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Carboranyl diphosphenes: synthesis, structure and reactivity†

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Carboranyl-diphosphenes {1-P-2-[C(^tBu) = N(Ar)]-1,2-C₂B₁₀H₁₀}₂ [Ar = Dmp (**6**) or Ph (**7**); Dmp = 2,6-Me₂C₆H₃, Ph = C₆H₅] are prepared in good yields by the reduction of iminocarboranyldichlorophosphines 1-PCl₂-2-[C(^tBu) = N(Ar)]-1,2-C₂B₁₀H₁₀ [where Ar = Dmp (**4**) or Ph (**5**)] with potassium graphite (KC₈) in THF. Compounds **6** and **7** have similar dimeric structures in the solid state as confirmed by single-crystal X-ray analyses. Their solution structures are, however, different on the basis of ³¹P NMR studies, which could be ascribed to the steric effects of Dmp over Ph. As a result, **6** and **7** exhibit different coordination chemistry toward W(CO)₅(THF). On the other hand, they show similar properties with oxidizing agents, giving a variety of phosphorus(III) compounds. The results indicate that **6** dissociates into carboranyl phosphinidene in THF.

Introduction

The chemistry of low-valent main group compounds has received much attention and is a rapidly developing research area of organometallic chemistry,^{1,2} which has not only promoted the understanding of the bonding interactions in main group compounds^{2,3} but also exhibited transition-metal-like behavior of these compounds to activate small molecules.⁴ Among these, low-valent phosphorus(I) compounds are among the most studied classes, including monomeric phosphinidenes (Lewis base⁵ or transition-metal⁶ stabilized) and diphosphenes^{7,8} (Fig. 1).

Diphosphenes (RP = PR), featuring small HOMO–LUMO energy gaps compared to their alkene analogues, have achieved remarkable advances in the last decades due to the development of diverse ligand sets with distinct stereoelectronic properties, enabling a comprehensive understanding of the structure, bonding, and reactivity within the diphosphene family.^{7,8} In 1981, the first isolation of diphosphene Mes*P = PMes* (Mes* = 2,4,6-^tBu₃C₆H₂) by Yoshifuji⁹ opened up the avenue for classical diphosphenes, which were kinetically stabilized by extremely bulky aryl or alkyl substituents.^{7,8} On

the other hand, plenty of diphosphenes with diverse Lewis base ligands, including non-carbon (B, Ga, Si, Ge, N, P) donors, stable N-heterocyclic carbenes (NHCs) and other singlet carbenes, were realized in recent years.⁸ Recent selected examples include the works of Yamashita^{10a} and Goicoechea^{10b} on boryl-substituted diphosphene compounds, a chiral 1,1'-binaphthyl diphosphene reported by Tsurusaki and Kamikawa,¹¹ vinyl-substituted diphosphenes^{12a,c} and a di-1,2-dihydro-1,2-diphosphete-substituted diphosphene^{12b} developed by Stephen and Ghadwal, a germlyliumylidene-substituted diphosphene synthesized by Driess,¹³ a gallium carbene-substituted diphosphene prepared by Goicoechea,¹⁴ and the utilization of diphosphenes as ligands for gold(I) species by Protasiewicz^{15a} and Jana^{15b} and for a lead(0) complex by Mo.^{15c}

In 2016, we described the preparation and reactivity of the imine-stabilized carboranyl phosphinidene 1,2-[C(^tBu) = N(2',6'-ⁱPr₂C₆H₃)P]-1,2-C₂B₁₀H₁₀ **1**.¹⁶ We wondered if the substituents on the iminocarborane ligand would influence the structures of the resulting phosphorus(I) compounds. With this in mind, new iminocarborane ligands with different aryl groups (Ar = Dmp and Ph) (Dmp = 2,6-Me₂C₆H₃, Ph = C₆H₅)

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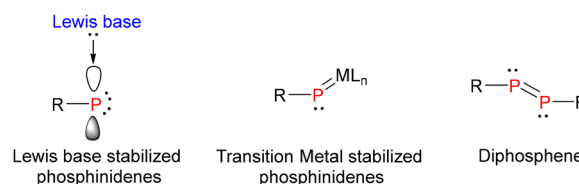


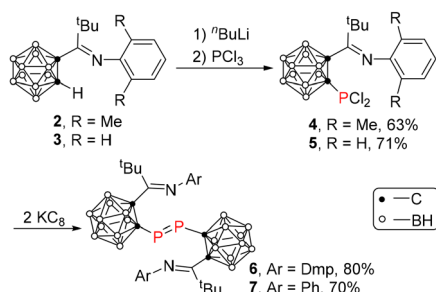
Fig. 1 Presentation of phosphorus(I) species.

were synthesized to study the steric effects of the aryl groups on carboranyl phosphorus(i) compounds. These results are reported in this article.

Results and discussion

The iminocarboranes **2** and **3** were prepared in 77%–80% yields by a salt elimination reaction of 1-Li-1,2-C₂B₁₀H₁₁ with ArN = C^tBuCl (Ar = Dmp¹⁷ or Ph¹⁸) in Et₂O. Treatment of **2** or **3** with 1 equiv. of *n*-BuLi in Et₂O, followed by the addition of 1 equiv. of PCl₃ afforded compounds **4** and **5** as yellow crystals in 63% and 70% yields, respectively. Reduction of **4** or **5** with 2 equiv. of potassium graphite (KC₈) in THF at room temperature afforded the corresponding carboranyl-diphosphene **6** or **7** as orange-yellow crystals in 70%–80% yields (Scheme 1). The phosphorus chemical shift of **6** was observed at 214.1 ppm, which was comparable to that of 210.5 ppm in **1**,¹⁶ suggesting the monomeric phosphinidene structure of **6** in solution. In contrast, it was shifted upfield significantly to –43.0 ppm for compound **7**, suggesting a dimeric diphosphene structure in solution probably due to the less steric hindrance of the Ph group.

