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Article

Activation of Alkynes by a Redox-Active Carboranyl Diphosphine and Formation of Boron-Containing Phosphacycles

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Cite This: *Inorg. Chem.* 2022, 61, 18568−18573

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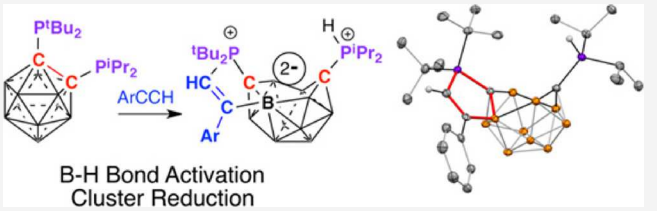
ABSTRACT: In this work, we report the reactivity of the carboranyl diphosphine, 1-P^{t}Bu$_2$−2-P^{i}Pr$_2$-C$_2$B$_{10}$H$_{10}$, with terminal alkynes, resulting in the formation of boron-containing phosphacycles. The reported system combines the nucleophilic activation of electron-deficient terminal alkynes via electron-rich phosphine groups with the redox behavior of carborane clusters to promote a sequence of metal-free intramolecular B−H bond activation and cyclization, creating an alkenylphosphonium cycle fused with a reduced open *nido*-carborane cluster.



INTRODUCTION

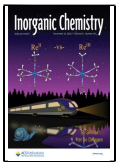
Icosahedral boron clusters have attracted renewed attention for their potential utilization in several key fields, including medicinal chemistry, ligand design and catalysis, luminescent materials, supramolecular chemistry, and battery electrolytes.[1−5] These clusters possess remarkable stability due to their unusual electronic structure, which features a high degree of electron delocalization that is often described as 3D aromaticity.[6−8] Neutral C$_2$B$_{10}$H$_{12}$ carborane clusters contain both C−H and B−H vertices, with the C−H bonds being weakly acidic (pK_a of *ortho*-C$_2$B$_{10}$H$_{12}$ is ca. 23). Thus, carbon vertex derivatization of these molecules largely relies on the deprotonation of cluster C−H bonds with strong bases followed by reactions with organic or inorganic electrophiles.[9,10] The relative ease of functionalization of carbon vertices results in the library of carborane derivatives being largely dominated by C-substituted clusters. In contrast, the carborane B−H bonds are rather strong, with a bond dissociation energy estimated at 118 kcal/mol (comparable to aromatic C−H bonds). The chemistry of these boron vertices shares similarities with arene chemistry, and the functionalization usually proceeds through electrophilic substitution promoted by Lewis acids or by oxidative addition to electron-rich late transition metal centers.[11,12] Recently, the development of new transition metal-catalyzed coupling methods has significantly expanded the library of B-substituted carboranyl derivatives.[13−16] In addition to *closo*-{C$_2$B$_{10}$} cages, there has been a significant progress in the selective B-H bond functionalization for *nido*-{C$_2$B$_9$} clusters.[17,18]

Metal-free bond activation, including organocatalysis, is emerging as a powerful method for the construction of new complex molecules.[19−21] For example, electron-rich phosphines have been recognized as efficient nucleophilic organocatalysts for the derivatization of electron-deficient alkynes.[22] Recently, the triarylphosphine-catalyzed C-alkenylation of C$_2$B$_{10}$H$_{12}$ has been reported by Xie and co-workers (Scheme 1a).[23] A related, intramolecular cyclization of a carborane-supported phosphine with an alkyne fragment, resulting in a carborane-fused phosphole, has been reported by Duan and co-workers (Scheme 1b).[24] This group also reported the intermolecular activation of electron-deficient alkynes by carboranyl monophosphines, which resulted in the deprotonation and subsequent derivatization of the remaining carborane C-vertex to form a five-member phosphacycle (Scheme 1c).[25] In all literature examples, functionalization of the remaining unsubstituted cluster C-H vertex was reported, in some cases, accompanied by deboronation of the cluster and conversion from a *closo*-{C$_2$B$_{10}$} to a *nido*-{C$_2$B$_9$} cage.

Recently, we reported an example of metal-free bond activation by the carboranyl diphosphine 1-P^{t}Bu$_2$−2-P^{i}Pr$_2$-C$_2$B$_{10}$H$_{10}$ (**1**).[26] This main group element system utilizes two basic phosphine sites and has the ability to cycle through the two-electron redox states of the carborane cluster to afford the ability to both donate electrons through the nucleophilic phosphine groups and accept electrons through cluster opening resulting in a concomitant increase in the C−P bond order.

