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Carbene Chemistry

Chemical Behaviour of a Prototype Boryl(phosphino)carbene

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Abstract: We recently disclosed the synthesis of a novel "push–pull" boryl(phosphino)carbene. To determine the influence of this substitution pattern on the chemical behaviour, a study into the reactivity of the prototype (**1**) of this new family of B(sp^2)-substituted phosphinocarbenes was undertaken. Carbene **1** exhibits one of the most common intramolecular rearrangements of singlet carbenes, involving a 1,2-mesityl shift, and typical [2+1] cycloaddition reactions with electron-poor acrylonitrile. A pronounced α,β-ambiphilic character was also shown by the reaction of **1** with benzaldehyde, leading to phosphorylalkene **4**. Due to its specific electronic properties, carbene **1** also exhibits unprecedented reactivity with chloroacrylonitrile, enabling the formation of bicyclo[1.1.0]phosphetanium salt **6** and borylcyclopropene **9**, which have been fully characterised by NMR spectroscopy and X-ray crystallography.

Introduction

Carbenes represent an important family of compounds, defined as neutral species featuring a divalent carbon atom with only six electrons in the valence shell, that have long been considered as transient intermediates. The isolation of a stable phosphino(silyl)carbene in 1988[1] and of a crystalline imidazol-2-ylidene compound in 1991,[2] in which two heteroatoms interact with the carbene centre, made real breakthroughs in this field. Since then, the chemistry of stabilised carbenes as synthetic reagents, ligands or organo-catalysts has become a very active area of investigation.[3] In this respect, the development of various stabilisation modes by modifying the substitution pattern at the carbon atom has been subject to detailed study. To date, stable singlet carbenes are predominantly π stabilised by the presence of at least one amino or phosphino group at the carbenic centre.[4] The reduced energetic cost for a nitrogen rather than a phosphorus atom to adopt a planar geometry, favouring the π interaction of the lone pair of the α-substituent with the p_π orbital at the carbenic carbon atom, renders amino groups significantly better π donors (or "push") than phosphino substituents.[5] In the case of stable non-cyclic carbenes, the second substituent at the carbenic centre (substituted heteroatom, alkyl or aryl group) determines the overall stabilisation mode, leading to "push–push", "push–spectator" or "push–pull" carbenes. While aminocarbenes are predominantly push–push[2] or push–spectator[6] stabilised, the push–pull mode is restricted to a limited number of phosphinocarbenes featuring an additional π-accepting group, which include silyl,[1] phosphonio[7] or 2,6-bis(trifluoromethyl)phenyl groups.[8] As a part of our research program aiming at extending this class of carbenes, we recently disclosed the synthesis of a prototype (**1**) of the push–pull boryl(phosphino)carbene family by deprotonation of the parent borylated methylenephosphonium salt (Figure 1).[9] With the presence of a B(sp^2)-containing boryl group adjacent to the carbenic centre in **1**, one could expect to induce a stabilising push–pull effect of greater magnitude (Figure 1).

The reactivity of stabilised carbenes depends on the singlet–triplet energy gap. With this in mind and because substituent effects govern the energetic positions of the frontier n_σ and p_π

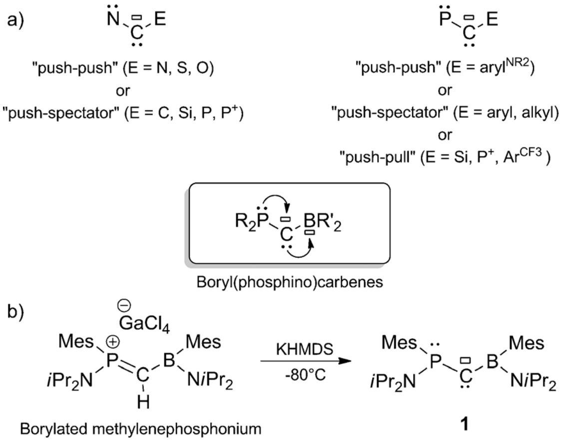

Figure 1. a) Push–push, push–spectator and push–pull stabilised carbenes. b) Synthesis of boryl(phosphino)carbene **1**.

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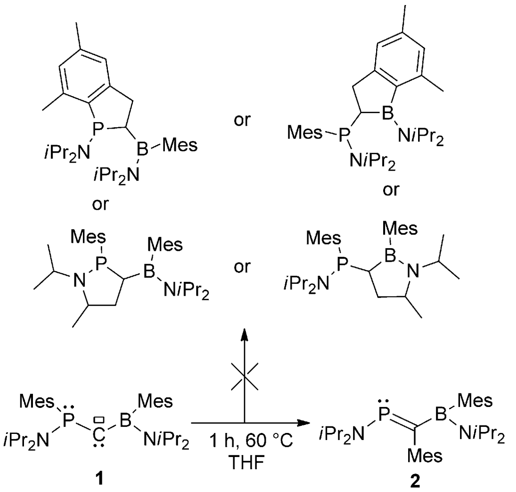
orbitals, a deeper investigation of the reactivity of boryl(phosphino)carbene **1** was undertaken. The aim is to better delineate its synthetic potential, and continue to investigate its behaviour towards small molecules, such as CO_2 and SO_2.[10]

Results and Discussion

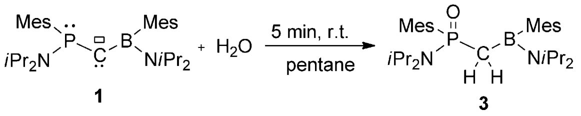
The reactivity of phosphinocarbenes mirrors the degree of carbene perturbation, which is directly linked to the substitution pattern at the carbenic centre; minor modifications of the electronic balance alter their stability. Push–pull phosphino(silyl)carbenes exhibit good thermal stability and drastic conditions are often needed to observe intramolecular C–H insertion reactions into appropriately located side chains.[1] With phosphino(aryl)carbenes, displaying a similar stabilisation mode, an intramolecular rearrangement through a 1,2-migration reaction is generally detected above approximately 80 °C,[11] which can also be induced at room temperature, under photolytic conditions. Boryl(phosphino)carbene **1** is in an intermediate situation since slow rearrangement into phosphaalkene **2**, involving 1,2-migration of the phosphorus mesityl group to the carbene centre, is observed at room temperature. Monitoring the transformation by ^{31}P NMR spectroscopy, in THF, at 25 °C, indicates that the reaction reaches completion after 24 h, whereas only 1 h is needed at 60 °C (Scheme 1). The resulting phosphaalkene, **2**, was isolated and fully characterised by multinuclear NMR spectroscopy. In the $^{31}P\{^1H\}$ NMR spectrum, compound **2** displays a deshielded singlet at $\delta = 231.7$ ppm, falling in the expected range for a $\lambda^2\sigma^3$-P-containing species. In the $^{13}C\{^1H\}$ NMR spectrum, the carbon bound to the phosphorus atom resonates at $\delta = 143.8$ ppm, with a coupling constant value ($^1J_{CP} = 61.2$ Hz) indicative of direct connectivity between these two atoms, as reported for phosphaalkenes.[12]

The absence of any reactivity with Lewis basic reagents, like *tert*-butylisocyanide[13] or PMe_3,[8,14] indicates poor electrophilic behaviour of boryl(phosphino)carbene **1**.



Scheme 1. Thermal rearrangement of boryl(phosphino)carbene **1** into phosphaalkene **2**.

