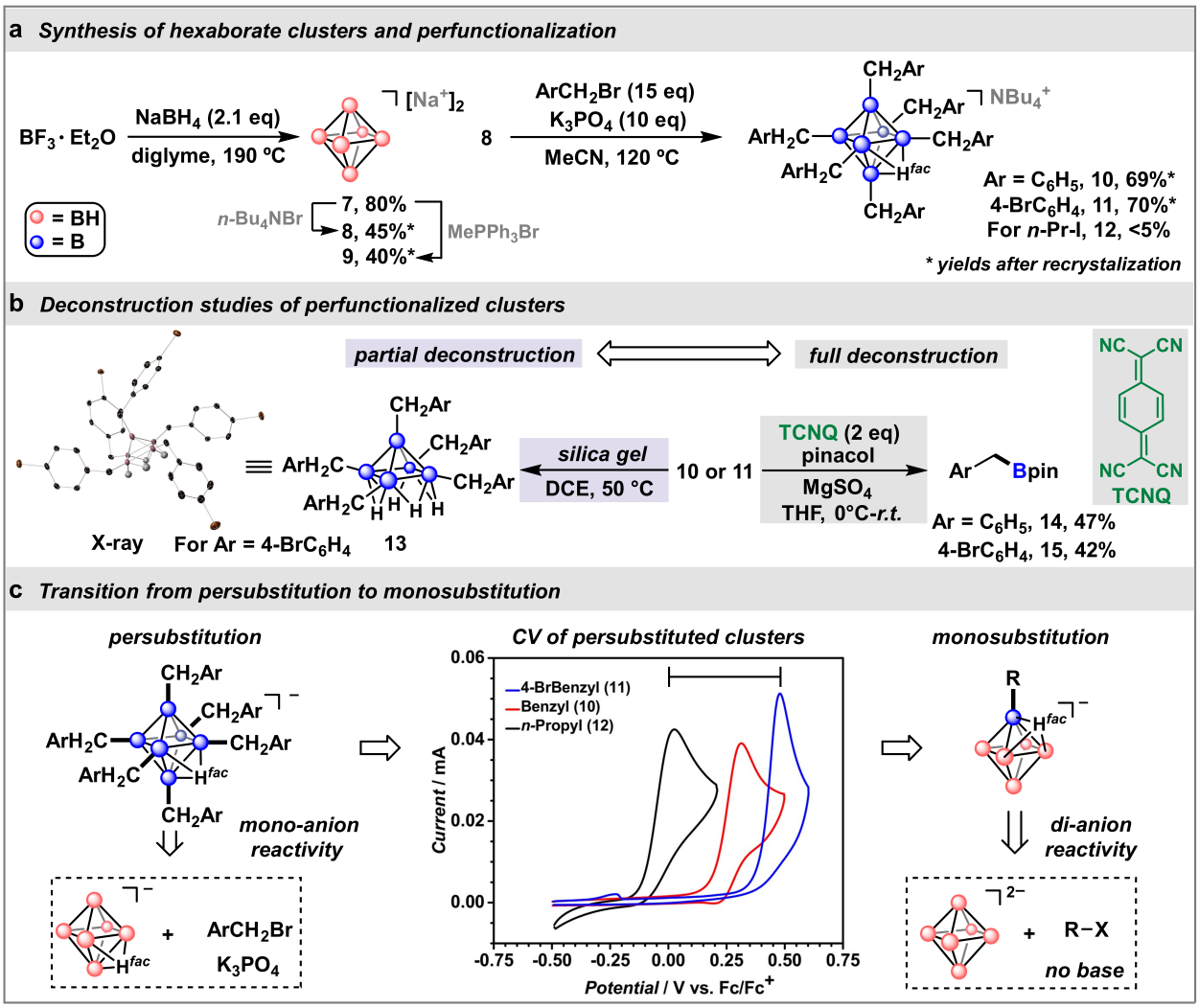

Fig. 2 Synthesis and deconstruction studies of perfunctionalized hexaborate anions. **a**, Preparation of monoanionic hexaborate cluster reagents (**8** and **9**) and their reactivity toward model electrophiles. **b**, Discovery of the selective cage deconstruction process of clusters **10** and **11**, leading to the intermediate **13**, which can be further degraded with TCNQ to produce tricoordinate alkyl boronate species (**14** and **15**). **c**, Oxidation potential variability (see cyclic voltammograms of **10**, **11** and **12**) of the perfunctionalized clusters leading to the alternative borylation strategy *via* a monosubstitution using dianionic $B_6H_6^{2-}$ reagent.

We thus hypothesized that *partial* cage substitution could alleviate these limitations (Fig. 2c). We investigated whether well-defined dianionic $B_6H_6^{2-}$ salts could be used for a base-free nucleophilic substitution, leading to the formation of monoalkylated compounds with similar oxidation potentials (Fig. 2c). The synthesis of the dianion **16** can be accomplished in a straightforward manner on a multi-gram scale by stirring **8** with NBu_4OH in the presence of the Na_2SO_4. Alternatively, **9** can be deprotonated with a phosphorane reagent (CH_2PPh_3) producing **17** in a nearly quantitative yield (Fig. 3a). Both of these dianion-based salts are bench stable solids that can be stored in a desiccator for over 2 months without any noticeable protonation to form the $B_6H_7^-$ monoanion.