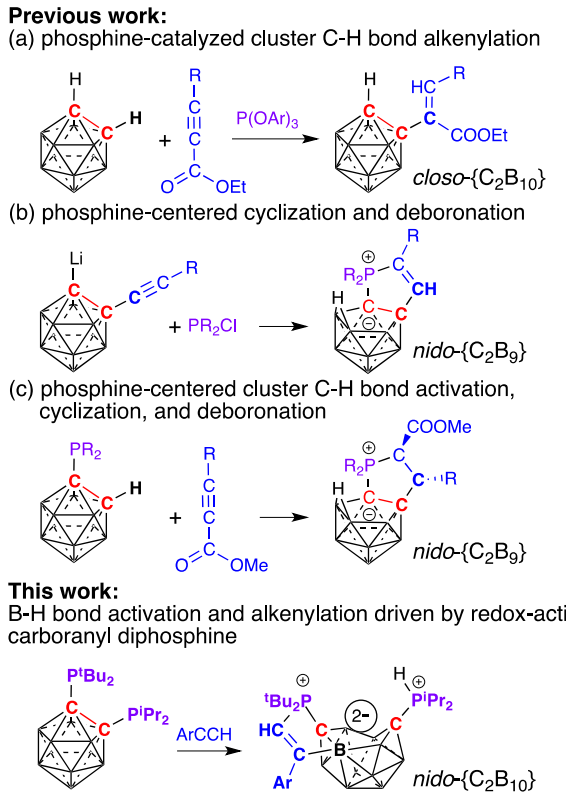
In our initial communication, we reported the reactivity of the redox-active carboranyl diphosphine system with main group hydrides and alcohols. The *closo*-carborane cage accepts two electrons and becomes a dianionic *nido*-{C$_2$B$_{10}$} cluster, and the two phosphines convert to phosphonium cations.

Received: August 14, 2022
Published: November 9, 2022



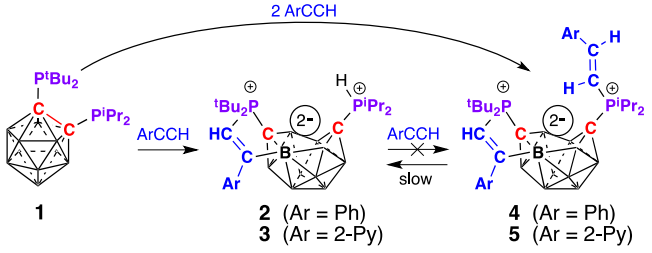
https://doi.org/10.1021/acs.inorgchem.2c02919
Inorg. Chem. 2022, 61, 18568−18573

Scheme 1. Reactivity of Carboranyl Phosphines with Alkynes



Overall reactivity may be described as the oxidative addition of the substrate to the whole molecule of **1**. In this work, we explored the reactivity of carboranyl diphosphine **1** with alkynes. We found that the synergy between the two electron-rich phosphine groups and the electron-accepting cluster leads to a cascade process, resulting in metal-free cage B−H bond activation and the formation of boron-containing fused phosphole-type zwitterionic cyclic products (Scheme 2).

Scheme 2. Reactivity of 1 with Phenylacetylene (Ar = Ph) and 2-Ethynylpyridine (Ar = 2-Py). Unlabeled Cluster Vertices = BH



RESULTS AND DISCUSSION

Carboranyl diphosphine **1** reacts with one equivalent of phenylacetylene at 70 °C to form a single product in 76% yield. The $^{31}P\{^{1}H\}$ nuclear magnetic resonance (NMR) spectrum of the product features two singlets, indicating an open cluster. A single crystal X-ray diffraction study revealed the structure of P(H)($^{i}Pr_2$)P(CHCPh)($^{t}Bu_2$)($C_2B_{10}H_9$) (**2**) (Figure 1) and confirmed the carborane cage is an open 12-vertex *nido*-cluster, which is reduced by two electrons. The cluster is C_2-

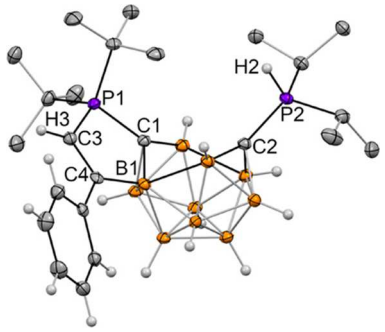


Figure 1. Displacement ellipsoid plot (50% probability) of the zwitterionic product P(H)($^{i}Pr_2$)P(CHCPh)($^{t}Bu_2$)($C_2B_{10}H_9$) (**2**). Hydrogen atoms of alkyl groups are not shown. Selected distances (Å): C1−P1 = 1.757(2), C2−P2 = 1.763(2), C3−P1 = 1.787(2), C3−C4 = 1.355(2).