The solid-state structures of **6** and **7** were confirmed by single-crystal X-ray analyses and are shown in Fig. 2 and 3, respectively. They are very similar, displaying diphosphene structures. The phosphorus atom is bonded to one cage-carbon atom and another phosphorus atom in a bent geometry with a C(2)–P(1)–P(1)# angle of 99.4(6)° in **6** and 98.8(1)° in



Scheme 1 Synthesis of carboranyl diphosphenes **6** and **7**.

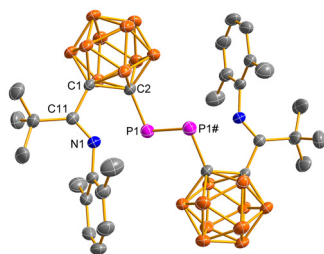


Fig. 2 Molecular structure of **6**. Selected bond lengths (Å) and angles (°): P(1)–P(1)# 2.037(1), C(1)–C(2) 1.730(2), P(1)–C(2) 1.871(2), C(11)–N(1) 1.262(2), C(11)–C(1) 1.545(2); C(2)–P(1)–P(1)# 99.4(1), N(1)–C(11)–C(1) 111.1(2), C(11)–C(1)–C(2) 113.8(2), C(1)–C(2)–P(1) 119.6(2).

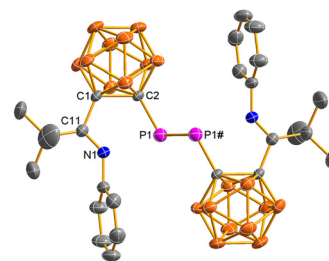


Fig. 3 Molecular structure of **7**. Selected bond lengths (Å) and angles (°): P(1)–P(1)# 2.037(2), C(1)–C(2) 1.729(3), P(1)–C(2) 1.876(2), C(11)–N(1) 1.262(3), C(11)–C(1) 1.535(3); C(2)–P(1)–P(1)# 98.8(1), N(1)–C(11)–C(1) 110.9(2), C(11)–C(1)–C(2) 113.7(2), C(1)–C(2)–P(1) 120.0(2).

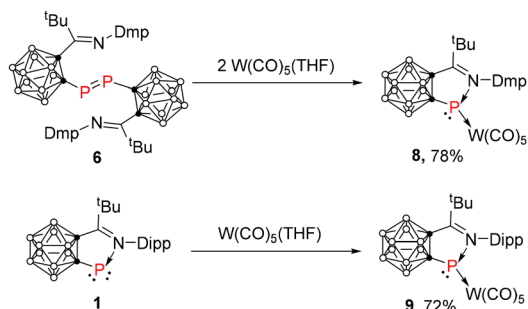
7, respectively, which are within the range of the corresponding C–P–P angles of diphosphenes [93.2(1)–114.9(1)°].¹⁹ The P(1)–P(1)# bond distances of 2.037(1) Å in **6** and 2.037(2) Å in **7** fall in the range of previously reported diphosphenes [1.985(3)–2.051(2) Å].^{19a,20} The P(1)–C(2) bond distances of 1.871(2) Å in **6** and 1.876(2) Å in **7** are comparable to those of 1.883(2) Å in **4** and **5**, respectively. The C(1)–C(2) distances of 1.730(2) Å in **6** and 1.729(3) Å in **7** are obviously elongated when compared to those of 1.702(3) Å in **4** and 1.699(3) Å in **5**, respectively, suggesting a partial *exo*- π bonding nature of the cage C–P bond.

It is noteworthy that the P(1)–N(1) distances of 2.520 Å in **6** and 2.500 Å in **7** are shorter than the sum of the van der Waals radii of phosphorus and nitrogen (3.55 Å),²¹ implying the presence of certain interactions between the phosphorus and nitrogen atoms.

In view of the solid-state structures and the ³¹P NMR chemical shifts of **1**, **6** and **7**, it was suggested that the size of the aryl group in the carboranyl imine moiety may play a role in the solution structures of the resulting compounds, monomeric carboranyl-phosphinidene vs. dimeric carboranyl-diphosphene. The experimental results indicated that the sterically hindered 2,6-diisopropylphenyl group led to a phosphinidene in both solution and solid state,¹⁶ whereas the phenyl group resulted in the formation of diphosphene **7** in both solution and solid-state as confirmed by single-crystal X-ray analysis and solution ³¹P NMR chemical shift. It was interesting to note that **6** with a moderate size substituent, 2,6-dimethylphenyl, existed as a dimeric carboranyl-diphosphene in the solid-state, but as a monomeric carboranyl-phosphinidene in solution. In this connection, we wondered if the addition of a Lewis acid could trap the monomeric phosphinidene.

Treatment of **6** with *in situ* generated W(CO)₅(THF), which was freshly prepared by UV irradiation of W(CO)₆ in THF for 24 h at room temperature, gave the desired complex **8** as purple crystals in 78% yield (Scheme 2). Its ³¹P NMR chemical shift was observed at 233.4 ppm. For comparison, **1** also reacted with W(CO)₅(THF) to afford the corresponding complex **9** as purple crystals in 72% yield with the phosphorus chemical shift being observed at 260.0 ppm (Scheme 2). However, no reaction was observed between **7** and





Scheme 2 Reaction of **1** or **6** with $W(CO)_5(THF)$.

$W(CO)_5(THF)$ under similar conditions as indicated by ^{31}P NMR, implying the presence of only the dimeric diphosphene in solution for **7**.