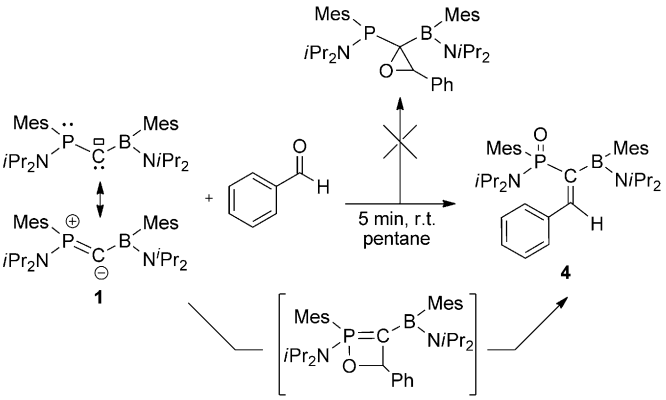
The more classical α,β-ambiphilic character resulting from the P_π–C_π interaction in phosphinocarbenes is, however, retained in compound **1**. Indeed, carbene **1** quickly reacts with a stoichiometric amount of water, quantitatively affording compound **3** (Scheme 2). In the $^{31}P\{^1H\}$ NMR spectrum, the phosphorus atom of the phosphine oxide moiety resonates at $\delta = 37.8$ ppm.[15,16] In the ^1H NMR spectrum, the two diastereotopic hydrogen atoms of the methylene group appear as a set of two doublets of doublets at $\delta = 2.31$ ($^2J_{HH} = 13.8$, $^2J_{HP} = 16.2$ Hz) and 2.69 ppm ($^2J_{HH} = 13.8$, $^2J_{HP} = 22.2$ Hz) in a 1:1 integration ratio.



Scheme 2. Hydrolysis reaction of boryl(phosphino)carbene **1**.

The reactions between the phosphino(silyl)carbene and aldehydes have been investigated, and two competitive processes were observed. With aromatic aldehydes, the reaction proceeds through a concerted [2+1] cycloaddition reaction to form a carbonyl group, leading to formation of oxiranes,[13] whereas with alkyl aldehydes a competitive pathway was observed through a [2+2]-like cycloaddition, providing a transient oxaphosphetene that rapidly transforms into the corresponding phosphorylated olefin.[17] The boryl(phosphino)carbene **1** reacts with benzaldehyde to produce exclusively the *Z* isomer of boryl(phosphoxide)alkene **4** (Scheme 3).

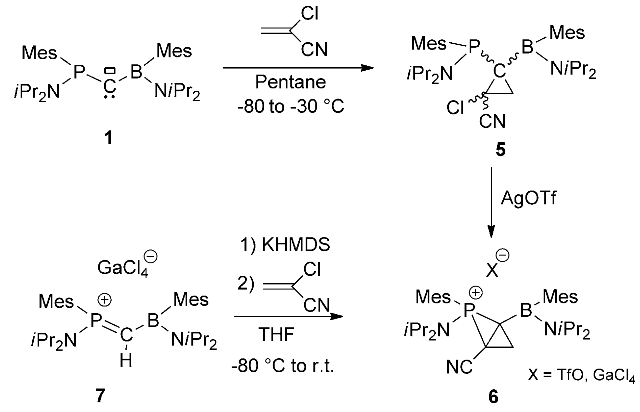
As previously observed with carbon and sulfur dioxide,[10] the olefinic derivative **4** could be rationalised by the formation of an intermediate oxaphosphetene through a Wittig-type reaction, illustrating the pronounced α,β-ambiphilic character of carbene **1**. Compound **4** was isolated and fully characterised by multinuclear NMR spectroscopy. In the $^{31}P\{^1H\}$ NMR spectrum, a singlet is observed at $\delta = 44.6$ ppm for the phosphine oxide moiety. The $^{13}C\{^1H\}$ NMR spectrum exhibits, in addition to the signals of the phenyl carbon atoms, a set of two doublets at $\delta = 137.2$ ($^1J_{CP} = 25.6$ Hz) and 143.9 ppm ($^2J_{CP} = 2.4$ Hz), corresponding to the ethylenic carbon atoms. In the ^1H NMR



Scheme 3. Reaction of boryl(phosphino)carbene **1** with benzaldehyde.

spectrum, the presence of a doublet at $\delta = 7.40$ ppm with a large coupling constant value ($^3J_{PH} = 44.5$ Hz) is in good agreement with a vinylic proton in a *trans* position to the phosphorus atom.

To get a more comprehensive view of the influence of the boryl moiety on the carbenic character of this prototype boryl(phosphino)carbene, we assessed the ability of **1** to undergo cyclopropanation reactions with electron-deficient olefins.[3b] In contrast to the case of phosphino(silyl)carbenes, carbene **1** does not react with styrene or methyl acrylate to give the corresponding cyclopropanes. This is probably due to the steric congestion around the carbene centre in **1**. In addition, the easy rearrangement of **1** into phosphaalkene **2** prevents any thermal activation of the cycloaddition process. Nevertheless, carbene **1** smoothly reacts with chloroacrylonitrile in pentane, at −30 °C (Scheme 4).



Scheme 4. Reaction of boryl(phosphino)carbene **1** with chloroacrylonitrile.

The resulting cyclopropane **5** was isolated in 55 % yield. The $^{31}P\{^1H\}$ NMR spectrum displays a set of singlets at $\delta = 49.0$ and 47.3 ppm, in a 77:23 integration ratio, indicative of the presence of two diastereomers. The observed diastereoselectivity of the cyclopropanation process contrasts with the case of phosphino(silyl)carbenes, which react diastereospecifically with acrylates, leading to the exclusive formation of the *syn* isomer.[13a, 18] However, the selectivity observed with carbene **1** is very similar to that obtained in the reaction of [2,6-bis(trifluoromethyl)phenyl](phosphino)carbene with chloroacrylonitrile.[11] The major isomer of **5** ($\delta_P = 49.0$ ppm) was analysed by multinuclear NMR spectroscopy. In the $^{11}B\{^1H\}$ NMR spectrum, a singlet is observed at $\delta = 43$ ppm. The ^1H NMR spectrum displays a multiplet at $\delta = 1.79$ and a doublet of doublets at 2.38 ppm ($^2J_{HH} = 3.3$, $^3J_{HP} = 6.0$ Hz) in a 1:1 ratio for the diastereotopic protons of the methylene group. The $^{13}C\{^1H\}$ NMR spectrum exhibits a set of doublets at $\delta = 39.2$ ($^1J_{CP} = 7.5$ Hz) and 29.7 ppm ($^2J_{CP} = 5.5$ Hz), corresponding to the PCB and methylenic carbon atoms, respectively. The X-ray structure of **5** was determined at −80 °C, revealing the presence of two diastereoisomers in the asymmetric unit, in a 55:45 ratio (Figure 2). The P1–C1 bond length (1.892(2) Å) is in agreement with that reported for P–C single bonds in phosphinocyclopropanes.[11, 18a] The B1–C1 bond is slightly longer than that reported for cyclopropyl–B(sp^2) linkages (1.52–1.56 Å),[19] probably for steric reasons.