symmetric,[27−30] giving rise to two enantiomers of **2** that co-crystallized as a racemate. The P($^{i}Pr_2$) group is protonated, and the P($^{t}Bu_2$) group is converted to an alkenylphosphonium center through the attachment of phenylacetylene. The *β*-carbon of the alkyne forms a bond with the carborane boron atom that was adjacent to the cluster carbon atoms in the parent *closo*- form. Structural metrics of **2** are consistent with a zwitterion/ylide description of the phosphorus centers with the P1−C1 and P2−C2 bond lengths being relatively short (1.757(2) Å and 1.763(2) Å, respectively). Within the planar five-membered phosphole-like cycle, the P1−C3 bond length is also short at 1.787(2) Å, the C3−C4 distance is 1.355(2) Å, corresponding to the double bond, and the C4−B1 bond length is 1.612(2) Å.

A similar electron-deficient alkyne, 2-ethynylpyridine, produced the isostructural product **3** upon reaction with **1** (see the Supporting Information for structural details). Monitoring with ^{31}P NMR spectroscopy showed the reaction proceeded even at room temperature, albeit slowly, and complete conversion was achieved by heating the reaction mixture at 70 °C. In contrast to the selective activation of terminal arylacetylenes mentioned above, the reaction of **1** and diethylacetylenedicarboxylate produced a mixture of at least seven phosphorus-containing products, according to ^{31}P NMR spectroscopy. Other disubstituted alkynes, such as diphenylacetylene or 1-phenyl-2-trimethylsilylacetylene, did not react with **1**. Alkyl-substituted terminal alkynes, such as 1-hexyne or trimethylsilylacetylene did not react with **1**. We found that if another noncarboranyl phosphine, such as triethylphosphine, was added to the reaction mixture, the formation of **2** still occurred, although significantly impeded. This observation suggests that the interaction of the phosphine groups of **1** with the alkyne is one of the initial steps of the reaction.

When more than one equivalent of phenylacetylene was present, the formation of a different single product was observed by ^{31}P NMR spectroscopy. The structure of the product was established by single crystal X-ray diffraction study as P(CHCHPh)($^{i}Pr_2$)P(CHCPh)($^{t}Bu_2$)($C_2B_{10}H_9$) (**4**) (Figure 2). One phenylacetylene molecule was activated analogously to **2**, forming a B−C bond with the cluster and completing the five-membered cycle, and an additional alkyne fragment connected to the P($^{i}Pr_2$) group as a phosphinoalkenyl moiety, with the substituents adopting a *trans*-orientation around the double bond. The structural metrics of the phosphole-like part of **4** are analogous to those of **2**. Compound **4** slowly converts

https://doi.org/10.1021/acs.inorgchem.2c02919
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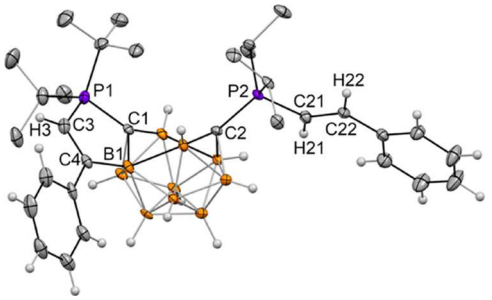


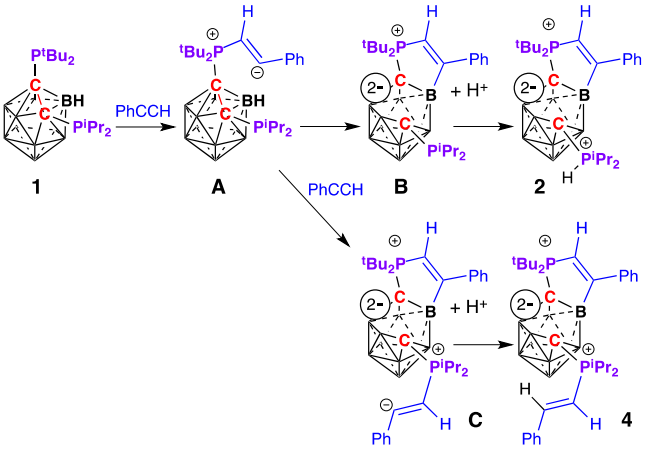
Figure 2. Displacement ellipsoid plot (50% probability) of the zwitterionic product P(CHCHPh)(^{i}Pr$_2$)P(CHCPh)(^{t}Bu$_2$)(C$_2$B$_{10}$H$_9$) (**4**). Hydrogen atoms of alkyl groups are not shown. Selected distances (Å): C1−P1 = 1.757(2), C2−P2 = 1.756(2), C3−P1 = 1.779(2), C3−C4 = 1.351(2), C21−P2 = 1.785(2), C21−C22 = 1.327(3).