The solid-state structures of **8** and **9** were confirmed by single-crystal X-ray analyses and are shown in Fig. 4. The P(1) atoms in **8** and **9** are σ -bonded to one cage carbon atom, one imine nitrogen atom and one tungsten atom in a trigonal pyramidal geometry. The five atoms (C1, C2, P1, N1, C11) of the *exo* five-membered ring are nearly co-planar (the sum of internal pentagon angles = 538.9° for **8** and 537.9° for **9**). The bond distances in the five-membered ring (C1, C2, P1, N1, and C11) in **8** and **9** are very close to each other, which are barely longer than the corresponding values observed in **1**.¹⁶

To better understand the dissociation of diphosphenes in solution, density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level of theory were performed. The optimized bond distances and angles of **1**, **6** and **7** are in very good agreement with the experimental values. The structures of monomeric phosphinidenes with 2,6-dimethylphenyl or phenyl groups, as well as diphosphene with a 2,6-diisopropyl group, were also optimized. In addition, the dissociation enthalpies and Gibbs free energies of carboranyl-diphosphenes into the corresponding monomeric carboranyl-phosphinidenes were calculated at the B3LYP/6-31G(d,p) level of theory (Fig. 5). The three reactions presented the dissociation of three different aryl substituted carboranyl-diphosphenes to the corresponding monomeric carboranyl-phosphinidenes, respectively (aryl = Dipp, Dmp and Ph). Eqn (1) shows a negative enthalpy change, whereas it is positive for both eqn (2) and (3) in Fig. 5. Though ΔG is negative for all three reactions, the values are quite different. The largest negative value of

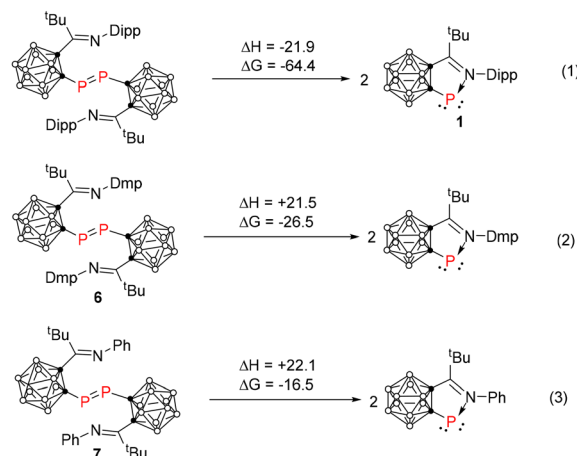


Fig. 5 The calculated dissociation enthalpy and Gibbs energy of carboranyl-diphosphenes (in kcal mol^{-1}) at the B3LYP/6-31G(d,p) level of theory.

Gibbs energy, as well as the negative value of enthalpy in eqn (1) implies that the sterically hindered 2,6-diisopropylphenyl group prohibits the formation of a dimer, leading to the isolation of the monomeric imine-stabilized phosphinidene **1**. On the other hand, the positive values of enthalpy in eqn (2) and (3) suggest that the less sterically demanding 2,6-dimethylphenyl and phenyl groups favor the formation of diphosphenes with the tendency of phenyl > 2,6-dimethylphenyl. On the other hand, the solvation of the P center might contribute to the stabilization of the monomeric 2,6-dimethylphenyl phosphinidene in solution.

We are interested in exploring the chemical properties of the resultant diphosphene compounds. Compound **6** reacted with 2 equiv. of $Cu(OAc)_2$ in THF at room temperature to afford a redox product, phosphine **10**, as colorless crystals in 60% yield (Scheme 3). Its ^{31}P NMR spectrum exhibited a

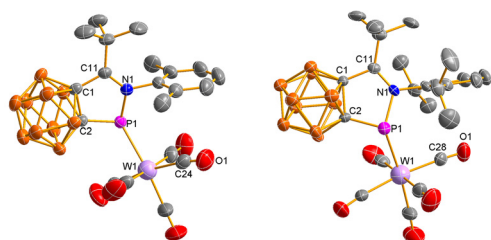
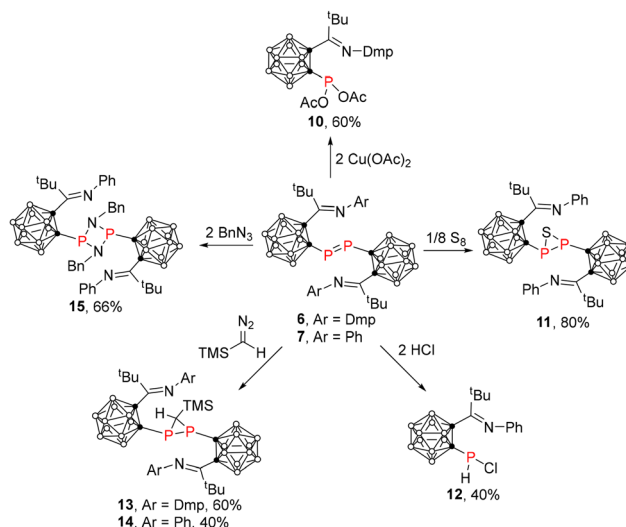


Fig. 4 Molecular structures of **8** (left) and **9** (right).



Scheme 3 Reactivity of **6** and **7**.



singlet at 95.5 ppm, which was similar to that of 105.8 ppm observed for a Dipp-substituted phosphine.¹⁶ Single-crystal X-ray analyses confirmed that the P(1) atom in **10** is σ -bonded to one cage carbon atom and two acetyl groups in a trigonal pyramidal geometry (Fig. 6). Treatment of **7** with 1 equiv. of sulfur (S) gave thiadiphosphirane **11** as yellow crystals in 80% yield (Scheme 3). This kind of reaction has been observed in aryl diphosphene compounds.²² Its ³¹P NMR chemical shift of –66.6 ppm was comparable to that of –82.4 ppm in the Dipp-substituted carboranyl thiadiphosphirane¹⁶ and those observed in aryl-thiadiphosphiranes.²² Single-crystal X-ray analyses show that the P(1) atom in **11** adopts a typical trigonal pyramidal geometry (Fig. 7). On the other hand, protonation of **7** with HCl in ether gave phosphine **12** as yellow crystals in 40% yield (Scheme 3). Its ³¹P NMR chemical shift was observed at 9.7 ppm as a doublet with $J_{\text{P-H}} = 256.0$ Hz. The solid-state structure of **12** was further confirmed by single-crystal X-ray analysis (Fig. S1†).