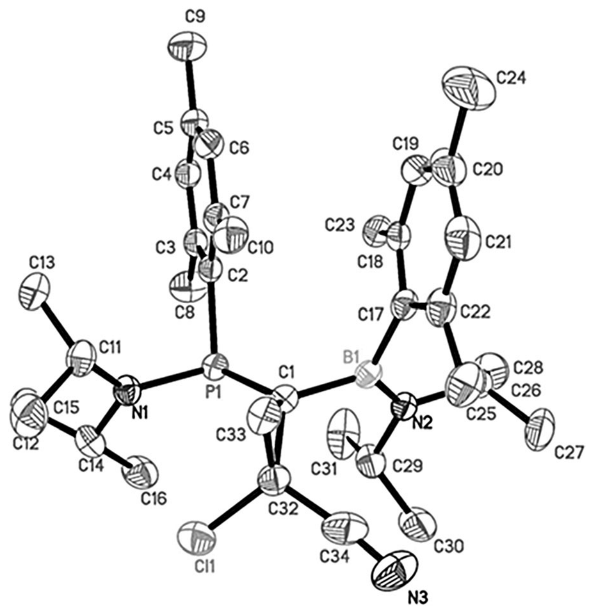


Figure 2. Molecular structure of **5** (*syn*-**5** featuring the chlorine *cis* to the phosphorus is represented here). Thermal ellipsoids were set at 50 % probability. Hydrogen atoms were omitted for clarity; selected bond lengths [Å] and angles [°]: C33–C32 1.491(2), C1–CC33 1.522(2), C1–C32 1.536(2), P1–N1 1.691(1), P1–C2 1.862(2), P1–C1 1.892(2), B1–N2 1.402(2), B1–C17 1.593(2), B1–C1 1.638(2); C32-C1-P1 117.45(11), C33-C1-C32 58.36(11), C32-C1-B1 117.05(13), N1-P1-C2 101.66(7), N1-P1-C1 111.52(7), C2-P1-C1 107.39(7), N2-B1-C17 121.27(14), N2-B1-C1 122.54(14), C17-B1-C1 116.09(13).

Interestingly, the presence of nucleophilic (P) and electrophilic (C–Cl) centres, allows the easy formation of an original bicyclic structure. Indeed, the addition of one equivalent of silver triflate to a solution of **5** in CH_2Cl_2, at −80 °C, leads to the formation of bicyclo[1.1.0]phosphetanium salt **6**, as a mixture of two isomers (67:33), characterised by two singlets at $\delta = 15.7$ and 7.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum (Scheme 4). The bicyclo[1.1.0]phosphetanium salt **6** can also be obtained directly from the methylene phosphonium salt **7**, which is the precursor of carbene **1**. In this case, deprotonation and cyclopropanation were performed in situ and stepwise, leading to the direct formation of the bicyclic structure **6**, which was isolated, in 60 % yield, as a mixture of two diastereomers in a 55:45 ratio. Probably, the salts formed in the first step catalyse the nucleophilic attack of the phosphine centre of the in situ generated phosphino cyclopropane **5**.

Diastereoselective crystallisation of the mixture of the two isomers of **6** from a saturated solution in toluene at −30 °C allowed the full characterisation of the major diastereomer ($\delta_P = 15.7$ ppm) and allowed us to deduce the spectroscopic data of the minor one ($\delta_P = 7.6$ ppm). The $^{11}B\{^1H\}$ NMR spectrum of the major diastereomer displays a signal at $\delta = 40$ ppm. In the ^1H NMR spectrum, two sets of signals are observed for the diastereotopic hydrogen atoms of the methylene bridge: doublets of doublets at $\delta = 3.11$ ($^2J_{HH} = 5.2$, $^3J_{HP} = 27.6$ Hz) and 2.99 ppm ($^2J_{HH} = 5.2$, $^3J_{HP} = 53.7$ Hz). The solid-state structure of the major diastereomer of **6** was determined by a single-crystal

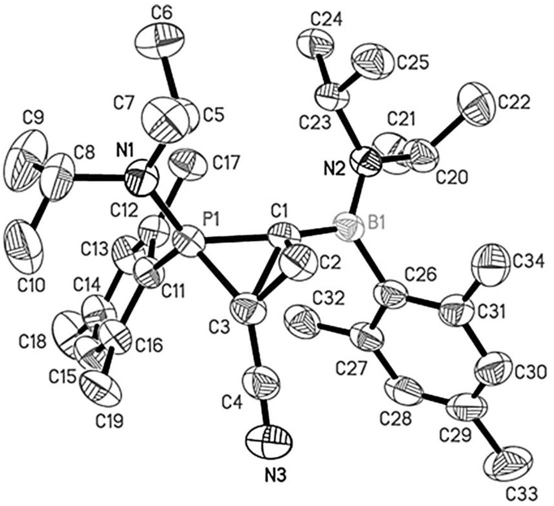


Figure 3. Molecular structure of **6**. Thermal ellipsoids were set at 50 % probability. Hydrogen atoms, $GaCl_4^-$ and solvent were omitted for clarity; selected bond lengths [Å] and angles [°]: P1–N1 1.625(3), P1–C1 1.770(3), P1–C3 1.784(3), P1–C11 1.786(3), N2–B1 1.391(4), N3–C4 1.147(5), C3–C4 1.434(5), B1–C1 1.605(5), C1–C2 1.540(5), C1–C3 1.614(4), C2–C3 1.484(4), B1–C26 1.588(5); N1-P1-C1 117.94(14), N1-P1-C3 128.46(15), C1-P1-C3 54.02(14), N1-P1-C11 113.99(14), C1-P1-C11 119.53(15), C3-P1-C11 110.51(15), N2-B1-C26 123.5(3), N2-B1-C1 119.7(3), C2-C3-C1 59.4(2), C2-C3-P1 99.8(2), C1-C3-P1 62.55(16), C26-B1-C1 116.6(3), C2-C1-B1 120.0(3), C2-C1-C3 56.1(2), B1-C1-C3 131.0(3), C2-C1-P1 98.2(2).

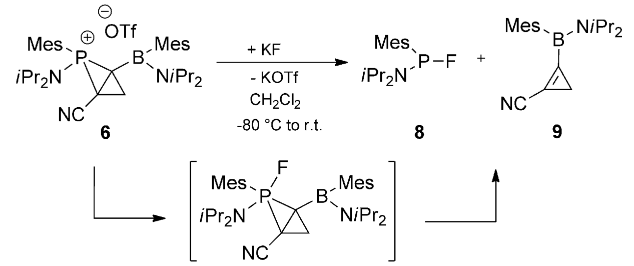
X-ray diffraction analysis at −80 °C, clearly showing the tetravalent environment of the phosphorus centre, and the bicyclic structure (Figure 3).

The intracyclic P–C bond lengths (1.770(3) and 1.784(3) Å) are shorter than those of classical P–C single bonds (1.80–1.90 Å) and lie between the bond lengths of phosphetanium salts (P–C ≈ 1.800 Å)[20] and those of phosphiranium cations (P–C ≈ 1.760 Å).[21] A similar trend is observed for the variation of the C1-P1-C3 bond angle (54.02(14)°), which also lies between that in phosphetanium (75–82°) and phosphiranium salts (47–52°).[20,21]

By analogy with the reactivity of phosphiranium salts, the ability of **6** to undergo the cheletropic extrusion of a phosphenium fragment was evaluated.[22] In the presence of diphenylacetylene or dimethyl acetylenedicarboxylate, no reaction was observed, even at an elevated temperature. In contrast, the addition of one equivalent of potassium fluoride to **6** led quantitatively to borylcyclopropene **9** and fluorophosphine **8**, which were fully characterised spectroscopically. In this case, instead of generating a transient phosphenium salt, the reaction probably involves the transient formation of a bicyclic phosphorane (Scheme 5).[23]

Conclusion

The chemical behaviour of the novel push–pull boryl(phosphino)carbene **1** was thoroughly evaluated through a range of appropriate reactions mirroring the different aspects generally encountered in stabilised carbenes. We have shown that carbene **1** is relatively stable but not to the same degree as phosphino(silyl)carbenes. Indeed, it slowly rearranges at room temperature into phosphaalkene **2** by a 1,2-mesityl migration to the carbenic centre. This boryl(phosphino)carbene (**1**) presents an important α,β-ambiphilic character, reacting with benzaldehyde and leading to the corresponding boryl(phosphoxide) alkene **4**, rather than the boryl(phosphino)oxirane. In addition, the absence of any reactivity towards Lewis bases indicates that **1** is weakly electrophilic. In contrast, it readily reacts with the electron-poor chloroacrylonitrile to give the corresponding [2+1] cycloadduct. The resulting boryl(phosphino)cyclopropane **5** displays interesting intramolecular reactivity, and can be converted into the bicyclo[1.1.0]phosphetanium salt **6**, featuring an original structure with two fused three-membered rings. The formal extrusion of a phosphenium fragment from the bicyclic structure **6** allows easy synthesis of borylcyclopropene **9** under mild conditions.



