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Chemical Behaviour of Prototypical Boryl(phosphino)carbene

Florie Lavigne,^[a] Eddy Maerten,^{*[a]} Gilles Alcaraz,^[b] Nathalie Saffon-Merceron,^[c]
and Antoine Baceiredo^{*[a]}

Dedication ((optional))

Abstract: We recently disclosed the synthesis of a novel "push-pull" boryl(phosphino)carbene. In order to delineate the influence of this substitution pattern on the chemical behaviour, the reactivity of the prototypical example (**1**) of this new family of B(sp²)-substituted phosphinocarbenes was undertaken. Carbene **1** exhibits one of the most common intramolecular rearrangement

of singlet carbenes involving a 1,2-mesityl shift, and a typical [2+1] cycloaddition reactions with electron poor acrylonitrile. A pronounced α,β -ambiphilic character was also evidenced by the reaction of **1** with benzaldehyde leading to phosphorylalkene **4**. Due to its specific electronic properties, **1** also exhibits an unprecedented reactivity with chloroacrylonitrile enabling the

formation of bicyclo[1.1.0]phosphetanium salts **6** and borylcyclopropene **9** which have been fully characterized by NMR spectroscopy and X-ray crystallography.

Keywords: Carbenes • [2+1] Cycloaddition • Wittig reaction • Phosphiranium • Borylcyclopropene

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 stabilized carbenes as synthetic reagents, ligands, or organo-catalysts has become a very active area of investigation.^[3] In this respect, the development of various stabilization modes by modifying the substitution pattern at the carbon atom has been subject to detailed study. To date, stable

singlet carbenes are predominantly π -stabilized by the presence of at least one amino or phosphino group at the carbenic centre.^[4] The reduced energetic cost for the nitrogen atom to adopt a planar geometry with respect to phosphorus, favour the π -interaction of the lone pair of the α -substituent with the p_π orbital at the carbenic carbon, 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 stabilization mode leading to "push-push", "push-spectator" or "push-pull" carbenes. While aminocarbenes are predominantly "push-push"^[2] or "push-spectator"^[6] stabilized, 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 the prototypical example (**1**) of the novel "push-pull" boryl(phosphino)carbene family by deprotonation of the parent borylated methylenephosphonium salt (Figure 1).^[9] With the presence of a B(sp²) containing boryl group adjacent to the carbenic centre in **1**, one could expect to induce a stabilizing "push-pull" effect of greater magnitude (Figure 1).

[a] Dr F. Lavigne, Dr E. Maerten, Dr A. Baceiredo
Université de Toulouse, UPS, and CNRS, LHFA UMR 5069, F-31062
Toulouse Cedex 9 (France)
Fax: (+)33-561558204
E-mail: baceired@chimie.ups-tlse.fr

[b] Dr G. Alcaraz,
LCC, UPR CNRS 8241, F-31077 Toulouse (France)

[c] Dr N. Saffon-Merceron,
Université de Toulouse, UPS, and CNRS, ICT FR 2599, F-31062 Toulouse
(France)