Furthermore, carboranyl-diphosphenes could undergo different cycloaddition reactions. Treatment of **6** or **7** with 1 equiv. of trimethylsilyldiazomethane afforded carboranyl-diphosphiranes **13** or **14** as yellow crystals in moderate yields *via* a [2 + 1] cycloaddition reaction (Scheme 3). The solid-state structures were further confirmed by single-crystal X-ray analyses. The representative structure of **14** was shown in Fig. 8. The [2 + 1 + 1] cycloaddition reaction of **7** with 2 equiv. of

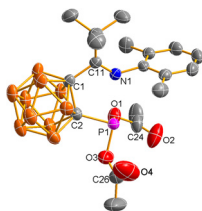


Fig. 6 Molecular structure of **10**. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.699(3), P(1)–C(2) 1.883(2), C(11)–N(1) 1.266(3), C(11)–C(1) 1.545(3), P(1)–O(1) 1.673(2), P(1)–O(3) 1.692(2); N(1)–C(11)–C(1) 109.9(2), C(11)–C(1)–C(2) 113.0(2), C(1)–C(2)–P(1) 118.0(2), C(2)–P(1)–O(1) 97.0(1), C(2)–P(1)–O(3) 93.7(2), O(1)–P(1)–O(3) 92.7(2).

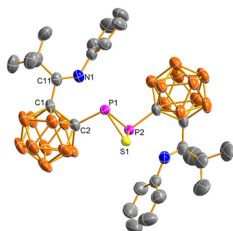


Fig. 7 Molecular structure of **11**. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.725(4), P(1)–C(2) 1.900(3), C(11)–N(1) 1.271(3), C(11)–C(1) 1.538(4), P(1)–P(2) 2.224(1), P(1)–S(1) 2.145(1), P(2)–S(1) 2.077(1); N(1)–C(11)–C(1) 110.6(2), C(11)–C(1)–C(2) 115.1(2), C(1)–C(2)–P(1) 116.8(2), C(2)–P(1)–P(2) 99.3(1), C(2)–P(1)–S(1) 99.7(1), S(1)–P(1)–P(2) 56.7(1), P(1)–S(1)–P(2) 63.6(1), S(1)–P(2)–P(1) 56.8(1).

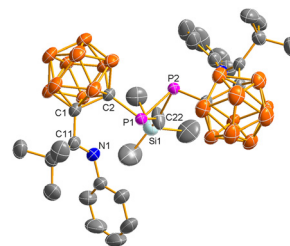


Fig. 8 Molecular structure of **14**. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.745(3), P(1)–C(2) 1.881(2), C(11)–N(1) 1.269(3), C(11)–C(1) 1.543(4), P(1)–P(2) 2.192(2), P(1)–C(22) 1.837(3); N(1)–C(11)–C(1) 110.4(2), C(11)–C(1)–C(2) 116.2(2), C(1)–C(2)–P(1) 117.1(2), C(2)–P(1)–P(2) 98.8(1), P(2)–P(1)–C(22) 53.4(1), P(1)–C(22)–P(2) 73.3(2).

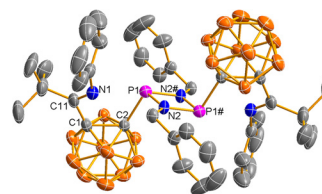


Fig. 9 Molecular structure of **15**. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.703(3), P(1)–C(2) 1.943(2), C(11)–N(1) 1.268(3), C(11)–C(1) 1.540(3), P(1)–N(2) 1.712(2), P(1)–N(2)# 1.723(23); N(1)–C(11)–C(1) 110.8(2), C(11)–C(1)–C(2) 113.8(2), C(1)–C(2)–P(1) 117.1(2), C(2)–P(1)–N(2) 102.8(1), C(2)–P(1)–N(2)# 102.2(1), N(2)–P(1)–N(2)# 80.6(1), P(1)–N(2)–P(1)# 99.4(1).

benzyl azide yielded carboranyl-cyclodiphosphazane **15** as pale yellow crystals in 66% yield (Scheme 3). This reaction may proceed *via* coupling of **7** with a benzyl nitrene (generated from benzyl azide) to form an azadiphosphiridine intermediate,²³ subsequently followed by coupling with another equiv. of benzyl nitrene to produce **15**. Its ³¹P NMR chemical shift was observed as a singlet at 195.2 ppm. Single-crystal X-ray analyses confirmed the formation of a four-membered coplanar heterocyclic ring (Fig. 9).

Conclusions

In summary, the structural diversity of the carboranyl phosphorus(i) compounds correlates with the steric properties of the aryl group and the strength of the N → P intramolecular interaction. The computational studies suggest that the aryl group in the carboranyl moiety can affect the N → P intramolecular interaction in compounds **1**, **6** and **7**. These observations are further evidenced by the ³¹P NMR chemical shifts of the carboranyl phosphorus(i) compounds, as well as the isolation of complex **8** *via* the reaction of **6** with W(CO)₅(THF). Furthermore, carboranyl-diphosphenes can undergo diverse reactions with Cu(OAc)₂, S₈, HCl, (TMS)CHN₂ and BnN₃ to give phosphines **10** to **15**. It is noteworthy that the reaction of diphosphenes with BnN₃ provides an alternative synthetic method to afford cyclodiphosphazanes, which have found



wide applications in coordination chemistry as versatile ligands and in supramolecular chemistry as scaffolds. In addition, the resulting carborane-phosphorus compounds might serve as valuable synthons for the development of 3D boron cluster-based heterocyclic systems, which exhibit unique photophysical properties and great potential in functional materials.²⁴

Experimental

General remarks

All procedures were carried out under a dry argon atmosphere using standard Schlenk and glovebox techniques. ¹H, ¹³C, ¹¹B and ³¹P NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400, 100, 128 and 162 MHz, respectively. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts and to external BF₃·OEt₂ (0.00 ppm) for boron chemical shifts. NMR multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad signal. Mass spectra were obtained on a Thermo Finnigan MAT 95 XL spectrometer. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. **1**¹⁶ and ArN = C^tBuCl (Ar = Dmp¹⁷ or Ph¹⁸) were prepared according to literature procedures. All other chemicals were purchased from Aldrich, J&K or Acros Chemical Co. and used as received unless otherwise specified.