Scheme 5. Reaction of bicyclo[1.1.0]phosphetanium salt **6** with KF.

In conclusion, due to its unique electronic properties, the push–pull boryl(phosphino)carbene **1** exhibits both classical and unprecedented reactivities. Our efforts to develop new push–pull models are still underway and will allow a better understanding of this type of reactivity.

Experimental Section

General procedures: All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques. Dry and oxygen-free solvents were used. ^{1}H, ^{11}B, ^{13}C and ^{31}P NMR spectra were recorded on Brucker Avance 400 or Avance 300 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to Me_4Si as an external standard. ^{31}P and ^{11}B NMR downfield chemical shifts are expressed in ppm relative to 85 % H_3PO_4 and $BF_3\cdot Et_2O$, respectively. IR spectra were recorded on a Varian 640-IR spectrophotometer. Mass spectra were recorded on a Hewlett Packard 5989A spectrometer. Carbene **1** and methylenephosphonium **7** were prepared according to a literature procedure.[9]

Phosphaalkene 2: Phosphaalkene **2** was obtained quantitatively by heating a solution of carbene **1** (72 mg, 0.15 mmol) in [D$_8$]THF (1 mL) at reflux for 1 h or by stirring the solution at room temperature for 24 h. The product was spectroscopically characterised without further purification. ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta=0.80$ (d, $^{3}J_{HH}=6.3$ Hz, 12H; PNCHCH_3), 0.85 (d, $^{3}J_{HH}=6.9$ Hz, 6H; BNCHCH_3), 1.09 (d, $^{3}J_{HH}=6.9$ Hz, 6H; BNCHCH_3), 1.76 (m, 6H; CH_{3ortho}B), 1.82 (m, 3H; CH_{3para}B), 1.97 (s, 6H; CH_{3ortho}Mes), 1.98 (s, 3H; CH_{3para}Mes), 3.22 (sept d, $^{3}J_{HH}=6.9$, $^{3}J_{PH}=13.5$ Hz, 2H; PNCHCH$_3$), 3.32 (sept, $^{3}J_{HH}=7.2$ Hz, 2H; BNCHCH$_3$), 6.32 (s, 2H; CH_{Ar}Mes), 6.46 ppm (s, 2H; CH_{Ar}B); ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]THF): $\delta=19.9$ (s; CH$_{3ortho}$Mes), 20.2 (s; CH$_{3para}$Mes), 21.3 (s; CH$_{3ortho}$B), 22.0

(s; *C*H$_{3para}$B), 22.9 (s; BNCH*C*H$_3$), 23.0 (s; PNCH*C*H$_3$), 23.5 (s; BNCH*C*H$_3$), 47.1 (s; BN*C*HCH$_3$), 48.1 (d, $^3J_{CP}$ = 3.1 Hz; PN*C*HCH$_3$), 126.3 (s; *C*H$_{Ar}$Mes), 127.4 (s; *C*H$_{Ar}$B), 133.3 (s; *C*$_{ortho}$Mes), 135.0 (s; *C*$_{ortho}$B), 139.1 (s; *C*$_{para}$B), 140.1 (s; *C*$_{para}$Mes), 143.8 ppm (d, $^1J_{CP}$ = 61.2 Hz; P*C*B); ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF): δ = 231.7 ppm; ^{11}B{^{1}H} NMR (128 MHz, [D$_8$]THF): δ = 42.6 ppm; HRMS (ESI$^+$): *m/z* calcd for C$_{31}$H$_{50}$BN$_2$P: 493.3883 [*M*+H]$^+$; found: 493.3872.

Phosphine oxide 3: At room temperature, water (2.5 μL, 0.14 mmol) was added to a solution of boryl(phosphino)carbene **1** (70 mg, 0.14 mmol) in pentane (2 mL). Within 5 min, the solution becomes cloudy. The precipitate was purified and filtered through a small layer of silica gel (eluent: ethanol). A yellow powder was obtained (44 mg, 62% yield). M.p. = 151–152 °C; ^{1}H NMR (300.1 MHz, C$_6$D$_6$): δ = 0.79 (d, $^3J_{HH}$ = 6.9 Hz, 3H; BNCHC*H*$_3$), 0.84 (d, $^3J_{HH}$ = 6.6 Hz, 3H; BNCHC*H*$_3$), 1.04 (d,$^3J_{HH}$ = 6.6 Hz, 6H; PNCHC*H*$_3$), 1.30 (d, $^3J_{HH}$ = 6.9 Hz, 6H; PNCHC*H*$_3$), 1.36 (d, $^3J_{HH}$ = 7.2 Hz, 3H; BNCHC*H*$_3$), 1.52 (d, $^3J_{HH}$ = 6.9 Hz, 3H; BNCHC*H*$_3$), 2.03 (s, 3H; C*H*$_{3ortho}$P), 2.15 (s, 3H; C*H*$_{3ortho}$B), 2.18 (s, 3H; C*H*$_{3ortho}$B), 2.24 (s, 3H; C*H*$_{3para}$B), 2.31 (dd, $^2J_{HH}$ = 14.1, $^2J_{HP}$ = 16.2 Hz, 1H; PC*H*$_2$B), 2.37 (s, 3H; C*H*$_{3para}$P), 2.68 (dd, $^2J_{HH}$ = 14.1, $^2J_{HP}$ = 22.8 Hz, 1H; PC*H*$_2$B), 2.88 (s, 3H; C*H*$_{3ortho}$P), 3.25 (sept, $^3J_{HH}$ = 7.5 Hz, 1H; BNC*H*CH3), 3.42 (sept, $^3J_{HH}$ = 6.9 Hz, 2H; PNC*H*CH$_3$), 3.60 (sept, $^3J_{HH}$ = 6.9 Hz, 1H; BNC*H*CH$_3$), 6.44 (s, 1H; C*H*$_{Ar}$P), 6.50 (s, 1H; C*H*$_{Ar}$B), 6.59 (s, 1H; C*H*$_{Ar}$B), 6.64 ppm (s, 1H; C*H*$_{Ar}$P); ^{13}C{^{1}H} NMR (75.1 MHz, C$_6$D$_6$): δ = 20.9 (s; *C*H$_{3ortho}$P), 21.2 (s; *C*H$_{3ortho}$B), 22.0 (s; BNCH*C*H$_3$), 22.1 (s; BNCH*C*H$_3$), 22.6 (s; *C*H$_{3ortho}$B), 22.9 (s; *C*H$_{3para}$P), 23.2 (s; *C*H$_{3para}$B), 23.2 (d, $^3J_{CP}$ = 2.2 Hz; PNCH*C*H$_3$), 23.6 (d, $^3J_{CP}$ = 2.8 Hz; PNCH*C*H$_3$), 24.4 (s; *C*H$_{3ortho}$P), 24.9 (s; BNCH*C*H$_3$), 25.0 (s; BNCH*C*H$_3$), 28.6 (d, $^1J_{CP}$ = 82.5 Hz; P*C*H$_2$B), 47.4 (d, $^2J_{CP}$ = 3.1 Hz; PN*C*HCH$_3$), 48.5 (s; BN*C*HCH$_3$), 50.4 (s; BN*C*HCH$_3$), 127.3 (s; *C*H$_{Ar}$B), 127.4 (s; *C*H$_{Ar}$B), 128.9 (d, $^1J_{CP}$ = 111.3 Hz; *C*$_{ipso}$P), 130.4 (d, $^3J_{CP}$ = 11.7 Hz; *C*H$_{Ar}$P), 131.4 (d, $^3J_{CP}$ = 12.9 Hz; *C*H$_{Ar}$P), 135.5 (s; *C*$_{ortho}$B), 137.7 (s; *C*$_{para}$B), 138.6 (s; *C*$_{ortho}$P), 139.5 (d, $^4J_{CP}$ = 2.6 Hz; *C*$_{para}$P), 139.7 (s; *C*$_{ortho}$B), 146.3 ppm (d, $^2J_{CP}$ = 10.1 Hz; *C*$_{ortho}$P); the carbon *ipso* to boron was not observed; ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ = 37.8 ppm (s); ^{11}B{^{1}H} NMR (96.3 MHz, C$_6$D$_6$): δ = 43.4 ppm (s); HRMS (ESI$^+$): *m/z* calcd for C$_{31}$H$_{52}$BN$_2$OP: 511.3989 [*M*+H]$^+$; found; 511.3991.