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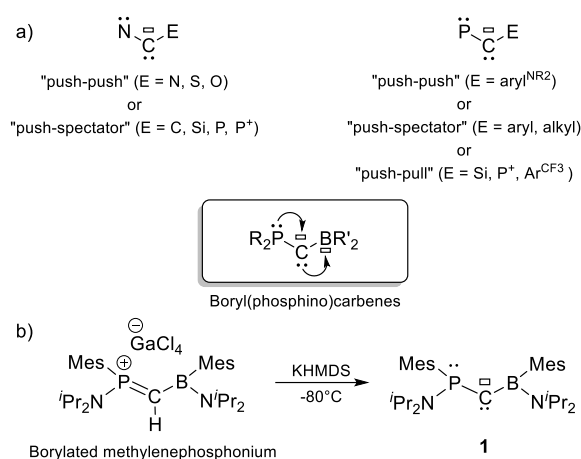
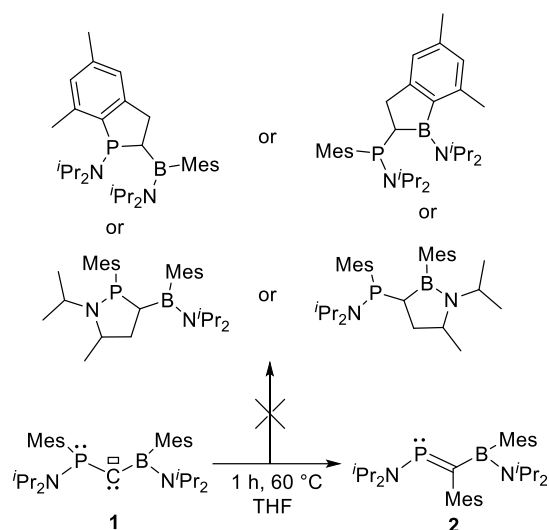


Figure 1: a) "Push-push", "push-spectator" and "push-pull" stabilized carbenes. b) Synthesis of boryl(phosphino)carbene **1**.

The reactivity of stabilized carbenes depends on the singlet-triplet energy gap. With this in mind and because substituent effects govern the energetic positions of the frontier orbitals n_σ and p_π , a deeper investigation of the reactivity of the boryl(phosphino)carbene **1** was undertaken. The aim is to better delineate its synthetic potential, in the continuation of our preliminary results concerning its comportment towards small molecules such as CO_2 and SO_2 .^[10]

Results and Discussion

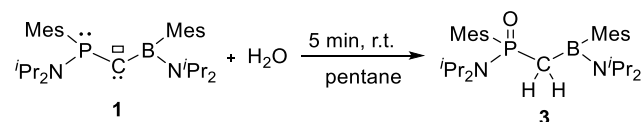
Reactivity of phosphinocarbenes mirrors the degree of the carbene perturbation that is directly linked to the substitution pattern at the carbenic centre; minor modifications of the electronic balance altering their stability. "Push-pull" phosphino(silyl)carbenes exhibit a good thermal stability and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



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

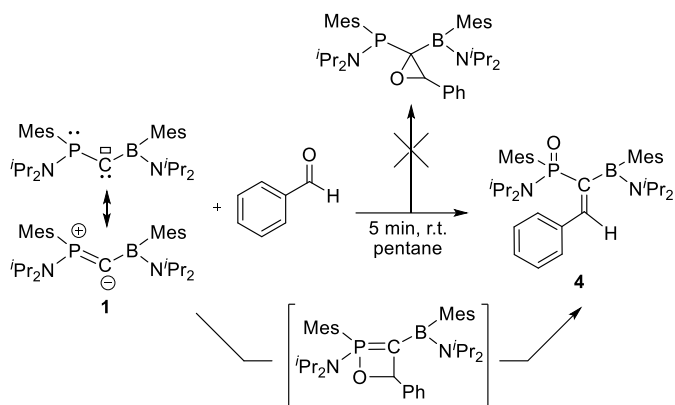
The absence of any reactivity with Lewis basic reagents, like *tert*-butylisocyanide^[13] or PMe_3 ,^[8,14] indicates a poor electrophilic behaviour of boryl(phosphino)carbene **1**.

The more classical α,β -ambiphilic character resulting from the $\text{P}\pi\text{-C}\pi$ interaction in phosphinocarbenes is however retained in **1**. Indeed, **1** quickly reacts with a stoichiometric amount of water, affording quantitatively compound **3** (Scheme 2). In the ³¹P{¹H} NMR, 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 doublet of doublets at $\delta = 2.31$ (²J_{HH} = 13.8 Hz, ²J_{HP} = 16.2 Hz) and $\delta = 2.69$ ppm (²J_{HH} = 13.8 Hz, ²J_{HP} = 22.2 Hz) in a 1:1 integration ratio.