X-ray structure determination. Single crystals were immersed in Paratone-N oil and sealed under argon in thin-walled glass capillaries. All data were collected at 296 K for **2–6** and **8–15** or 297 K for **7** on a Bruker D8 Venture diffractometer or a Bruker Kappa ApexII Duo diffractometer using Mo-K α radiation. An empirical absorption correction was applied using the SADABS program.²⁵ All structures were solved by direct methods and subsequent Fourier difference techniques and were refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.²⁶ All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and refinement are given in Table S1.†

Preparation of 2. To an ether (50 mL) solution of *o*-C₂B₁₀H₁₂ (2.30 g, 16.0 mmol), *n*-BuLi (1.6 M, 10.0 mL, 16.0 mmol) was slowly added *via* a syringe at 0 °C under stirring. The mixture was allowed to slowly warm to room temperature and stirred at room temperature for 2 h, to which (2,6-Me₂C₆H₃)N=C^t(Bu)Cl (3.60 g, 16.0 mmol) was slowly added. The reaction mixture was stirred at room temperature overnight. After the removal of the solvent, column chromatographic separation (silica gel, 230–400 mesh) using hexane/AcOEt (40:1) as the eluent afforded **2** as a pale yellow solid (4.20 g, 80%). ¹H NMR (400 MHz, CDCl₃): δ 1.21 (s, 9H; CMe₃), 1.99 (s, 6H; Me) 4.61 (br s, 1H; cage CH), 6.85 (t, J = 7.2 Hz, 1H; aromatic CH), 6.96 (d, J = 7.2 Hz, 2H; aromatic CH). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 18.6 (Me), 29.4 (CMe₃), 45.5 (s, CMe₃), 63.7 (cage C),

78.2 (cage C), 121.6, 122.5, 127.8, 146.6 (aromatic C), 162.0 (C=N). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -13.7 (2B), -11.3 (2B), -9.0 (4B), -3.1 (1B), -2.2 (1B). HRMS: m/z calcd for C₁₅H₂₉¹⁰B₂¹¹B₈N⁺: 331.3305. Found: 331.3308.

Preparation of 3. Compound **3** was prepared in a similar manner to that of **2** using *o*-C₂B₁₀H₁₂ (2.30 g, 16.0 mmol), *n*-BuLi (1.6 M, 10.0 mL, 16.0 mmol) and PhN=C^t(Bu)Cl (3.1 g, 16.0 mmol) as a pale yellow solid (3.90 g, 80%). ¹H NMR (400 MHz, CDCl₃): δ 1.25 (s, 9H; CMe₃), 4.68 (br s, 1H; cage CH), 6.51 (d, J = 7.6 Hz, 2H; aromatic CH), 6.99 (t, J = 7.6 Hz, 1H; aromatic CH), 7.27 (t, J = 8.0 Hz, 2H; aromatic CH). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 31.4 (CMe₃), 45.4 (s, CMe₃), 63.5 (cage C), 78.3 (cage C), 115.6, 122.7, 128.8, 148.8 (aromatic C), 163.0 (C=N). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -14.1 (2B), -11.7 (2B); -9.2 (4B), -3.4 (1B), -2.6 (1B). HRMS: m/z calcd for C₁₃H₂₅¹⁰B₂¹¹B₈N⁺: 303.2991. Found: 303.2994.

Preparation of 4. To an ether solution (20 mL) of **2** (0.79 g, 2.4 mmol), a hexane solution of *n*-BuLi (1.6 M, 1.5 mL, 2.4 mmol) was slowly added *via* a syringe at 0 °C under stirring. The reaction mixture was allowed to warm to room temperature and stirred overnight. PCl₃ (0.25 mL, 2.9 mmol) was then added *via* a syringe at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for 4 h. After the removal of the precipitate by filtration, the filtrate was concentrated to about 5 mL, to which *n*-hexane (2 mL) was added. Compound **4** was isolated as orange crystals after the solution stood at room temperature overnight (0.65 g, 63%). ¹H NMR (400 MHz, C₆D₆): δ 0.79 (s, 9H; CMe₃), 1.80 (s, 6H; Me), 6.72 (d, J = 6.8 Hz, 2H; aromatic CH), 6.78 (d, J = 6.4 Hz, 1H; aromatic CH). ¹³C{¹H} NMR (100 MHz, C₆D₆): δ 19.3, 19.4 (Me), 29.4 (CMe₃), 44.6 (CMe₃), 85.9 (d, J = 12.2 Hz, cage C), 87.1 (cage C), 125.7, 126.5, 128.8, 142.0 (aromatic C), 168.8 (C=N). ¹¹B{¹H} NMR (128 MHz, C₆D₆): δ -13.6 (2B), -6.9 (6B), -0.1 (2B). ³¹P NMR (162 MHz, C₆D₆): 89.2. Anal. calcd for C₁₅H₂₈¹⁰B₂¹¹B₈Cl₂NP: C 41.67, H 6.53, N 3.24. Found: C 41.94, H 6.83, N 3.17.