Phosphorylalkene 4: At room temperature, benzaldehyde (58.2 μL, 0.57 mmol) was added to a solution of boryl(phosphino)carbene **1** (200 mg, 0.41 mmol) in pentane (3 mL). Within 5 min, the solution turned yellow. After evaporation of the solvent, the product was purified by filtration through a small layer of silica gel (eluent: diethyl ether). A yellow powder was obtained (150 mg 61% yield). M.p. = 120–122 °C; ^{1}H NMR (300.1 MHz, CDCl$_3$): δ = 0.95 (d, $^3J_{HH}$ = 6.0 Hz, 3H; BNCHC*H*$_3$), 1.27 (d, $^3J_{HH}$ = 6.9 Hz, 3H; PNCHC*H*$_3$), 1.33 (d, $^3J_{HH}$ = 6.9 Hz, 3H; PNCHC*H*$_3$), 1.35 (d, $^3J_{HH}$ = 7.5 Hz, 3H; PNCHC*H*$_3$), 1.36 (d, $^3J_{HH}$ = 7.0 Hz, 3H; BNCHC*H*$_3$), 1.39 (d, $^3J_{HH}$ = 6.5 Hz, 3H; BNCHC*H*$_3$), 1.59 (d, $^3J_{HH}$ = 6.0 Hz, 3H; BNCHC*H*$_3$), 1.67 (d, $^3J_{HH}$ = 7.2 Hz, 3H; PNCHC*H*$_3$), 1.89 (s, 3H; C*H*$_{3ortho}$P), 2.00 (s, 3H; C*H*$_{3para}$B), 2.06 (s, 3H; C*H*$_{3ortho}$B), 2.13 (s, 3H; C*H*$_{3para}$P), 2.22 (s, 3H; C*H*$_{3ortho}$B), 2.80 (s, 3H; C*H*$_{3ortho}$P), 3.39 (m, 1H; BNC*H*CH$_3$), 3.65 (m, 1H; BNC*H*CH$_3$), 4.00 (sept, $^3J_{HH}$ = 7.5 Hz, 1H; PNC*H*CH$_3$), 4.33 (sept, $^3J_{HH}$ = 7.0 Hz, 1H; PNC*H*CH$_3$), 6.06 (s, 1H; C*H*$_{Ar}$B), 6.07 (s, 1H; C*H*$_{Ar}$P), 6.44 (s, 1H; C*H*$_{Ar}$P), 6.69 (s, 1H; C*H*$_{Ar}$B), 7.39 (m, 3H; C*H*$_{Ar}$Ph), 7.40 (d, $^3J_{PH}$ = 44.5 Hz, 1H; PC=C*H*Ph), 7.89 ppm (m, 2H; C*H*$_{Ar}$Ph); ^{13}C{^{1}H} NMR (75.1 MHz, CDCl$_3$): δ = 20.8 (d, $^5J_{CP}$ = 4.5 Hz; *C*H$_{3para}$P), 20.9 (s; *C*H$_{3ortho}$B), 22.1 (s; BNCH*C*H$_3$), 22.5 (s; PNCH*C*H$_3$), 23.0 (s; *C*H$_{3ortho}$B), 23.1 (s; PNCH*C*H$_3$), 23.3 (s; BNCH*C*H$_3$), 23.9 (d, $^3J_{CP}$ = 4.1 Hz; *C*H$_{3ortho}$P), 24.0 (s; BNCH*C*H$_3$), 24.1 (d, $^3J_{CP}$ = 3.7 Hz; *C*H$_{3ortho}$P), 25.0 (s; *C*H$_{3para}$B), 25.7 (s; PNCH*C*H$_3$), 26.8 (s; BNCH*C*H$_3$), 26.9 (s; PNCH*C*H$_3$), 46.6 (s; BN*C*HCH$_3$), 48.4 (s; BN*C*HCH$_3$), 51.3 (s; PN*C*HCH$_3$), 51.4 (s; PN*C*HCH$_3$), 126.5 (s; *C*H$_{Ar}$P), 127.1 (s; *C*H$_{Ar}$P), 127.9 (s; *C*H$_{Ar}$Ph), 128.0 (d, $^1J_{CP}$ = 111.4 Hz; *C*$_{ipso}$P), 128.9 (s; *C*H$_{Ar}$B), 129.7 (s; *C*H$_{Ar}$B), 130.7 (d, $^4J_{CP}$ = 1.4 Hz; *C*H$_{Ar}$Ph), 135.3 (s; *C*$_{ortho}$B), 137.2 (d, $^1J_{CP}$ = 25.6 Hz; P*C*B), 138.8 (d, $^4J_{CP}$ = 2.6 Hz; *C*$_{para}$P), 138.9 (s; *C*$_{para}$B), 140.4 (s; *C*$_{ortho}$B), 140.9 (d, $^2J_{CP}$ = 12.4 Hz; *C*$_{ortho}$P), 143.8 (s; *C*$_{ortho}$P), 143.9 ppm (d, $^2J_{CP}$ = 2.4 Hz; PC=*C*H); the carbon *ipso* to boron was not observed; ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ = 44.6 ppm (s); ^{11}B{^{1}H} NMR (96.3 MHz, CDCl$_3$): δ = 45.1 ppm (s); HRMS (ESI$^+$): *m/z* calcd for C$_{38}$H$_{56}$BN$_2$OP: 621.4121 [*M*+Na]$^+$; found: 621.4132.

