

Metal-Free Bond Activation by Carboranyl Diphosphines

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ABSTRACT: We report metal-free bond activation by the carboranyl diphosphine 1- P^tBu_2 -2- P^iPr_2 - $C_2B_{10}H_{10}$. This main group element system contains basic binding sites and possesses the ability to cycle through two-electron redox states. The reported reactions with selected main group hydrides and alcohols occur via the formal oxidation of the phosphine groups and concomitant reduction of the boron cage. These transformations, which are driven by the cooperation between the electron-donating exohedral substituents and the electron-accepting cluster, differ from those of “regular” phosphines and are reminiscent of oxidative addition to transition metal centers, thus representing a new approach to metal-free bond activation.

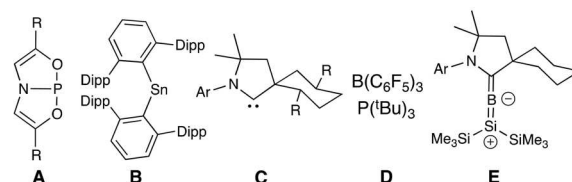
Activation of strong bonds has been the driver of organometallic chemistry since the early development of transition metal catalysis. Recently, significant attention has been focused on the conceptually similar metal-free redox bond activation inspired by discoveries from Power, Bertrand, Stephan, Braunschweig, Radosevich, and others (Scheme 1A–E).^{1–13} For example, cycling between P(III) and P(V) states in geometrically constrained phosphorus compounds affords the possibility of oxidative addition and reductive elimination in a way that mimics the reactivity of transition metal complexes.¹⁴

The redox transformations in main group systems can be centered on a single atom, as in the example of oxidative addition to trivalent phosphorus, or they can occur through the participation of larger fragments. Carborane clusters, including neutral $C_2B_{10}H_{12}$, have attracted increasing attention due to new applications in luminescent materials, batteries, ligand design, and catalysis.^{15–22} The *ortho*-carborane *closo*- $\{C_2B_{10}\}$ cluster can accept two electrons with conversion to the open *nido*- $\{C_2B_{10}\}$ isomers. This redox capability has been recently utilized in ligand design, for example by Welch and co-workers, who proposed that a reduced open cluster assists the activation of aromatic C–C bonds at the connected ruthenium center (Scheme 1F),²³ and by Xie and co-workers, who reported B–B bond formation upon the reduction of carborane with coordinated haloborylene (Scheme 1G).²⁴ Furthermore, Menard, Hayton, and co-workers demonstrated that changes in the geometry of the carborane cluster upon reduction resulted in marked differences in the ligand bite angle and chelation abilities, facilitating the redox-controlled extraction of uranyl ion (Scheme 1H).²⁵

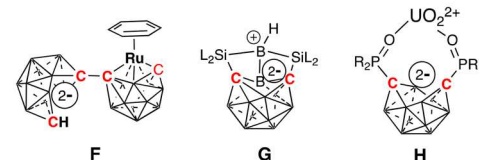
The carbon atoms of *ortho*- $C_2B_{10}H_{12}$ form single bonds to exohedral substituents, and π -back-donation from those groups to the cluster can increase the exohedral bond order and weaken the intracuster C–C bond.^{26,27} Recently, there was a report of opening of the *ortho*- $\{C_2B_{10}\}$ cage upon the reaction of carboranyl diphosphines with HCl, leading to the formation of a zwitterionic *nido*-cluster that contains two phosphonium centers (Scheme 1I).²⁸ Albeit complicated by side reactions

Scheme 1. Selected Examples of Redox Reactivity in Main Group Systems, Including Carboranes

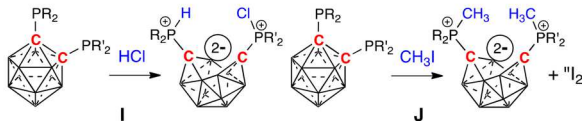
examples of metal-like redox-active main group systems:



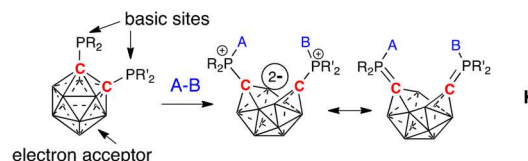
redox-active carborane clusters as ligands:



carboranyl diphosphine cluster opening upon protonation or alkylation:



metal-free bond activation driven by redox-active carboranyl diphosphines:



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and only partial conversion, similar reactivity has been observed between a carboranyl diphosphine and methyl iodide: the phosphorus centers become methylated and the carborane cage opens.²⁹ Concomitant formation of I_2 has been proposed as a source of electrons for the cluster reduction (Scheme 1J).