to **2** upon standing in solution at room temperature, but **2** does not convert to **4** in the presence of additional phenylacetylene (Scheme 2). Analogously, the reaction of 2.1 equiv of 2-ethynylpyridine and **1** at 70 °C produced the product (**5**), which is isostructural to **4**. Like compound **4**, compound **5** similarly slowly converts to **3** upon standing in solution, which precluded its isolation in the pure form (ca. 95% purity according to NMR spectroscopy). Nevertheless, we have been able to determine its crystal structure (see the Supporting Information), which is analogous to **4**.

Phosphines have been known to attack electron-deficient alkynes, leading to the formation of vinylphosphonium intermediates.[31,32] Recently, the reaction of carboranyl monophosphines and acetylenedicarboxylates was reported, wherein the remaining relatively acidic C−H bond of the cluster was deprotonated and a new C−C bond between the alkyne and carborane was formed.[25] Although the outcome of that reaction was complicated by the loss of one boron vertex and the eventual formation of an 11-vertex *nido*-cluster, the overall transformation is conceptually analogous to the activation of alkynes by electron-rich phosphines for subsequent reactions with nucleophiles. In the case presented herein, the synergy between the redox capability of carborane and the electronically conjugated phosphine groups at each cluster carbon atom was utilized in reactions with electron-deficient alkynes, ultimately leading to the activation of the B−H bond of the cluster. Importantly, the observed reactivity is completely analogous to our recently reported examples of bond-activation of main group hydrides and alcohols by **1**, which also led to the formation of zwitterions with two phosphonium centers and a dianionic cluster.[26] The synthesis of **2**−**5** features regioselective metal-free B−H bond activation with the formation of a direct C−B bond. Notably, the carborane cluster retained all its 12 vertices and was converted to its C_2-symmetric *nido*- form through two- electron reduction.

We propose that the following sequence of steps leads to the observed formation of **2**−**5** by combining nucleophilic organocatalytic reactivity and the redox behavior of the inorganic cluster (Scheme 3). The first step of this transformation can be considered as phosphine-promoted activation of the alkyne,[33] where the more electron-rich P(^{t}Bu$_2$) group acts as a nucleophile to attack the alkyne, forming the P−C bond and the carbanionic intermediate **A**. Notably, this regioselectivity with respect to the phosphine groups was

Scheme 3. Proposed Mechanism for the Formation of 2 and 4



observed in all cases. The nucleophilic, geometrically constrained intermediate then attacks the proximal B−H bond of the cluster, forming the C−B bond. The attack occurs at the boron atom that is adjacent to the two carbon atoms, as this is the most electron-deficient B-vertex. We found that the formation of **2** proceeds slightly faster for 4-methoxyphenylacetylene than for phenylacetylene, which is, in turn, significantly faster than 4-fluorophenylacetylene. This behavior may be caused by stronger nucleophilicity of the intermediate **A** when the alkyne substituent cannot efficiently stabilize the carbanion, thus promoting the attack on the B−H bond of the cluster. The *closo*-carborane cluster receives two electrons from the B−H bond, oxidizing the formally hydridic (B)H hydrogen atom to a proton, forming the intermediate **B**.[34] This proton eventually migrates to the remaining basic P(^{i}Pr$_2$) group, forming another phosphonium center. Importantly, when the deuterium-labeled phenylacetylene,[35] PhCCD, was used in the reaction with **1**, the P(^{i}Pr$_2$) group in the product **2** contained a P−H instead of a P−D bond. This observation confirms that this proton originates from the cluster B−H bond and not from deprotonation of the alkyne. The ultimate results of these steps are B−H bond activation, formation of two phosphonium cations, and the cluster-opening two-electron reduction of carborane.

In the presence of excess phenylacetylene, the final step of the reaction (protonation of the second phosphine group) is in competition with the nucleophilic attack of the phosphorous atom on the alkyne to form a phosphinoalkenyl moiety instead. This proposed reaction sequence is supported by the fact that the addition of phenylacetylene to **2** does not result in the conversion to **4**, an observation which can be explained by the fact that **2** already contains two phosphonium cations, and therefore possesses no nucleophilic centers to activate another equivalent of alkyne. Furthermore, the formation of **4** is facilitated in the presence of an external base (triethylamine), which presumably binds the proton formed in the B−H bond activation. The reverse transformation of **4** to **2** occurs slowly (several weeks), possibly through alkyne elimination from the phosphonium alkenyl fragment, generating free phenylacetylene and a protonated P(^{i}Pr$_2$) group.