Preparation of 5. **5** was prepared as pale yellow crystals (0.69 g, 71%) in a similar manner to that of **4** using **3** (0.73 g, 2.4 mmol), *n*-BuLi (1.6 M, 1.5 mL, 2.4 mmol) and PCl₃ (0.25 mL, 2.9 mmol). ¹H NMR (400 MHz, C₆D₆): δ 0.73 (s, 9H; CMe₃), 6.23 (d, J = 7.2 Hz, 2H; aromatic CH), 6.84 (t, J = 7.2 Hz, 1H; aromatic CH), 6.91 (t, J = 7.2 Hz, 2H; aromatic CH). ¹³C{¹H} NMR (100 MHz, C₆D₆): δ 29.9 (CMe₃), 44.5 (CMe₃), 85.0 (d, J = 12.2 Hz, cage C) 87.0 (d, J = 131.8 Hz, cage C), 120.6, 126.0, 128.4, 142.4 (aromatic C), 169.5 (C=N). ¹¹B{¹H} NMR (128 MHz, C₆D₆): δ -10.1 (4B), -8.1 (4B), -1.8 (1B), -0.1 (1B). ³¹P NMR (162 MHz, C₆D₆): 109.3. Anal. calcd for C₁₃H₂₄¹⁰B₂¹¹B₈Cl₂NP: C 38.62, H 5.98, N 3.46. Found: C 39.07, H 6.07, N 2.93.

Preparation of 6. A THF solution (20 mL) of **4** (518 mg, 1.2 mmol) was slowly added to a mixture of KC₈ (324 mg, 2.4 mmol) in THF at room temperature, and the reaction mixture was stirred overnight at room temperature. The color of the solution was changed to orange yellow. After filtration, the orange yellow filtrate was concentrated to about 5 mL. Compound **6** was isolated as orange yellow crystals after the



solution stood at room temperature overnight (347 mg, 80%). ^1H NMR (400 MHz, C_6D_6): δ 1.23 (s, 18H; CMe_3), 2.26 (s, 12 H; Me_2), 7.08 (d, J = 8.8 Hz, 4H; aromatic CH), 7.24 (t, J = 7.2 Hz, 2H; aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 18.5 (*Me*), 30.4 (CMe_3), 45.2 (CMe_3), 86.5 (d, J_{PC} = 85.0 Hz, cage C) 87.6 (cage C), 121.8, 122.7, 128.8, 146.8 (aromatic C), 161.9 ($\text{C}\equiv\text{N}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ -11.9 (4B), -9.9 (6B), -8.4 (6B), -6.7 (4B). ^{31}P NMR (162 MHz, C_6D_6): 214.1. Anal. calcd for $\text{C}_{30}\text{H}_{56}^{10}\text{B}_4^{11}\text{B}_{16}\text{N}_2\text{P}_2$: C 49.84, H 7.81, N 3.88. Found: C 50.46, H 7.69, N 3.37.

Preparation of 7. 7 was prepared as orange yellow crystals (280 mg, 70%) in a similar manner to that of 6 using 5 (485 mg, 1.2 mmol) and KC_8 (324 mg, 2.4 mmol) in THF. ^1H NMR (400 MHz, C_6D_6): δ 0.87 (s, 18H; CMe_3), 6.59 (m, J = 6.8 Hz, 4H; aromatic CH), 6.82 (m, 6H; aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 31.3 (CMe_3), 45.2 (CMe_3), 85.9 (d, J = 62.0 Hz, cage C), 86.9 (cage C), 115.8, 122.8, 128.8, 149.1 (aromatic C), 163.0 ($\text{C}\equiv\text{N}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ -9.5 (8B), -8.2 (10B), -4.9 (2B). ^{31}P NMR (162 MHz, C_6D_6): -43.0. Anal. calcd for $\text{C}_{26}\text{H}_{48}^{10}\text{B}_4^{11}\text{B}_{16}\text{N}_2\text{P}_2$: C 46.83, H 7.26, N 4.20. Found: C 46.89, H 7.40, N 4.29.

Preparation of 8. Compound 6 (72.2 mg, 0.1 mmol), $\text{W}(\text{CO})_6$ (70.4 mg, 0.2 mmol) and THF (1 mL) were mixed in a closable Schlenk tube. The resulting mixture was irradiated with Xe light (300 W, 290–1500 nm) under argon for 24 h at room temperature. The color was changed from orange yellow to reddish purple. The ^{31}P NMR spectrum indicated a complete conversion of 6. After the removal of the solvent, the residue was recrystallized from hexane (3 mL) at room temperature to give 8 as reddish purple crystals (106.9 mg, 78%). ^1H NMR (400 MHz, C_6D_6): δ 0.73 (s, 9H; CMe_3), 1.89 (s, 6H; CHMe_2), 6.60 (d, J = 7.6 Hz, 2H; aromatic CH), 6.81 (t, J = 7.6 Hz, 1H; aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 18.8 (d, J = 5.5 Hz, *Me*), 30.2 (d, J = 6.4 Hz, CMe_3), 44.7 (d, J = 10.4 Hz, CMe_3), 83.7 (d, J = 65.2 Hz, cage C), 85.4 (d, J = 13.0 Hz, cage C), 122.7, 130.2, 133.7, 137.8 (aromatic C), 164.6 (d, J = 31.0 Hz, $\text{C}\equiv\text{N}$), 191.1, 196.2 (CO), 200.6 (d, J = 21.9 Hz, CO). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ -10.4 (5B), -8.3 (4B), -4.5 (1B). ^{31}P NMR (162 MHz, C_6D_6): δ 233.4. HRMS: m/z calcd for $\text{C}_{20}\text{H}_{28}^{10}\text{B}_2^{11}\text{B}_8\text{NO}_5\text{PW}^+$: 685.2190. Found: 685.2190.