Conceptually, carboranyl diphosphines represent a metal-free cluster-containing molecular framework that combines two important features normally reserved for transition metals: the simultaneous ability to accept electrons to cycle through two-electron redox states and the ability to donate electrons through Lewis basic binding sites (Scheme 1K). Results reported herein demonstrate that the synergy between these two properties opens a new reactivity manifold in a metal-free main group element system, which mimics the chemistry of transition metals (coordination of a substrate and two-electron oxidative addition concomitant with activation of substrate bonds) with main group hydrides and alcohols.

In this work, we aimed to maximize both the electron-donating ability of the phosphorus centers and their steric hindrance. We hypothesized that the combination of these two properties would lead to the lengthening of the C–C bond of the cluster and predispose the cage to opening upon reduction. A carboranyl diphosphine with two adjacent P^iBu_2 groups is yet unknown, presumably due to steric obstacles.³⁰ Stepwise deprotonation of the C–H bonds of $C_2B_{10}H_{12}$ and reactions with P^iBu_2Cl and P^iPr_2Cl led to the formation of 1- P^iBu_2 -2- P^iPr_2 - $C_2B_{10}H_{10}$ (**1**). The $^{31}P\{^1H\}$ NMR spectrum of **1** contains two doublets at 28.1 and 69.7 ppm ($^3J_{PP} = 90$ Hz). Single crystal X-ray diffraction confirmed the expected connectivity (Figure 1). The cluster carbon–carbon bond in **1** is elongated at 1.832(2) Å, which is significantly longer than that of the parent *ortho*- $C_2B_{10}H_{12}$ cage (1.624(8) Å)³¹ and is in fact the longest reported C1–C2 distance for carboranyl diphosphines.³²

The DFT calculations³³ demonstrated that the HOMO and HOMO–1 of **1** are largely localized at the phosphorus atoms, representing their lone pairs. Fragments that are σ -antibonding for the intracluster C–C bond and π -bonding for the C–P bonds are the major contributors to the LUMO (Figure 1). These results corroborate the hypothesis that **1** is able to both donate electrons through the phosphine groups and accept electrons through concomitant cluster opening and increase in C–P bond order.

The cyclic voltammogram of **1** in THF has one reduction event at $E_{pc} = -1.84$ V and one oxidation event at $E_{pa} = -0.13$ V vs $FeCp_2^{+/0}$. The cyclic voltammograms of *ortho*- $C_2B_{10}H_{12}$ and many of its derivatives often exhibit an unresolved two-electron reduction wave and an oxidation wave with lower current values.³⁴ At least six distinct geometries for the dianionic *nido*-12-vertex carborane clusters have been described, with significant structural rearrangements occurring during cluster opening upon reduction.³⁵ Because of these cluster bond-breaking transformations, the CV traces often appear as quasi-reversible or irreversible processes.^{36–38}

Reduction of **1** with sodium metal in THF led to the clean formation of a diamagnetic product **2**, which exhibited two singlets at 39.7 and 65.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The absence of ^{31}P – ^{31}P coupling in the spectrum of **2** alluded to the separation of phosphorus nuclei via cleavage of the cluster C–C bond. We were not able to grow single crystals of **2**. Instead, we synthesized a related carboranyl diphosphine 1,2-(P^iPr_2) $_2$ - $C_2B_{10}H_{10}$ (**3**)³⁹ and reduced it under analogous