The simultaneous presence of two electron-rich phosphine groups on the redox-active carborane cluster is crucial for the observed B−H bond activation and cyclization. If the phosphine group is not attached to the cluster, as in the

https://doi.org/10.1021/acs.inorgchem.2c02919
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protocol developed by Xie and co-workers,[23] then the carborane C−H vertex undergoes deprotonation and alkenylation. If only one phosphine group is connected to the cluster, as in the case reported by Duan and co-workers, the C−H bond of carborane is likewise deprotonated, and a putative cyclic ylide, which is unstable to deboronation, forms and eventually transforms into a saturated five-membered phosphorus-containing heterocycle.[24,25,36] In the case reported herein, the presence of two phosphine groups on the cluster unlocks the redox behavior of the carborane cage, resulting in the intramolecular oxidation of the B−H bond and formation of the phosphorus and boron-containing heterocycle.

Since the *nido*-product **2** contains a reduced cluster with 14 skeletal electron pairs (SEPs), we decided to probe the possibility of two-electron oxidation back to the 13 SEP *closo*-form.[37] Notably, we have previously demonstrated such re-oxidation for the isostructural *nido*-cluster of the chemically reduced dianionic $\mathbf{1}^{2-}$ with $[FeCp_2]PF_6$, which could be conveniently monitored by ^{31}P NMR spectroscopy, as the dianionic open-cage cluster exhibited two singlets in the spectrum, and the neutral closed-cage featured two doublets due to ^{31}P-^{31}P coupling.[26] The reaction of **2** and 2 equiv of $[FeCp_2]PF_6$ in tetrahydrofuran led to a mixture of products, with the predominant component possessing two singlet signals in the ^{31}P NMR spectra at 30.4 and 71.8 ppm, indicating the absence of coupling between phosphorus centers. A single crystal X-ray diffraction study revealed the structure of zwitterionic $P(^iPr_2)P(CHCPh)(^tBu_2)(C_2B_{10}H_{10})$ **6** (Figure 3). Surprisingly, **6** still contained the negatively

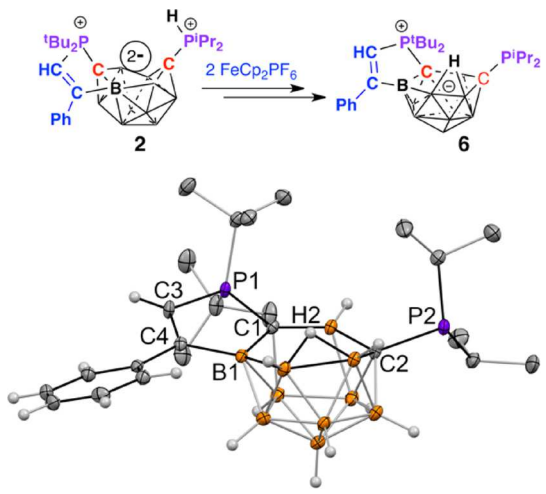

Figure 3. Synthesis and the displacement ellipsoid plot (50% probability) of the *nido*-7,9-$\{C_2B_{10}\}$ cage isomer product $P(^iPr_2)P(CHCPh)(^tBu_2)(C_2B_{10}H_{10})$ (**6**). Hydrogen atoms of alkyl groups are not shown. Selected distances (Å): C1−P1 = 1.794(1), C2−P2 = 1.865(1), C3−P1 = 1.773(1), C3−C4 = 1.350(2).

charged, reduced 12-vertex *nido*-cluster, albeit a different cage isomer than that in **2**. This C_s-symmetric cluster isomer *nido*-7,9-$\{C_2B_{10}\}$ has been previously obtained upon the reduction of carborane $C_2B_{10}H_{12}$ with sodium metal and subsequent protonation.[38,39] The five-membered phosphonium-containing cycle in **6** remained unchanged from that in **2**. The other phosphorus center in the $(H)P(^iPr_2)$ group of **2** lost its proton, which migrated to the open face of the cluster to form the bridging B−H−B fragment in **6**. We were not able to isolate oxidation products from the reaction of **2** with ferrocenium but observed apparent isomerization instead. This peculiar outcome prompted us to estimate the relative stability of isomers **2** and **6**. The density function theory calculations[40] with the PBE0 hybrid functional and TZP basis set revealed that the compound **6** is more stable than **2** by only 0.3 kcal/mol. It is possible that the oxidation of **2** is an initial step of the isomerization transformation.