Cyclopropane *syn*-and *anti*-5: 2-Chloroacrylonitrile (3 equiv, 48.7 μL, 0.60 mmol) was slowly added to a solution of carbene **1** (100 mg, 0.20 mmol) in pentane (1.5 mL) at −80 °C. The solution was warmed to −30 °C, stirred at this temperature for 24 h, filtered and the solvent was removed under vacuum. Extraction with pentane (2×5 mL) was performed and cyclopropane **5** was purified by silica gel chromatography with pentane as the eluent. A mixture of two diastereoisomers was obtained in a 77:23 ratio, as indicated by ^{31}P NMR spectroscopy (64 mg, 55% yield). White crystals of **5** in a 55:45 ratio of isomers (estimated by ^{31}P NMR analysis) could be obtained from a saturated solution in pentane at −40 °C. IR (THF): $\tilde{\nu}$ = 2305 cm^{-1}.

Major diastereomer: ^{1}H NMR (300.1 MHz, C$_6$D$_6$): δ = 0.31 (m, 3H; BNCHC*H*$_3$), 1.00 (d, $^3J_{HH}$ = 6.9 Hz, 3H; BNCHC*H*$_3$), 1.01 (d, $^3J_{HH}$ = 6.9 Hz, 3H; BNCHC*H*$_3$), 1.09 (d, $^3J_{HH}$ = 7.2 Hz, 3H; PNCHC*H*$_3$), 1.18 (d, $^3J_{HH}$ = 7.2 Hz, 3H; PNCHC*H*$_3$), 1.26 (s, 3H; C*H*$_{3ortho}$B), 1.46 (m, 3H; BNCHC*H*$_3$), 1.69 (d, $^3J_{HH}$ = 6.6 Hz, 3H; PNCHC*H*$_3$), 1.74 (s, 3H; C*H*$_{3ortho}$P), 1.78 (d, $^3J_{HH}$ = 7.2 Hz, 3H; PNCHC*H*$_3$), 1.79 (m, 1H; C*H*$_{2cycle}$), 2.08 (s, 3H; C*H*$_{3para}$P), 2.13 (s, 3H; C*H*$_{3para}$B), 2.38 (dd, $^2J_{HH}$ = 3.3, $^3J_{HP}$ = 6.0 Hz, 1H; C*H*$_{2cycle}$), 2.45 (s, 3H; C*H*$_{3ortho}$B), 2.81 (d, $^4J_{HP}$ = 3.6 Hz, 3H; C*H*$_{3ortho}$P), 3.13 (m, 1H; BNC*H*CH$_3$), 3.61 (m, 1H; BNC*H*CH$_3$), 3.82 (sept, $^3J_{HH}$ = 7.2 Hz, 1H; PNC*H*CH$_3$), 5.19 (sept d, $^3J_{HH}$ = 6.6, $^3J_{HP}$ = 2.7 Hz, 1H; PNC*H*CH$_3$), 6.44 (s, 1H; C*H*$_{Ar}$B), 6.54 (m, 1H; C*H*$_{Ar}$P), 6.69 (s, 1H C*H*$_{Ar}$B), 6.76 ppm (d, $^4J_{HP}$ = 6.3 Hz, 1H; C*H*$_{Ar}$P); ^{13}C{^{1}H} NMR (75.1 MHz, C$_6$D$_6$): δ = 20.4 (s; BNCH*C*H$_3$), 20.8 (s; *C*H$_{3para}$P), 21.0 (s; *C*H$_{3para}$B), 22.2 (s; *C*H$_{3ortho}$B), 23.3 (m; *C*H$_{3ortho}$P), 23.4 (s; PNCH*C*H$_3$), 23.5 (s; PNCH*C*H$_3$), 24.5 (s; *C*H$_{3ortho}$P), 25.0 (s; BNCH*C*H$_3$), 25.2 (s; *C*H$_{3ortho}$B), 25.5 (s; BNCH*C*H$_3$), 25.6 (s; PNCH*C*H$_3$), 26.1 (s; BNCH*C*H$_3$), 29.1 (d, $^3J_{CP}$ = 8.9 Hz; PNCH*C*H$_3$), 29.7 (d, $^2J_{CP}$ = 5.5 Hz; *C*H$_{2cycle}$), 39.2 (d, $^1J_{CP}$ = 7.5 Hz; P*C*B), 50.1 (s; BN*C*HCH$_3$), 51.8 (s; BN*C*HCH$_3$), 52.0 (s; PN*C*HCH$_3$), 52.3 (s; PN*C*HCH$_3$), 119.9 (s; *C*N), 128.2 (s; *C*H$_{Ar}$B), 128.3 (s; *C*H$_{Ar}$B), 129.8 (d, $^3J_{CP}$ = 7.7 Hz; *C*H$_{Ar}$P), 131.9 (s; *C*H$_{Ar}$P), 134.8 (d, $^1J_{CP}$ = 21.9 Hz; *C*$_{ipso}$P), 136.4 (s; *C*$_{para}$B), 138.5 (s; *C*$_{ortho}$B), 138.8 (s; *C*$_{para}$P), 140.6 (s; *C*$_{ortho}$ B), 143.3 (d, $^2J_{CP}$ = 3.3 Hz; *C*$_{ortho}$P), 144.1 ppm (m; *C*$_{ortho}$P); the bridgehead carbon atom alpha to the nitrile was not observed; ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ = 49.0 ppm (s); ^{11}B{^{1}H} NMR (96.3 MHz, C$_6$D$_6$): δ = 42.6 ppm (s).

Minor Diastereomer: ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ = 47.3 ppm (s).

Bicyclo[1.1.0]phosphetanium salt 6: A solution of silver triflate (57 mg, 0.22 mmol) in CH$_2$Cl$_2$ (1 mL) was added to a solution of cyclopropane **5** (130 mg, 0.22 mmol) in CH$_2$Cl$_2$ (2 mL) at −80 °C. The solution was slowly warmed to room temperature (4 h) and filtered. After removal of the solvent, crude compound **6** was washed with pentane (3×3 mL). Compound **6** was obtained as a white powder, containing two diastereoisomers in a ratio of 67:33 (85 mg, 55% yield). HRMS (ESI$^+$): *m/z* calcd for C$_{34}$H$_{52}$BClN$_3$P: 580.3759 [*M*+H]$^+$; found: 580.3763; the counter-anion was found to be chlorine by HRMS.

Major diastereomer: 67% yield; IR (THF): $\tilde{\nu}$ = 2150 cm^{-1}; ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 3H; BNCHC*H*$_3$), 1.21 (d, $^3J_{HH}$ = 7.2 Hz, 3H; BNCHC*H*$_3$), 1.22 (d, $^3J_{HH}$ = 7.2 Hz, 6H; PNCHC*H*$_3$), 1.24 (s, 3H; C*H*$_{3ortho}$B), 1.38 (d, $^3J_{HH}$ = 6.8 Hz, 6H; PNCHC*H*$_3$), 1.51 (d, $^3J_{HH}$ = 7.2 Hz, 3H; BNCHC*H*$_3$), 1.52 (d, $^3J_{HH}$ =