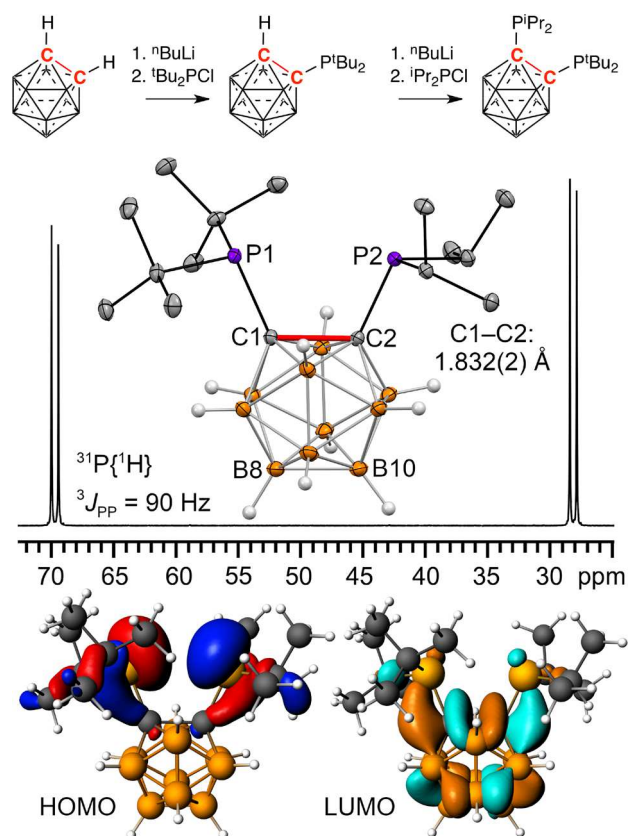


Figure 1. (Top) The synthesis, the $^{31}P\{^1H\}$ NMR spectrum, and the displacement ellipsoid plot (50% probability) of carboranyl diphosphine **1**. Hydrogen atoms of alkyl groups are not shown. (Bottom) Plots of HOMO and LUMO of **1** (isovalue 0.035).

conditions, obtaining **4**. The X-ray diffraction study of **4** revealed its formulation as $Na_2(THF)_3[(P^iPr_2)_2(C_2B_{10}H_{10})]$ (Figure 2). The carborane cage opened upon two-electron reduction, forming the *nido*-cluster with cleavage of the carbon–carbon bond (C1...C2 distance = 2.934(2) Å). This cluster isomer exhibits C_2 -symmetric geometry.²⁸ Similarly to **1**, the cyclic voltammogram of **3** in THF exhibited one

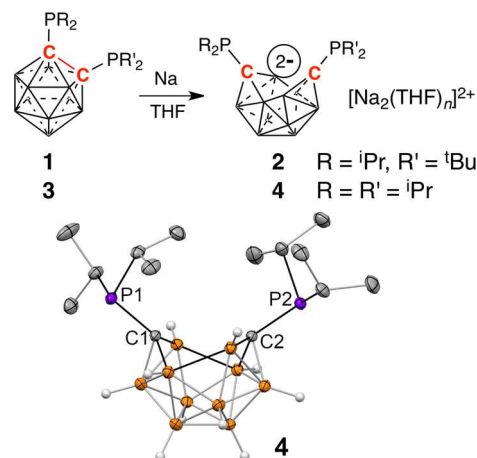


Figure 2. Reduction of **1** and **3** with sodium metal. Unlabeled cluster vertices = BH. The displacement ellipsoid plot (50% probability) of the dianionic carboranyl diphosphine **4**. Sodium cations with coordinated THF molecules as well as hydrogen atoms of alkyl groups are not shown.

reduction event at $E_{pc} = -1.88$ V and one oxidation event at $E_{pa} = -0.59$ V vs $\text{FcCp}_2^{*/0}$. The reduced dianionic phosphine **2** is air-sensitive in solution and converts to a mixture of the parent *closo*-cluster **1** and unidentified products upon exposure to air, as evidenced by ^{31}P NMR spectroscopy. The reaction of **2** and $[\text{FeCp}_2]\text{PF}_6$ produced **1**.