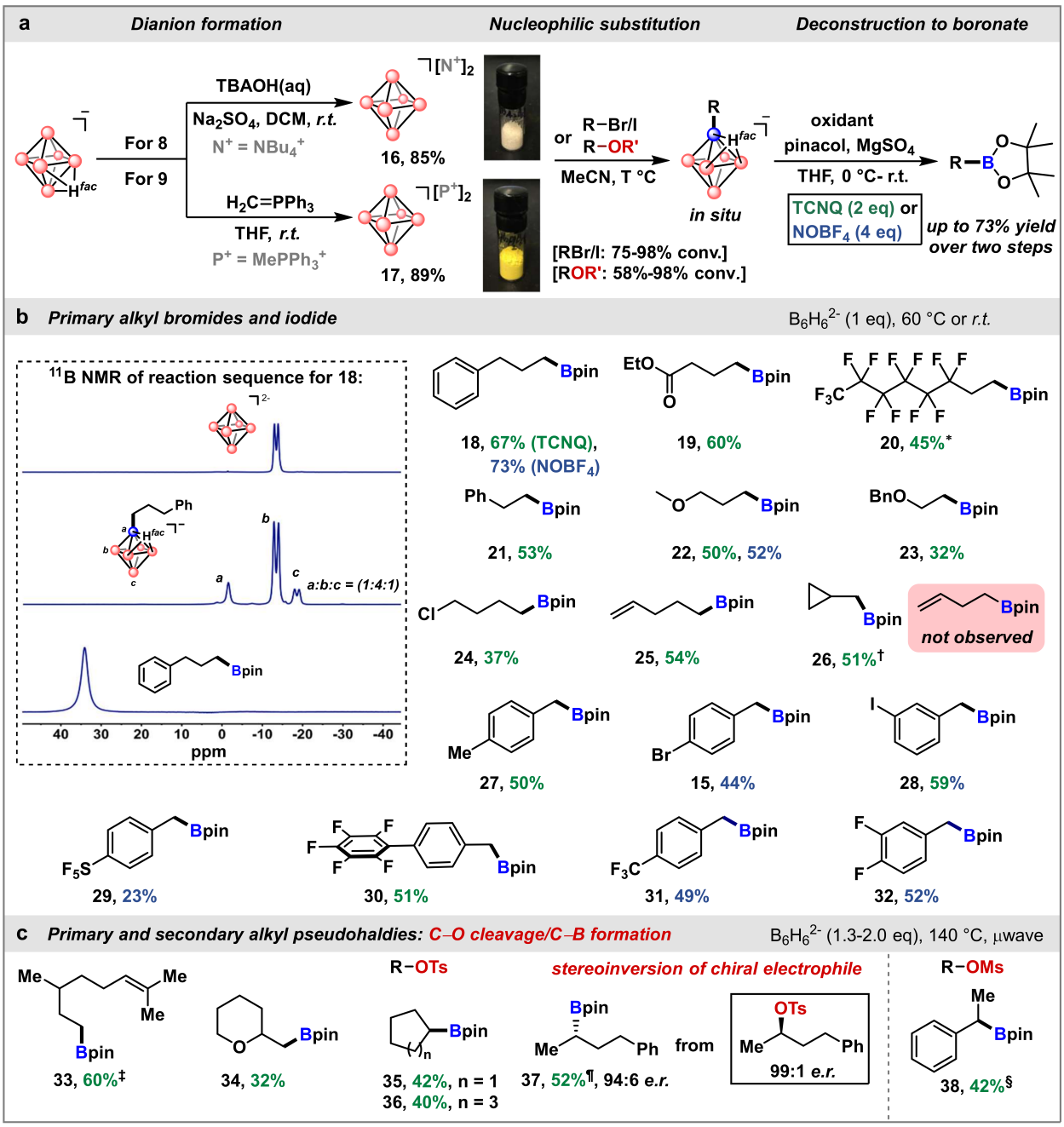

Fig. 3 Borylation/cage deconstruction strategy with dianionic hexaborates. a, Preparation of $B_6H_6^{2-}$ reagents and their subsequent use in borylation of organic electrophiles. **b**, Substrate scope of alkyl halides. Standard reaction conditions: $B_6H_6^{2-}$ (1.0 equiv), alkyl halide (0.4 mmol, 1.0 equiv), MeCN (2 mL). For unactivated alkyl bromides, 60 °C heating. For benzyl bromides, room temperature. Pinacol (10 equiv), $MgSO_4$ (12 equiv), THF (2 mL), 0 °C to room temperature for deconstruction. Isolated yields are calculated after cage deconstruction. Inset: ^{11}B NMR spectra for the synthesis sequence: hexaborate dianion (top); monosubstituted hexaborate (middle); purified alkyl–Bpin (bottom). **c**, Substrate scope of alkyl pseudohalides. Reaction conditions: $B_6H_6^{2-}$ (1.3-2.0 equiv), μwave heating at 140 °C. †Using alkyl iodide (2

equiv). † $B_6H_6^{2-}$ (1.5 equiv) and μwave heating at 110 °C. ‡Using oil bath heating at 80 °C. ¶ μwave heating at 90 °C.§ Using oil bath heating at 60 °C.

Consistent with our hypothesis, **16** and **17** undergo nucleophilic substitution with a wide variety of alkyl-based electrophiles producing the corresponding mono-substituted $[B_6H_5RH^{fac}]^-$ species (Fig. 3b). Importantly, these reactions take place under mild conditions by simply combining a dianionic reagent together with an electrophile substrate in a variety of non-protic organic solvents. No other additives are required to forge a B–C bond *via* this strategy. The unpurified products from these transformations can be directly subjected to oxidative deconstruction of the cluster with TCNQ or nitrosonium tetrafluoroborate ($NOBF_4$) in the presence of pinacol, ultimately producing the corresponding alkyl pinacol boronate esters.