6.8 Hz, 3 H; BNCHCH_3), 2.14 (s, 3 H; C$H_{3\mathrm{para}}$B), 2.28 (s, 3 H; C$H_{3\mathrm{ortho}}$B), 2.44 (s, 3 H; C$H_{3\mathrm{para}}$P), 2.76 (s, 3 H; C$H_{3\mathrm{ortho}}$P), 2.89 (s, 3 H; C$H_{3\mathrm{ortho}}$P), 2.99 (dd, $^{2}J_{HH}=5.2$, $^{3}J_{HP}=53.7$ Hz, 1 H; C$H_{2\mathrm{cycle}}$), 3.11 (dd, $^{2}J_{HH}=5.2$, $^{3}J_{HP}=27.6$ Hz, 1 H; C$H_{2\mathrm{cycle}}$), 3.72 (sept d, $^{3}J_{HH}=6.4$, $^{3}J_{HP}=13.2$ Hz, 2 H; PNCHCH$_3$), 3.77 (sept, $^{3}J_{HH}=6.8$ Hz, 1 H; BNCHCH$_3$), 4.47 (sept, $^{3}J_{HH}=7.2$ Hz, 1 H; BNCHCH$_3$), 6.54 (s, 1 H; CH_{Ar}B), 6.73 (s, 1 H; CH_{Ar}B), 7.23 (d, $^{4}J_{PH}=6.4$ Hz, 1 H; CH_{Ar}P), 7.24 ppm (d, $^{4}J_{PH}=6.0$ Hz, 1 H; CH_{Ar}P); ^{13}C{^{1}H} NMR (100.1 MHz, CDCl$_3$): $\delta=20.9$ (s; $CH_{3\mathrm{para}}$B), 21.6 (s; $CH_{3\mathrm{para}}$P), 21.7 (s; BNCHCH$_3$), 22.6 (s; $CH_{3\mathrm{ortho}}$B), 22.9 (s; $CH_{3\mathrm{ortho}}$P), 23.0 (s; PNCHCH$_3$), 23.1 (s; PNCHCH$_3$), 23.2 (s; BNCHCH$_3$), 23.3 (s; $CH_{3\mathrm{ortho}}$B), 24.0 (s; $CH_{3\mathrm{ortho}}$P), 24.7 (s; BNCHCH$_3$), 25.6 (s; BNCHCH$_3$), 27.6 (d, $^{1}J_{CP}=48.5$ Hz; PCB), 34.8 (d, $^{2}J_{CP}=2.2$ Hz; $CH_{2\mathrm{cycle}}$), 50.5 (s; BNCHCH$_3$), 52.9 (s; PNCHCH$_3$), 54.0 (s; BNCHCH$_3$), 110.8 (s; CN), 116.7 (d, $^{1}J_{CP}=125.4$ Hz; C_{ipso}P), 127.7 (s; CH_{Ar}B), 127.9 (s; CH_{Ar}B), 130.6 (d, $^{3}J_{CP}=14.0$ Hz; CH_{Ar}P), 131.7 (d, $^{3}J_{CP}=13.6$ Hz; CH_{Ar}P), 137.5 (s; C_{ortho}B), 138.4 (s; C_{para}B), 138.7 (s; C_{ortho}B), 142.4 (d, $^{2}J_{CP}=12.3$ Hz; C_{ortho}P), 143.6 (d, $^{2}J_{CP}=12.0$ Hz; C_{ortho}P), 148.4 ppm (d, $^{4}J_{CP}=2.6$ Hz; C_{para}P); the bridgehead carbon atom alpha to the nitrile was not observed; ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): $\delta=15.7$ ppm (s); ^{11}B{^{1}H} NMR (128.4 MHz, CDCl$_3$): $\delta=40.4$ ppm (s).

Minor diastereomer: 33 % yield; product not isolated; NMR spectra were deduced from analysis of the mixture; ^{1}H NMR (400.1 MHz, CDCl$_3$): $\delta=1.13$ (d, $^{3}J_{HH}=6.8$ Hz, 3 H; BNCHCH_3), 1.17 (d, $^{3}J_{HH}=6.8$ Hz, 3 H; BNCHCH_3), 1.38 (d, $^{3}J_{HH}=6.8$ Hz, 6 H; PNCHCH_3), 1.39 (d, $^{3}J_{HH}=6.8$ Hz, 6 H; PNCHCH_3), 1.42 (d, $^{3}J_{HH}=6.8$ Hz, 3 H; BNCHCH_3), 1.50 (d, $^{3}J_{HH}=6.4$ Hz, 3 H; BNCHCH_3), 2.21 (m, 2 H; C$H_{2\mathrm{cycle}}$), 2.24 (s, 3 H; C$H_{3\mathrm{ortho}}$B), 2.25 (s, 3 H; C$H_{3\mathrm{ortho}}$B), 2.31 (s, 3 H; C$H_{3\mathrm{para}}$B), 2.38 (s, 3 H; C$H_{3\mathrm{ortho}}$P), 2.39 (s, 3 H; C$H_{3\mathrm{para}}$P), 2.58 (s, 3 H; C$H_{3\mathrm{ortho}}$P), 3.71 (m, 1 H; BNCHCH$_3$), 3.99 (sept d, $^{3}J_{HH}=6.8$, $^{3}J_{HP}=13.6$ Hz, 2 H; PNCHCH$_3$), 4.38 (sept, $^{3}J_{HH}=6.8$ Hz, 1 H; BNCHCH$_3$), 6.81 (s, 1 H; CH_{Ar}B), 6.84 (s, 1 H; CH_{Ar}B), 7.15 ppm (d, $^{4}J_{PH}=6.4$ Hz, 2 H; CH_{Ar}P); ^{13}C NMR (100.1 MHz, CDCl$_3$): $\delta=6.9$ (d, $^{1}J_{CP}=63.2$ Hz; PCB), 21.0 (s; $CH_{3\mathrm{ortho}}$B), 21.6 (s; $CH_{3\mathrm{para}}$P), 21.7 (s; $CH_{3\mathrm{ortho}}$P), 21.8 (s; BNCHCH$_3$), 22.1 (d, $^{2}J_{CP}=13.1$ Hz; $CH_{2\mathrm{cycle}}$), 22.6 (s; BNCHCH$_3$), 23.6 (s; PNCHCH$_3$), 23.8 (s; $CH_{3\mathrm{ortho}}$B), 23.9 (s; $CH_{3\mathrm{para}}$B), 24.0 (s; $CH_{3\mathrm{ortho}}$P), 24.1 (s; BNCHCH$_3$), 24.2 (s; PNCHCH$_3$), 24.3 (s; BNCHCH$_3$), 49.8 (s; BNCHCH$_3$), 51.8 (d, $^{2}J_{CP}=2.8$ Hz; PNCHCH$_3$), 53.7 (s; BNCHCH$_3$), 106.9 (d, $^{1}J_{CP}=102.3$ Hz; C_{ipso}P), 112.5 (s; CN), 128.0 (s; CH_{Ar}B), 128.5 (s; CH_{Ar}B), 130.6 (d, $^{3}J_{CP}=14.0$ Hz; CH_{Ar}P), 138.4 (s; C_{para}B), 138.7 (s; C_{ortho}B), 139.0 (s; C_{ortho}B), 143.9 (d, $^{2}J_{CP}=13.7$ Hz; C_{ortho}P), 144.8 (d, $^{2}J_{CP}=9.9$ Hz; C_{ortho}P), 148.9 ppm (d, $^{4}J_{CP}=2.8$ Hz; C_{para}P); the bridgehead carbon atom alpha to the nitrile was not observed; ^{31}P{^{1}H} NMR (161.9 MHz, CDCl$_3$): $\delta=7.6$ ppm (s); ^{11}B{^{1}H} NMR (128.4 MHz, CDCl$_3$): $\delta=41.2$ ppm (s).