CONCLUSIONS

In summary, we demonstrated the activation of electron-deficient alkynes by a redox-active carborane cluster possessing two electron-rich phosphine groups. The observed transformation is an interplay of the nucleophilic reactivity of phosphines coupled with the electron-accepting ability of the carborane cluster, resulting in B−H bond activation and the formation of phosphine- and boron-containing heterocycles.

MATERIALS AND METHODS

All synthetic manipulations, unless stated otherwise, were carried out either in a nitrogen-filled Vacuum Atmospheres (VAC) drybox or on a dual manifold Schlenk-style vacuum line. The solvents were sparged with nitrogen, passed through activated alumina, and stored over activated 4 Å Linde-type molecular sieves. Benzene-d^6, $CDCl_3$, and CD_2Cl_2 were degassed and stored over activated 4 Å Linde-type molecular sieves. NMR spectra were recorded using Varian spectrometers at 400 (^{1}H), 100 (^{13}C), and 128 (^{11}B) MHz, reported in δ (parts per million) and referenced to the residual $^1H/^{13}C$ signals of the deuterated solvent or an external $BF_3(Et_2O)$ ($^{11}B(\delta)$: 0.0 ppm) standard. *J* values are given in Hz. Elemental analysis was provided by Midwest Microlab.

$(P^tBu_2)(P^iPr_2)(C_2B_{10}H_{10})$ (**1**) was prepared according to a previously reported literature procedure. *Ortho*-carborane $C_2B_{10}H_{12}$ (Boron Specialties), *n*-butyllithium solution (*n*-BuLi, 2.5 M solution in hexane), phenylacetylene, and 2-ethynylpyridine were used as received.

Synthesis of $P(H)(^iPr_2)P(CHCPh)(^tBu_2)(C_2B_{10}H_9)$ (2). A portion of **1** (0.050 g, 0.124 mmol) was dissolved in 1 mL of benzene and phenylacetylene (0.014 g, 0.136 mmol, 1.1 equiv) was added. The reaction mixture was stirred for 5 days at 70 °C. The sample was dried under vacuum and washed with hexanes (2 mL × 3) resulting in a light brown solid (yield: 0.047 g, 76%).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 65.0 (s, 1P, $P(C(CH_3)_3)_2$), 43.8 (s, 1P, $P(CH(CH_3)_2)_2$). **^{31}P NMR** (CD_2Cl_2): δ 66.9 (s, 1P, $P(C(CH_3)_3)_2$), 45.7 (d, $^1J_{P-H}$ = 421 Hz, 1P, $P(CH(CH_3)_2)_2$). **$^1H\{^{31}P\}$ NMR** (CD_2Cl_2): δ 7.51−7.30 (m, 5H, *Ph*CCH), 5.93 (s, 1H, *H*-$P(CH(CH_3)_2)_2$), 5.41 (s, 1H, PhCC*H*), 2.62 (m, 1H, P-$(CH(CH_3)_2)_2$), 2.48 (m, 1H, $P(CH(CH_3)_2)_2$), 1.46 (d, 18H, $P(C(CH_3)_3)_2$), 1.39 (m, 12H, $P(CH(CH_3)_2)_2$). **$^{11}B\{^1H\}$ NMR** (CD_2Cl_2): δ 26.0 (*B*H), 22.6 (*B*H), 2.1 (*B*H), 1.2 (*B*H), −8.6 (*B*C), −9.4(*B*H), −16.1 (*B*H), −17.3 (*B*H). **^{13}C NMR** (C_6D_6): δ 141.4 (d, $^2J_{C-P}$ = 20 Hz, PhCCH), 127.9 (s, *Ph*CCH), 127.7 (s, *Ph*CCH), 127.6 (s, *Ph*CCH), 116.8 (d, $^1J_{C-P}$ = 82 Hz, PhCCH), 35.8 (d, $^1J_{C-P}$ = 44 Hz, $P(C(CH_3)_3)_2$), 35.8 (d, $^1J_{C-P}$ = 37 Hz, $P(C(CH_3)_3)_2$), 29.0 (s, $P(C(CH_3)_3)_2$), 28.2 (s, $P(C(CH_3)_3)_2$), 23.8 (d, $^1J_{C-P}$ = 46 Hz, $P(CH(CH_3)_2)_2$), 23.6 (d, $^1J_{C-P}$ = 47 Hz, $P(CH(CH_3)_2)_2$), 18.3 (d, $^2J_{C-P}$ = 2 Hz, $P(CH(CH_3)_2)_2$), 18.2 (d, $^2J_{C-P}$ = 2 Hz, P(CH-$(CH_3)_2)_2$), 17.9 (d, $^2J_{C-P}$ = 2 Hz, $P(CH(CH_3)_2)_2$), 17.4 (d, $^2J_{C-P}$ = 3 Hz, $P(CH(CH_3)_2)_2$). Anal. calcd for $C_{24}H_{48}B_{10}P_2$: C, 56.89; H, 9.55. Found: C, 56.64; H, 9.89.