Primary alkyl bromides and iodide containing various functional groups such as ester (**19**), perfluoroalkyl (**20**), alkyl ether (**22**, **23**) and halide (**24**) substituents were successfully converted to the corresponding boronic esters using the substitution/cage deconstruction sequence. Phenethyl bromide, which is susceptible to elimination under basic conditions, is tolerated under the developed protocol (**21**). A substrate bearing a terminal olefin was also converted directly to the boronic ester with no evidence of olefin reduction (*e.g.*, hydroboration) (**25**). For benzyl bromides containing aryl bromide and iodide substituents, only C_{sp}^3–Br bonds were borylated (**15**, **28**). Interestingly, substrates bearing active sites for nucleophilic aromatic substitution (S_NAr) such as pentafluorophenyl and difluorophenyl groups (**30**, **32**) remained intact under the developed conditions.

Recently, there have been a growing number of reports using oxygen-containing electrophiles (pseudohalides) to replace alkyl halides as cross-coupling partners[19]. However, in metal-catalyzed borylations of alkyl electrophiles, pseudohalides are rarely reported as substrates due to the reduced reactivity of C_{sp}^3–O bonds towards activation by several metal-based catalysts commonly employed under borylation conditions[20]. In our case, the substitution of both primary and secondary alkyl–OTs/OMs substrates by $B_6H_6^{2-}$ (**16**) proceeded smoothly in the absence of any metal salts or halide additives; subsequent cage deconstruction produced the corresponding pinacol boronate ester compounds (**33**-**38**) (Fig. 3c).

To shed light on the nature of the cluster-based nucleophilic substitution, we investigated whether the discovered transformation showed hallmarks of radical reaction pathways. Bromomethylcyclopropane has been previously employed as a standard radical probe in various metal-catalyzed borylations, where in the presence of radical species, ring-opened 3-butenylboronate was isolated as the major product[21,22]. In contrast, after subjecting the same electrophile to our optimized reaction conditions, no ring-opened species were observed either in the reaction mixture after monofunctionalization or in the resulting borylated product **26**. This observation suggests that a radical mechanism for B–C bond formation is unlikely. Additionally, when enantiopure (*R*)-2-OTs-4-phenylbutane was applied in our protocol, enantio-enriched alkyl boronate **37** was obtained with inversion of stereochemistry (94:6 *e.r.*), suggesting an apparent S_N2 substitution mechanism. This observation stands in stark contrast to existing metal-catalyzed systems, in which racemic borylated products are observed due to the intermediacy of alkyl radicals, therefore impeding general approaches to stereospecific borylation through chiral induction[22,23]. Importantly, this borylation strategy provides a new chiral auxiliary-free pathway to generate enantio-enriched alkyl boronates from chiral alcohol derivatives[24,25].