Preparation of 9. This compound was prepared as reddish purple crystals (53.4 mg, 72%) in a similar manner to that of 8 from 1 (41.7 g, 0.1 mmol) and $\text{W}(\text{CO})_6$ (35.2 mg, 0.1 mmol). ^1H NMR (400 MHz, C_6D_6): δ 0.85 (s, 9H; CMe_3), 0.96 (d, J = 6.8 Hz, 6H; CHMe_2), 1.27 (d, J = 6.8 Hz, 6H; CHMe_2), 2.74 (m, 2H; CHMe_2), 6.81 (d, J = 8.0 Hz, 2H; aromatic CH), 7.00 (t, J = 8.0 Hz, 1H; aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 24.6, 25.6, 28.6 (CMe_3 , CHMe_2), 30.2 (CHMe_2), 45.9 (d, J = 10.5 Hz, CMe_3), 83.5 (d, J = 61.7 Hz, cage C), 85.2 (d, J = 12.5 Hz, cage C), 123.1, 123.8, 125.8, 131.5 (aromatic C), 135.2 (d, J = 9.4 Hz, aromatic C), 143.9 (aromatic C), 165.1 (d, J = 35.4 Hz, $\text{C}\equiv\text{N}$), 195.9 (CO), 199.7 (d, J = 25.2 Hz, CO). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ -10.0 (4B), -8.3 (4B), -4.2 (2B). ^{31}P NMR (162 MHz, C_6D_6): δ 260.0. HRMS: m/z calcd for $\text{C}_{24}\text{H}_{36}^{10}\text{B}_2^{11}\text{B}_8\text{NO}_5\text{PW}^+$: 741.2817. Found: 741.2814.

Preparation of 10. To a THF solution (15 mL) of 6 (72.2 mg, 0.1 mmol) was added $\text{Cu}(\text{OAc})_2$ (36.4 mg, 0.2 mmol) at room

temperature, and the mixture was stirred at room temperature overnight. The color of the solution was changed from orange yellow to deep brown. The ^{31}P NMR spectrum indicated a complete conversion of 6. After the removal of the solvent, the resulting mixture was dissolved in *n*-hexane (20 mL). After the removal of the precipitate, the hexane solution was concentrated to about 5 mL. Compound 10 was isolated as colorless crystals after slow evaporation of the solvent at room temperature (57.5 mg, 60%). ^1H NMR (400 MHz, CD_2Cl_2): δ 1.25 (s, 9H; CMe_3), 1.95 (s, 6H; *Me*), 2.12 (s, 6H; OCMe), 6.99 (m, 3H; aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, CD_2Cl_2): δ 19.7 (d, J = 2.8 Hz, OCMe), 21.9 (*Me*), 29.6 (CMe_3), 45.1 (CMe_3), 84.0 (d, J = 85.8 Hz, cage C), 85.4 (d, J = 9.7 Hz, cage C), 124.8, 125.0, 128.6, 143.4 (aromatic C), 165.9 ($\text{C}\equiv\text{N}$), 170.0 (d, J = 10.8 Hz, CO). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CD_2Cl_2): δ -11.0 (4B), -8.7 (4B), -2.0 (2B). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 95.5. HRMS: m/z calcd for $\text{C}_{19}\text{H}_{34}^{10}\text{B}_2^{11}\text{B}_8\text{NO}_4\text{P}^+$: 479.3233. Found: 479.3237.

Preparation of 11. To a THF solution (15 mL) of 7 (66.6 mg, 0.1 mmol) was added S_8 (3.2 mg, 0.0125 mmol) at room temperature, and the reaction mixture was stirred at room temperature overnight. The ^{31}P NMR spectrum indicated a complete conversion of 7. After the removal of the solvent, the resulting yellow powder was dissolved in toluene (5 mL). Compound 11 was isolated as yellow crystals after slow evaporation of the solvent at room temperature (55.8 mg, 80%). ^1H NMR (400 MHz, C_6D_6): δ 0.90 (s, 9H; CMe_3), 1.09 (s, 9H; CMe_3), 6.93 (m, 6H; aromatic CH), 7.09 (m, 4H; aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, C_6D_6): δ 30.8, 31.1 (CMe_3), 46.1 (CMe_3), 87.4 (cage C), 115.1, 115.8, 122.8, 123.3, 128.8, 148.3 (aromatic C), 159.6 ($\text{C}\equiv\text{N}$); another cage C was not observed. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ -7.5 (8B), -5.8 (8B), -0.4 (4B). ^{31}P NMR (162 MHz, C_6D_6): δ -66.6. Anal. calcd for $\text{C}_{26}\text{H}_{48}^{10}\text{B}_4^{11}\text{B}_{16}\text{N}_2\text{P}_2\text{S}\cdot 0.5\text{C}_7\text{H}_8$: C 47.56, H 7.04, N 3.76. Found: C 47.54, H 7.26, N 3.54.

Preparation of 12. To a THF solution (20 mL) of 7 (66.6 mg, 0.1 mmol), an ether solution of HCl (1.0 M, 0.2 mL, 0.2 mmol) was slowly added *via* a syringe at 0 °C under stirring. The reaction mixture was allowed to warm to room temperature and stirred overnight. The ^{31}P NMR spectrum indicated a complete conversion of 7. After the removal of the solvent, the resulting yellow powder was dissolved in toluene (5 mL). Compound 12 was isolated as light yellow crystals after slow evaporation of the solvent at room temperature (29.6 mg, 40%). ^1H NMR (400 MHz, C_6D_6): δ 0.71 (s, 9H; CMe_3), 6.01 (d, J = 7.2 Hz, 1H; aromatic CH), 6.25 (d, J = 7.6 Hz, 1H; aromatic CH), 6.34 (d, J_{HP} = 254.0 Hz, 1H; PH), 6.84 (m, 3H; aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ (400 MHz, C_6D_6): δ 30.7 (CMe_3), 44.1 (CMe_3), 79.5 (d, J = 81.0 Hz, cage C), 83.2 (d, J = 9.0 Hz, cage C), 120.0, 121.1, 126.5, 128.9, 142.0 (aromatic C), 171.3 ($\text{C}\equiv\text{N}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ -9.8 (4B), -7.7 (3B), -4.7 (1B), -2.7 (1B), 0.3 (1B). ^{31}P NMR (162 MHz, C_6D_6): δ 9.7 (d, J_{PH} = 256.0 Hz). HRMS: m/z calcd for $\text{C}_{13}\text{H}_{25}^{10}\text{B}_2^{11}\text{B}_8\text{ClNP}^+$: 369.2411. Found: 369.2413.