Synthesis of $P(H)(^iPr_2)P(CHCPy)(^tBu_2)(C_2B_{10}H_9)$ (3). A portion of compound **1** (0.050 g, 0.12 mmol) was dissolved in 1 mL of benzene and 2-ethynylpyridine was added (11 μL, 0.11 mmol, 0.9 equiv). The reaction mixture was heated for 4 h at 70 °C. Volatiles were removed under vacuum, and the solid was washed with 5 mL hexanes and 5 mL diethyl ether. The product was extracted with 3 mL DCM and dried under vacuum, yielding an orange/brown solid. Yield: 0.024 g, 42%.

https://doi.org/10.1021/acs.inorgchem.2c02919
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$^{31}P\{^{1}H\}$ **NMR** ($CDCl_3$): δ 65.44 (s, 1P, $P(C(CH_3)_3)_2$), 43.74 (s, 1P, H-$P(CH(CH_3)_2)_2$). ^{31}**P NMR** ($CDCl_3$): δ 65.62 (s, 1P, $P(C(CH_3)_3)_2$), 44.23 (d, $^{1}J_{P-H}$ = 439 Hz, 1P, H-$P(CH(CH_3)_2)_2$). ^{1}**H NMR** ($CDCl_3$): δ 8.64 (d, *Py*CCH, 1H), 8.24 (m, *Py*CCH, 1H), 7.65 (m, *Py*CCH, 1H), 7.27 (d, $^{2}J_{P-H}$ = 27 Hz, *Py*CCH, 1H), 5.37 (d, $^{1}J_{P-H}$ = 434 Hz, PyCC*H*), 2.51 (m, 2H, $P(CH(CH_3)_2)_2$), 1.62 (d, 18H, $P(C(CH_3)_3)_2$), 1.34 (m, 12H, $P(CH(CH_3)_2)_2$). $^{11}B\{^{1}H\}$ **NMR** ($CDCl_3$): δ 27.71 (*B*H), 23.61 (*B*H), 2.29 (*B*H), 1.11 (*B*H), −8.75 (*B*H), −16.04 (*B*C), −17.40 (*B*H), −18.36 (*B*H). ^{13}**C NMR** ($CDCl_3$): 151.6 (d, $^{2}J_{C-P}$ = 20 Hz, PyCCH), 145.2 (s, *Py*CCH), 144.3 (s, *Py*CCH), 140.6 (s, *Py*CCH), 132.0 (d, $^{1}J_{C-P}$ = 76 Hz, PyCCH), 129.1 (s, *Py*CCH), 124.7 (s, *Py*CCH),37.0 (d, $^{1}J_{C-P}$ = 43 Hz, $P(C(CH_3)_3)_2$), 36.4 (d, $^{1}J_{C-P}$ = 35 Hz, $P(C(CH_3)_3)_2$), 29.2 (s, $P(C(CH_3)_3)_2$), 28.3 (s, $P(C(CH_3)_3)_2$), 23.9 (d, $^{1}J_{C-P}$ = 27 Hz, $P(CH(CH_3)_2)_2$), 23.5 (d, $^{1}J_{C-P}$ = 28 Hz, $P(CH(CH_3)_2)_2$), 18.6 (d, $^{2}J_{C-P}$ = 18 Hz, $P(CH(CH_3)_2)_2$), 17.8 (d, $^{2}J_{C-P}$ = 34 Hz, $P(CH(CH_3)_2)_2$).

Synthesis of P(CHCHPh)(^{i}Pr$_2$)P(CHCPh)(^{t}Bu$_2$)($C_2B_{10}H_9$) (4). A portion of **1** (0.050 g, 0.124 mmol) was dissolved in 1 mL of benzene and phenylacetylene (0.031 g, 0.310 mmol, 2.5 equiv) was added. The reaction mixture was stirred for 5 days at 70 °C. The sample was dried completely and washed with hexanes (2 mL × 3) resulting in a light brown solid (yield: 0.034 g, 46%). Compound **4** slowly converted to **2** upon standing in dichloromethane solution.