After the redox behavior of diphosphines **1** and **2** was probed, we tested our hypothesis of cooperative reactivity of the two electron-donating exohedral phosphorus centers and the electron-accepting boron cage in the reactions with main group hydrides. The reaction of **1** and 2.1 equiv of HSn^nBu_3 in benzene at 70°C led to the formation of white solid product **5**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** exhibited two singlets at 42.9 and 60.7 ppm, indicating the reduction of the boron cluster accompanied by the cleavage of its C–C bond. The ^1H NMR spectrum of **5** contained two signals corresponding to P–H bonds at 5.22 ($^1J_{\text{PH}} = 437$ Hz) and 5.46 ($^1J_{\text{PH}} = 432$ Hz) ppm. The ^{119}Sn NMR spectrum of the reaction mixture indicated the reductive coupling of tin centers with the formation of $^n\text{Bu}_3\text{Sn}^--\text{Sn}^n\text{Bu}_3$.⁴⁰ The colorless product of the reaction is sparingly soluble in benzene and was isolated in 97% yield. Crystal structure study revealed the zwitterionic **5** containing an open C_2 -symmetric *nido*-cluster and protonated phosphines (Figure 3). The C1–P1 and C2–P2 bonds in **5** are

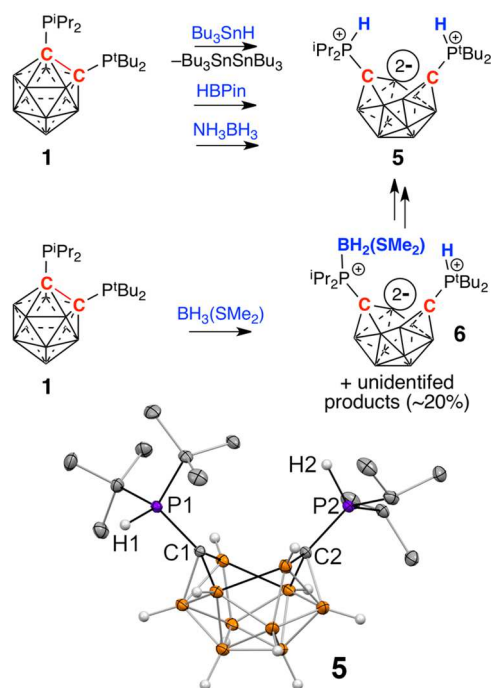


Figure 3. Reactivity of **1** with main group hydrides. Unlabeled cluster vertices = BH. The displacement ellipsoid plot (50% probability) of the zwitterionic product **5**. Hydrogen atoms of alkyl groups are not shown.

shortened (1.751(1) and 1.747(1) Å, respectively, which can be compared to the corresponding C–P bond lengths of 1.915(1) and 1.878(1) Å in the parent **1**), indicating their partial ylide character. The C1...C2 distance in **5** is 2.906(1) Å.

Zwitterionic compound **5** is also the product of the reaction of **1** and pinacolborane with the conversion occurring slowly at 70°C . ^{11}B NMR spectra of the reaction mixture of **1** and HBPIn exhibited the gradual appearance of a new broad signal at 21 ppm that has been previously assigned to a combination

of B_2Pin_3 , pinBOBpin, and HOBpin. These products have been reported to form upon thermal decomposition of HBPIn borane and B_2pin_2 diborane.⁴¹ Only traces of B_2pin_2 ($\delta = 30$ ppm) were observed in the ^{11}B NMR spectrum.

The reaction of **1** and $\text{BH}_3\cdot\text{SMe}_2$ at room temperature initially produced several open-cage products according to ^{31}P NMR spectroscopy, which convert to **5** upon heating or standing at room temperature. We were able to obtain single crystals of the major intermediate product **6**, which exhibits a sharp singlet at 61.1 ppm and a broad signal at 22.2 ppm. Its crystal structure provided an insight into the reactivity of **1** with boranes (Figure 3 and Figure S-30 in the Supporting Information). The intermediate features the same C_2 -symmetric open cluster geometry as **5**. The P^iBu_2 group is protonated and the P^iPr_2 group is bound to the $\text{BH}_2(\text{SMe}_2)$ fragment. This intermediate product eventually converts to **5** in DCM solution.

Similarly, the reaction of **1** and ammonia borane led to slow formation of **5** upon heating at 70°C . Notably, the same open-cluster deuterated phosphonium compound **5** formed immediately upon addition of deoxygenated D_2O to a solution of the chemically reduced dianionic phosphine **2** in THF.