Preparation of 13. To a THF solution (20 mL) of 6 (144.4 mg, 0.2 mmol), a hexane solution of trimethylsilyldiazomethane (2.0 M, 0.1 mL, 0.2 mmol) was slowly added at room tempera-



ture, and the mixture was stirred at room temperature overnight. The ^{31}P NMR spectrum indicated a complete conversion of **6**. After the removal of the solvent, the resulting yellow powder was dissolved in toluene (5 mL). Compound **13** was isolated as yellow crystals after slow evaporation of the solvent at room temperature (97.1 mg, 60%). ^1H NMR (400 MHz, C_6D_6): δ −0.20 (s, 9H; SiMe_3), 0.29 (s, 1H; CHTMS), 0.97 (s, 18H; CMe_3), 1.88 (s, 3H; Me), 1.89 (s, 3H; Me), 2.27 (s, 3H; Me), 2.35 (s, 3H; Me), 6.83 (m, 6H; aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, C_6D_6): δ −0.66, 0.44 (SiMe_3), 19.4 (CHTMS), 28.6 (CMe_3), 45.6, 45.4 (CMe_3), 121.5, 122.0, 122.1, 122.3, 122.4, 122.5, 127.6, 127.9, 128.0, 128.3, 145.8, 146.3 (aromatic CH), 161.2, 162.1 ($\text{C}=\text{N}$); the signals of cage *C* were not observed. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ −7.7 (12B), −1.0 (8B). ^{31}P NMR (162 MHz, C_6D_6): δ −120.3 (d, J = 171.7 Hz; 1P), −90.3 (d, J = 171.7 Hz; 1P). HRMS: m/z calcd for $(\text{C}_{34}\text{H}_{66}^{10}\text{B}_4^{11}\text{B}_{16}\text{N}_2\text{P}_2\text{Si} + \text{Na})^+$: 831.6369. Found: 831.6384.

Preparation of 14. This compound was prepared in a similar manner to that of **13** as yellow crystals (60.2 mg, 40%) from **7** (133.2 mg, 0.2 mmol) and trimethylsilyldiazomethane (2.0 M, 0.1 mL, 0.2 mmol). ^1H NMR (400 MHz, C_6D_6): δ −0.17 (s, 9H; SiMe_3), 0.29 (s, 1H; CHTMS), 0.96 (s, 18H; CMe_3), 6.77 (m, 3H; aromatic CH), 6.98 (m, 7H; aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, C_6D_6): δ 2.12 (SiMe_3), 21.4 (CHTMS), 31.2, 31.3 (CMe_3), 46.3, 46.4 (CMe_3), 85.7 (d, J = 114 Hz, cage *C*), 87.8 (d, J = 13.0 Hz, cage *C*), 115.8, 117.7, 123.3, 123.5, 125.7, 129.3, 147.3, 147.4 (aromatic CH), 162.0, 162.4 ($\text{C}=\text{N}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ −8.9 (12B), −2.1 (8B). ^{31}P NMR (162 MHz, C_6D_6): δ −123.2 (d, J = 178.2 Hz; 1P), −88.3 (d, J = 178.2 Hz; 1P). HRMS: m/z calcd for $(\text{C}_{30}\text{H}_{58}^{10}\text{B}_4^{11}\text{B}_{16}\text{N}_2\text{P}_2\text{Si} + \text{Na})^+$: 775.5743. Found: 775.5762.

Preparation of 15. To a THF solution of **7** (66.6 mg, 0.1 mmol) (20 mL), benzyl azide (26.6 mg, 0.2 mmol) was slowly added at room temperature, and the mixture was stirred at room temperature overnight. The ^{31}P NMR spectrum indicated a complete conversion of **7**. After the removal of the solvent, the resulting yellow powder was dissolved in toluene (5 mL) to give **15** as yellow crystals after slow evaporation of the solvent at room temperature (57.9 mg, 66%). ^1H NMR (400 MHz, CD_2Cl_2): δ 1.01 (s, 18H; CMe_3), 2.34 (s, 4H; CH_2Ph), 6.39 (d, J = 7.6 Hz, 4H; aromatic CH), 7.26 (m, 12H; aromatic CH), 7.34 (d, J = 7.6 Hz, 4H; aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, CD_2Cl_2): δ 31.2 (CMe_3), 45.7 (CMe_3), 49.7 (CH_2Ph), 66.0 (cage *C*), 84.6 (cage *C*), 118.6, 123.8, 125.6, 127.5, 128.3, 128.4, 128.5, 129.3, 136.6, 146.0 (aromatic CH), 162.0 ($\text{C}=\text{N}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CD_2Cl_2): δ −8.9 (12B), −2.1 (8B). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 195.2. Anal. calcd for $\text{C}_{40}\text{H}_{62}^{10}\text{B}_4^{11}\text{B}_{16}\text{N}_4\text{P}_2$: C 54.78, H 7.13, N 6.39. Found: C 54.35, H 7.35, N 6.64.

Author contributions

J. Z. and Z. X. directed and conceived this project. T. L. C. conducted the experiments. All authors discussed the results and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers 2446505–2446518 for 2–15.† Experimental details and spectral data are available in the ESI.†

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