$^{31}P\{^{1}H\}$ **NMR** (CD_2Cl_2): δ 64.3 (s, 1P, $P(C(CH_3)_3)_2$), 29.6 (s, 1P, $P(CH(CH_3)_2)_2$). $^{11}B\{^{1}H\}$ **NMR** (CD_2Cl_2): δ 25.6 (*B*H), 2.0 (*B*H), −2.4 (*B*H), −8.6 (*B*C), −10.7 (*B*H), −16.6 (*B*H), −18.7 (*B*H). ^{1}**H NMR** (CD_2Cl_2): δ 7.45−7.21 (m, 10H, *Ph*CCH & *Ph*CHCH), 6.36 (d, $^{2}J_{H-P}$ = 31 Hz, 1H, PhCHC*H*), 6.36 (d, $^{3}J_{H-P}$ = 5 Hz, 1H, PhC*H*CH), 5.83 (d, $^{2}J_{H-P}$ = 32 Hz, 1H, PhCC*H*), 2.56 (m, 2H, $P(CH(CH_3)_2)_2$), 1.46 (d, 18H, $P(C(CH_3)_3)_2$), 1.39 (m, 12H, $P(CH(CH_3)_2)_2$). ^{13}**C NMR** (C_6D_6): δ 141.5 (d, $^{2}J_{C-P}$ = 20 Hz, PhCCH), 135.1 (d, $^{2}J_{C-P}$ = 16 Hz, PhCCH), 139.4−127.5 (s, *Ph*CCH), 116.6 (d, $^{1}J_{C-P}$ = 83 Hz, PhCCH), 35.7 (d, $^{1}J_{C-P}$ = 37 Hz, $P(C(CH_3)_3)_2$), 35.6 (d, $^{1}J_{C-P}$ = 44 Hz, $P(C(CH_3)_3)_2$), 29.2 (s, $P(C(CH_3)_3)_2$), 28.4 (s, $P(C(CH_3)_3)_2$), 25.6 (d, $^{1}J_{C-P}$ = 36 Hz, $P(CH(CH_3)_2)_2$), 25.0 (d, $^{1}J_{C-P}$ = 33 Hz, $P(CH(CH_3)_2)_2$), 17.0 (d, $^{2}J_{C-P}$ = 3 Hz, $P(CH(CH_3)_2)_2$), 16.7 (d, $^{2}J_{C-P}$ = 3 Hz, $P(CH(CH_3)_2)_2$). Anal. calcd for $C_{32}H_{54}B_{10}P_2$: C, 63.13; H, 8.94. Found: C, 62.65; H, 9.51.

Synthesis of P(CHCHPy)(^{i}Pr$_2$)P(CHCPy)(^{t}Bu$_2$)($C_2B_{10}H_9$) (5). A portion of compound **1** (0.050 g, 0.12 mmol) was dissolved in 1 mL of benzene and 1 mL of THF. 2-Ethynylpyridine (50 μL, 0.49 mmol, 4 equiv) and triethylamine (17 μL, 0.12 mmol, 1 equiv) were added. The reaction mixture was stirred at room temperature for 15 min, then volatiles were removed under vacuum. The sample was washed with 5 mL of hexanes and 3 mL diethyl ether, and the product was extracted with chloroform. Yield: 57 mg, 78%. Compound **5** slowly decomposes in solution at room temperature and could be isolated in ca. 96% purity.

$^{31}P\{^{1}H\}$ **NMR** ($CDCl_3$): δ 64.4 (s, 1P, $P(C(CH_3)_3)_2$), 50.7 (s, 1P, $P(CH(CH_3)_2)_2$). $^{11}B\{^{1}H\}$ **NMR** ($CDCl_3$): δ 19.4 (*B*H), 15.8 (*B*H), 2.4 (*B*H), −6.9 (*B*C), −16.2 (*B*H), −21.3 (*B*H).

Formation of P(^{i}Pr$_2$)P(CHCPh)(^{t}Bu$_2$)($C_2B_{10}H_{10}$) (6). A portion of **2** (0.032 mg, 0.063 mmol) was dissolved in 1 mL of dichloromethane. A solution of $[FeCp_2]BF_4$ (0.034 g, 0.125 mmol, 2 equiv) in 2 mL of dichloromethane was added. The reaction mixture changed color from dark blue to light-brown within 15 min of stirring at room temperature. Reduction of solution volume to ca. 1 mL and layering with cyclohexanes produced colorless single crystals suitable for an X-ray diffraction experiment.

$^{31}P\{^{1}H\}$ **NMR** ($CDCl_3$): δ 71.8 (s, 1P, $P(C(CH_3)_3)_2$), 30.4 (s, 1P, $P(CH(CH_3)_2)_2$).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c02919.

Characterization data (NMR spectra and crystallographic details), displacement ellipsoid plots, and computational method details (PDF)

Accession Codes

CCDC 2084267 and 2193431−2193434 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.

■ ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under grants CHE-1654301 and CHE-2154828.

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https://doi.org/10.1021/acs.inorgchem.2c02919
Inorg. Chem. 2022, 61, 18568−18573