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

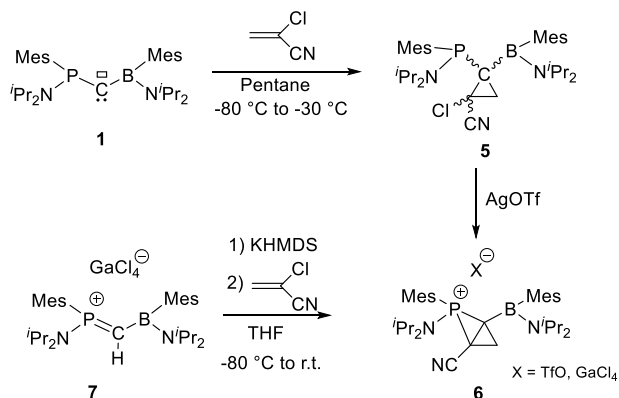
The reactions between the phosphino(silyl)carbene and aldehydes have been investigated, and two competitive processes were observed. With aromatic aldehydes, the reaction proceeds via a concerted [2+1] cycloaddition to carbonyl leading to oxiranes,^[13] while with alkyl aldehydes a competitive pathway was observed via 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 *Z*-isomer of boryl(phosphoxide)alkene **4** (Scheme 3).



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

As previously observed with carbon and sulfur dioxide,^[10] the olefinic derivative **4** could be rationalized by the formation of an intermediate oxaphosphetene via a Wittig type reaction, illustrating the pronounced α,β -ambiphilic character of **1**. Compound **4** was isolated and fully characterized by multinuclear NMR spectroscopy. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, a singlet is observed at $\delta = 44.6$ ppm for the phosphine oxide moiety. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibits, in addition to the signals of the phenyl carbon atoms, a set of two doublets at $\delta = 137.2$ ppm ($^1J_{\text{CP}} = 25.6$ Hz) and $\delta = 143.9$ ppm ($^2J_{\text{CP}} = 2.4$ Hz) corresponding to the ethylenic carbon atoms. In the ^1H NMR spectrum, the presence of a doublet at $\delta = 7.40$ ppm with a large coupling constant value ($^3J_{\text{PH}} = 44.5$ Hz) is in good agreement with a vinylic proton in *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 prototypical 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 phosphalkene **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 obtained in 55 % isolated yield. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a set of singlets at $\delta = 49.0$ and 47.3 ppm, in a 77 : 23 respective integration ratio, indicative of the presence two diastereomers. The observed diastereoselectivity of the cyclopropanation process contrasts to 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 obtain in the reaction of (2,6-bis(trifluoromethyl)phenyl)(phosphino)carbene with chloroacrylonitrile.^[11] The major isomer of **5** ($\delta_{\text{P}} = 49.0$ ppm) was analyzed by multinuclear NMR. In the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum, a singlet is observed at $\delta = 43$ ppm. The ^1H NMR displays a multiplet at $\delta = 1.79$ ppm and a doublet of doublets at $\delta = 2.38$ ppm ($^2J_{\text{HH}} = 3.3$ Hz, $^3J_{\text{HP}} = 6.0$ Hz) in a 1:1 ratio for the diastereotopic protons of the methylene group. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibits a set of doublets at $\delta = 39.2$ ($^1J_{\text{CP}} = 7.5$ Hz) and $\delta = 29.7$ ppm ($^2J_{\text{CP}} = 5.5$ 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 the two diastereoisomers in the asymmetric unit, in a 55 : 45 ratio (Figure 2). The P1-C1 bond distance (1.892(2) Å) is in agreement with that reported for P-C single bonds in phosphino cyclopropanes.^[11, 18a] The B1-C1 bond is slightly longer than that reported for a cyclopropyl-B(sp²) linkages (1.52 Å-1.56 Å),^[19] probably for steric reasons.