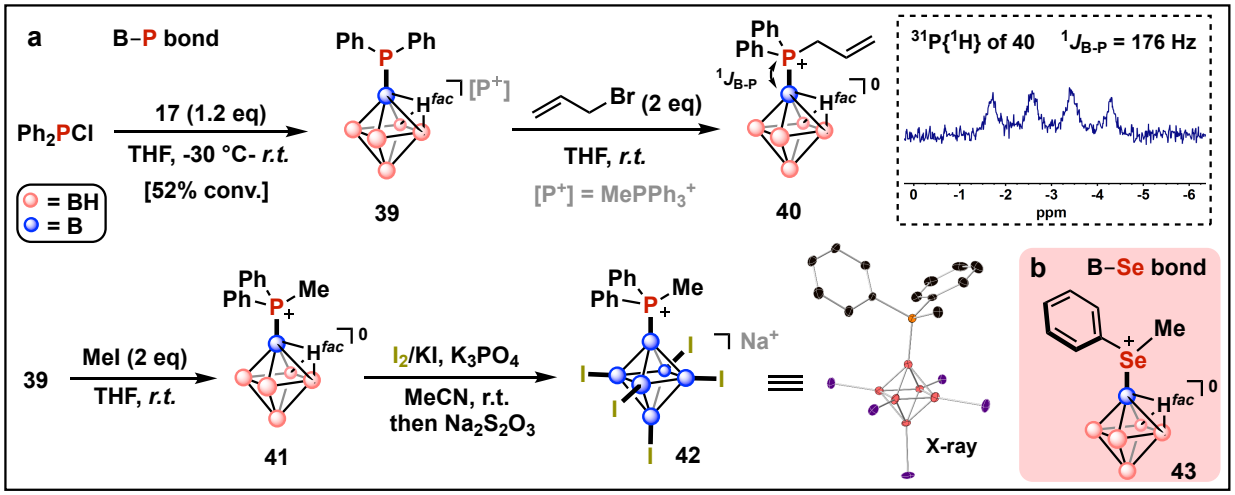

Fig. 4 Reaction of dianionic hexaborate with main group electrophiles. **a**, Transformations leading to the formation of clusters with B–P bonds (**40-42)**. **b**, Hexaborate cluster featuring a B–Se bond (**43,** see SI for synthesis and characterization details).

Undesired side reactions, including apparent one-electron reduction chemistry, have been observed with other classes of nucleophilic boron reagents in the presence of alkyl-based electrophiles[26]; in addition, some of these species also exhibit reducing behavior toward main group electrophiles[27]. Interestingly, during the course of our investigations, we never observed any apparent reduction products stemming from the reactions of hexaborate and alkyl electrophiles, which implies that under the developed conditions this nucleophilic source of boron is significantly less reducing. We therefore were curious whether the nucleophilic behavior of the hexaborate reagent could be extended to reactions with main group electrophiles to forge B-heteroatom bonds (Fig. 4). Traditionally, main group boranes (*e.g.*, phosphinoboranes) are prepared using electrophilic boron-based reagents[28]. Interested in reversing the role of boron reagents in these bond formations, we combined **17** and Ph_2PCl, resulting in the formation of diphenylphosphine-substituted hexaborate **39** (Fig. 4a), as judged by multinuclear NMR spectroscopy. Subsequent treatment with allyl bromide followed by workup permitted the isolation of **40** as a zwitterionic hexaborate containing an exopolyhedral P–B bond. The methylation of phosphorus, generating zwitterionic **41**, followed by iodination produced a heteroleptic penta-iodinated cluster **42,** which we were able to characterize by multinuclear NMR spectroscopy and single crystal X-ray diffraction, further confirming the proposed B–P connectivity. These results contrast previous observations of nearly quantitative reduction and formation of the corresponding diphosphine ($Ph_2P–PPh_2$) when **1** was treated with Ph_2PCl[27]. Consistent with the non-reducing, nucleophilic nature of the hexaborate anion, **17** undergoes a clean transformation with PhSeCl reagent forging a substituted cluster **43** with an exopolyhedral B–Se bond (Fig. 4b).

Overall, we have discovered that small polyhedral boron clusters featuring a sterically unprotected B_6-based cluster core possess a strong, yet non-reducing nucleophilicity that can be leveraged for the borylation of various organic and main group electrophiles. This led us to the development of a simple protocol, whereby carbon-based electrophiles can be transformed into the corresponding tricoordinate boron ester species without the use of metal catalysis. This work

highlights how boron-rich clusters can expand the toolkit of main group reagents[29-47] ultimately aiding in the development of organic synthesis through new modes of reactivity.

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Author contributions

X. M., J. C. A. and A. M. S. designed the project and the experiments. X. M., J. C. A., N. A. B. performed the synthesis and characterization, K. O. K. and D. J. assisted with the analytical characterization, A. U., K. Q. and M. K. contributed to the validation of the synthetic methodology. A. L. R. performed X-ray crystallographic studies. X. C., K. L. B and K. N. H. designed and performed computational studies. A. M. S., X. M., J. C.A. and N.A.B co-wrote the manuscript. All authors discussed the data and commented on the manuscript during its preparation.

Additional information

Supplementary information is available for this paper. Correspondence and requests for materials should be addressed to A.M.S.

Competing financial interests

The authors declare no competing financial interests.