*Alternative procedure for synthesis of **6***: Methylene phosphonium **7** (645 mg, 0.92 mmol) was dissolved in THF (6 mL). The solution was cooled to −80 °C and a solution of potassium hexamethyldisilazide (KHMDS, 275 mg, 1.38 mmol) in THF (2 mL) was added dropwise (185 mg, 0.92 mmol). After 30 min at −80 °C, excess 2-chloroacrylonitrile was added and then the solution was warmed to room temperature and stirred overnight. A brown precipitate appeared. The solvent was evaporated under vacuum and the crude product was washed with pentane (4×5 mL). Compound **6** was isolated as a light-brown powder (417 mg, 60 % yield) in a 55:45 diastereoisomeric ratio (^{31}P NMR). White crystals of the major isomer were obtained, at −30 °C, from a saturated solution in toluene. Major diastereomer: 55 % yield; ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): $\delta=15.7$ ppm (s). Minor diastereomer: 45 % yield; ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): $\delta=7.6$ ppm (s).

Fluorophosphine 8 and borylcyclopropene 9: A solution of KF (5 mg, 0.09 mmol) in [D$_8$]THF (0.5 mL) was added to a solution of **6** (30 mg, 0.04 mmol, 67:33 mixture) in [D$_8$]THF (0.6 mL). The solution was stirred for 48 h at room temperature to quantitatively afford fluorophosphine **8** and borylcyclopropene **9**.

*Fluorophosphine **8***: HRMS (ESI$^+$): *m/z* calcd for $C_{15}H_{25}NFP$:270.1787 $[M+H]^+$; found: 270.1756; ^{1}H NMR (500.3 MHz, [D$_8$]THF): $\delta=1.01$ (d, $^{3}J_{HH}=10.0$ Hz, 12 H; NCHCH_3), 2.27 (s, 3 H; C$H_{3\mathrm{para}}$), 2.44 (d, $^{4}J_{HP}=2.5$ Hz, 6 H; C$H_{3\mathrm{ortho}}$), 2.91 (sept, $^{3}J_{HH}=5.0$ Hz, 2 H; NCHCH$_3$), 6.86 ppm (d, $^{4}J_{HH}=1{,}6$ Hz, 2 H; CH_{Ar}); ^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]THF): $\delta=20.0$ (s; $CH_{3\mathrm{para}}$), 21.1 (s; $CH_{3\mathrm{ortho}}$), 22.7 (s; NCHCH$_3$), 45.0 (s; NCHCH$_3$), 129.9 (m; CH_{Ar}), 138.8 (s; C_{para}), 140.7 ppm (d, $^{2}J_{CP}=21.3$ Hz; C_{ortho}); the *ipso* carbon could not be observed; ^{31}P{^{1}H} NMR (202.5 MHz, [D$_8$]THF): $\delta=151.2$ ppm (d, $^{1}J_{PF}=984.2$ Hz); ^{19}F NMR (282.4 MHz, [D$_8$]THF): $\delta=-113.8$ ppm (d, $^{1}J_{PF}=984.2$ Hz).

*Borylcyclopropene **9***: HRMS (ESI$^+$): *m/z* calcd for $C_{19}H_{27}BN_2$: 295.2346 $[M+H]^+$; found: 295.2345; IR (THF): $\tilde{\upsilon}=2236$ cm^{-1} (CN); ^{1}H NMR (500.3 MHz, [D$_8$]THF): $\delta=1.16$ (d, $^{3}J_{HH}=10.0$ Hz, 6 H; NCHCH_3), 1.34 (d, $^{3}J_{HH}=10.0$ Hz, 6 H; NCHCH_3), 1.50 (s, 2 H; C$H_{2\mathrm{cycle}}$), 2.24 (s, 3 H; C$H_{3\mathrm{para}}$), 2.29 (s, 6 H; C$H_{3\mathrm{ortho}}$), 3.60 (m, 1 H; NCHCH$_3$), 3.74 (sept, $^{3}J_{HH}=10.0$ Hz, 1 H; NCHCH$_3$), 6.78 ppm (s, 2 H; CH_{Ar}); ^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]THF): $\delta=12.7$ (s; $CH_{2\mathrm{cycle}}$), 20.2 (s; $CH_{3\mathrm{para}}$), 20.7 (s; NCHCH$_3$), 21.1 (s; $CH_{3\mathrm{orho}}$), 24.5 (m; NCHCH$_3$), 45.3 (s; NCHCH$_3$), 51.8 (s; NCHCH$_3$), 96.2 (s; CCN), 112.1 (s; CN), 127.1 (s; $CH_{\mathrm{Ar.}}$), 136.8 (s; C_{para}), 137.9 ppm (s; C_{ortho}); the carbon *ipso* to boron and the bridgehead carbon atom alpha to boron were not observed; ^{11}B{^{1}H} NMR (160.5 MHz, [D$_8$]THF): $\delta=38.5$ ppm (s).

X-ray structural analysis: The data for the structures for **5** and **6** were collected on a Bruker-AXS Quazar APEX II diffractometer by using a 30 W air-cooled microfocus source (ImS) with focusing multilayer optics (**5**) and on a Brucker-AXS SMART APEX II diffractometer (**6**) at a temperature of 193(2) K, with Mo$_{K\alpha}$ radiation (wavelength = 0.71073 Å) by using phi and omega scans. The details of data collection and crystal structure refinements are summarised in

Table 1. Crystal data and structure refinement for compounds **5** and **6**.

	5	6
empirical formula	$C_{34}H_{52}BClN_3P$	$C_{48}H_{68}BCl_4GaN_3P$
formula weight	580.02	940.35
temperature [K]	193(2)	193(2)
wavelength [Å]	0.71073	0.71073
crystal system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a [Å]	11.0429(5)	11.3645(2)
b [Å]	34.2430(13)	12.5065(2)
c [Å]	9.6712(4)	20.1667(4)
α [°]	90	75.4480(10)
β [°]	110.854(2)	88.6350(10)
γ [°]	90	67.2530(10)
volume [Å^3]	3417.5(2)	2549.91(8)
Z	4	2
ρ_{calcd} [g cm^{-3}]	1.127	1.225
μ (Mo$_{K\alpha}$) [mm^{-1}]	0.185	0.814
F(000)	1256	992
crystal size [mm^3]	0.10×0.10×0.08	0.40×0.20×0.08
reflections collected	38 108	33 382
independent reflections	6881	10 215
R_{int}	0.0373	0.0458
max. and min. transmission	0.9854 and 0.9818	0.9377 and 0.7365
data/restraints/parameters	6881/43/403	10 215/397/648
goodness-of-fit on F^2	1.057	1.050
$R1$ [$I>2\sigma(I)$]	0.0414	0.0568
$wR2$ [$I>2\sigma(I)$]	0.1021	0.1434
$R1$ (all data)	0.0569	0.0956
$wR2$ (all data)	0.1099	0.1631
larg. diff. peak and hole [e Å^{-3}]	0.231 and −0.228	0.498 and −0.391

Table 1. The data were integrated with SAINT and an empirical absorption correction with SADABS was applied.[24] The structures were solved by direct methods using SHELXS-97[25] and refined by using the least-squares method on F^2.[25] All non-hydrogen atoms were treated anisotropically. All hydrogen atoms attached to carbon atoms were fixed geometrically and treated as riding on their parent atoms with C–H = 0.95 (aromatic), 0.98 (CH_3), 0.99 (CH_2) or 1.0 Å (CH) with $U_{iso}(H) = 1.2U_{eq}(CH, CH_2)$ or $U_{iso}(H) = 1.5U_{eq}(CH_3)$. CCDC-951086 (**5**) and CCDC-951087 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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