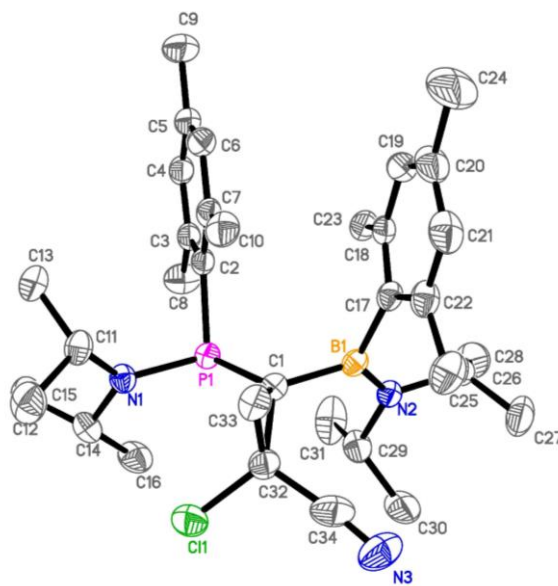


Figure 2. Molecular structure of **5** (*syn*-**5** featuring the chlorine *cis* to the phosphorus as represented here). Thermal ellipsoids set at 50% probability. H atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: C33-C32: 1.491(2); C1-C33: 1.522(2); C1-C32: 1.536(2); P1-N1: 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 a nucleophilic (P) and an electrophilic (C-Cl) centres, allows the easy formation of an original bicyclic structure. Indeed, the addition of one equivalent of silver triflate to a CH_2Cl_2 solution of **5**, at -80 °C, leads to the formation of bicyclo[1.1.0]phosphetanium salt **6**, as a mixture of two isomers (67 : 33) characterized by two singlets at $\delta = 15.7$ and 7.6 ppm in the $^{31}\text{P}\{^1\text{H}\}$ 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 catalyze the nucleophilic attack of the phosphine centre of the in situ generated phosphino cyclopropane **5**.

Diastereoselective crystallization of the mixture of the two isomers of **6** from a saturated toluene solution at $-30\text{ }^{\circ}\text{C}$, allowed the full characterization of the major diastereomer ($\delta_{\text{P}} = 15.7\text{ ppm}$) and to deduce the spectroscopic data of the minor one ($\delta_{\text{P}} = 7.6\text{ ppm}$). The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the major diastereomer displays a signal at $\delta = 40\text{ ppm}$. In the ^1H NMR spectrum, two sets of signals are observed for the diastereotopic hydrogen atoms of the methylene bridge: doublet of doublets at $\delta = 3.11$ ($^2J_{\text{HH}} = 5.2\text{ Hz}$, $^3J_{\text{HP}} = 27.6\text{ Hz}$) and 2.99 ppm ($^2J_{\text{HH}} = 5.2\text{ Hz}$, $^3J_{\text{HP}} = 53.7\text{ Hz}$). The solid state structure of the major diastereomer of **6** was determined by a single crystal X-ray diffraction analysis at $-80\text{ }^{\circ}\text{C}$, clearly showing the tetravalent environment of phosphorus centre, and the bicyclic structure (Figure 3).

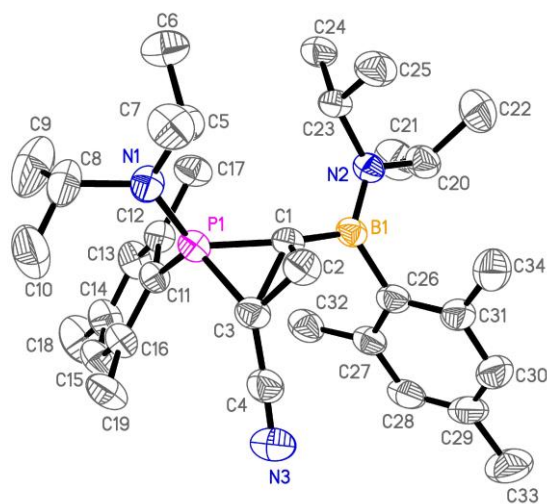
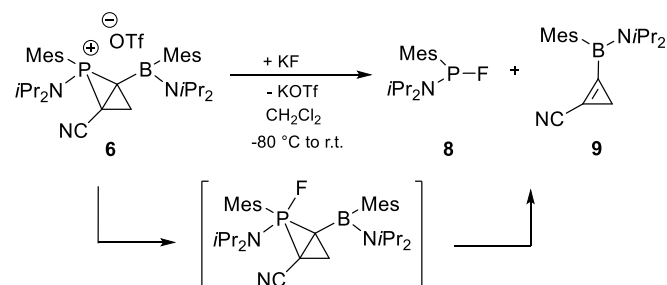