Dehydrogenation of boranes has been mostly reported for transition metal compounds.^{42,43} New main group systems, including frustrated Lewis pairs, emerged, which can also affect the formation of B–N and B–P bonds from boranes or aminoboranes.^{44,45} In the example presented herein, the carboranyl diphosphine molecule provides two electrons for the substrate upon the conversion of two phosphines to phosphonium cations and the transformation from the *closo*- to the *nido*-cluster. The cooperation of the exohedral substituents and the redox-active cluster is crucial for this unique reactivity, as evidenced by the fact that trialkyl- or triarylphosphines alone do not induce dehydrogenation of boranes.

The unusual reactivity of diphosphine **1** with main group hydrides prompted the exploration of other, conceptually similar, “oxidative addition”-type transformations. The reaction of **1** with excess methanol in the presence of 0.2 equiv of tosylic acid at room temperature led to clean formation of a new product that exhibited two singlet signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. X-ray diffraction experiment revealed the formation of the zwitterionic product $\text{P}^i\text{Bu}_2(\text{OMe})\text{--P}^i\text{Pr}_2(\text{H})\text{--}(\text{C}_2\text{B}_{10}\text{H}_{10})$ (**7**) (Figure 4). Analogously to **4–6**, the cluster is open and two phosphonium cations are present. Only the single isomer **7**, which contains the protonated P^iPr_2 group and the methoxy-bound P^iBu_2 group, formed. A similar transformation was observed for **1** and isopropanol in the presence of tosylic acid. According to the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the product of the reaction exhibits two singlet signals at 41.0 and 75.4 ppm, with the former signal converting into a doublet in the ^1H -coupled ^{31}P NMR spectrum, indicating its protonation. The reaction of **1** and 3,5-dimethylphenol did not proceed under analogous conditions, suggesting that the nucleophilicity of the alcohol is important for this reaction.

The sequence of steps involved in the activation of alcohols by **1** is not known at present and the role of the acid is not clear. We found that the reaction of **1** and methanol does not proceed when no acid is added. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a mixture of 1 equiv of tosylic acid and **1** contains the set of two doublets at 6.7 and 35.2 ppm ($^3J_{\text{PP}} = 108$ Hz). The signal at 6.7 ppm converts into the doublet of doublets in the ^1H -coupled ^{31}P NMR spectrum, indicating that tosylic acid

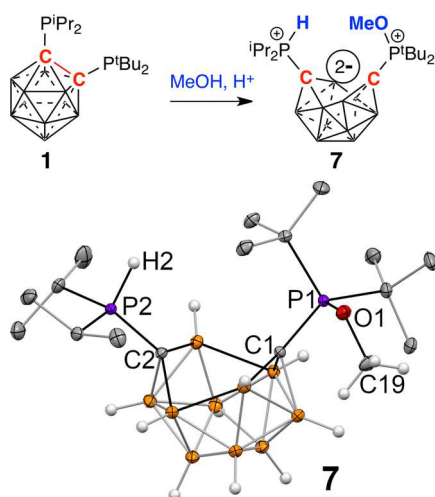


Figure 4. Reactivity of **1** with methanol in the presence of tosylic acid at room temperature. Unlabeled cluster vertices = BH. The displacement ellipsoid plot (50% probability) of the zwitterionic product **7**. Hydrogen atoms of alkyl groups are not shown.

protonates one of the phosphine groups of **1** while the cluster remains in the neutral closed form.

In conclusion, the unusual reactivity of carboranyl diphosphine **1** reported herein demonstrates the synergy between the electron-donating phosphine groups and the electron-accepting carborane cluster. The *closo*-carborane cage accepts two electrons and becomes the dianionic *nido*-cluster with the two phosphines converting to phosphonium cations. The resulting zwitterionic products are stable and exhibit ylide-type phosphorus-cluster interactions. Overall reactivity may be described as the oxidative addition of substrates (main group hydrides and alcohols) to the whole molecule of diphosphine **1**. These findings put forward a new mode of metal-free bond activation reactions by a main group cluster system. Further studies of the novel reactivity of this class of compounds are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c05387>.

Experimental details, characterization data (NMR spectra, cyclic voltammetry data, and crystallographic data), and computational details (PDF)

Accession Codes

CCDC 2084262–2084266 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.

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Notes

The authors declare no competing financial interest.

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