Figure 3. Molecular structure of **6**. Thermal ellipsoids set at 50% probability. H atoms and GaCl_4^- and solvent were omitted for clarity; selected bond lengths [\AA] and angles [$^{\circ}$]: P1-N1: 1.625(3); P1-C1: 1.770(3); P1-C3: 1.784(3); P1-C11: 1.786(3); N2-B1: 1.391(4); N3-C4: 1.147(5); C3-C4: 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).

The intracyclic P-C bond distances (1.770(3) \AA and 1.784(3) \AA) are shorter than those of classical P-C single bonds (1.80 - 1.90 \AA) and lie between the distances of phosphetanium salts (P-C \sim 1.800 \AA)^[20] and those of phosphiranium cations (P-C \sim 1.760 \AA).^[21] A similar trend is observed for the variation of the C1-P1-C3 angle (54.02(14) $^{\circ}$) for the phosphetanium (75–82 $^{\circ}$) and phosphiranium salts (47–52 $^{\circ}$).^[20,21]

By analogy with the reactivity of phosphiranium salts, the ability of **6** to undergo the cheletropic extrusion of a phosphonium fragment was evaluated.^[22] In the presence of diphenylacetylene or dimethyl acetylenedicarboxylate, no reaction was observed, even at

elevated temperature. In contrast, the addition of one equivalent of potassium fluoride to **6** lead quantitatively to borylcyclopropene **9** and fluorophosphine **8** that were fully characterized spectroscopically. In this case, instead of generating a transient phosphonium salt, the reaction probably involves the transient formation of a bicyclic phosphorane (Scheme 5).^[23]



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

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 stabilized carbenes. We have shown that carbene **1** is relatively stable, but not to the same degree compared to phosphino(silyl)carbenes. Indeed, it slowly rearranges at room temperature into phosphalkene **2** via a 1,2-mesityl migration to the carbenic centre. This boryl(phosphino)carbene **1** presents an important α,β -ambiphilic character since it reacts with benzaldehyde 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 an interesting intramolecular reactivity, and it can be converted into the bicyclo[1.1.0]phosphetanium salt **6** featuring an original structure with two fused three membered rings. The extrusion of a phosphonium fragment, formally, from the bicyclic structure **6** allows an easy synthesis of borylcyclopropene **9** in mild conditions.

In conclusion, due to unique electronic properties, the "push-pull" boryl(phosphino)carbene **1** exhibits both classical and unprecedented reactivities. Our efforts for developing new "push-pull" models is underway and will allow 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. ^1H , ^{11}B , ^{13}C and ^{31}P NMR spectra were recorded on Bruker Avance 400 or Avance 300 spectrometers. ^1H NMR and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to Me_4Si as external standard. ^{31}P NMR and ^{11}B NMR downfield chemical are expressed in ppm relative to 85 % H_3PO_4 and $\text{BF}_3\cdot\text{Et}_2\text{O}$, respectively. IR spectra were recorded on a Varian 640-IR. Mass spectra were recorded on Hewlett Packard 5989A. Carbene **1** and methylenephosphonium **7** were prepared according to a literature procedure.^[9]

Phosphaalkene 2: Phosphaalkene **2** was obtained quantitatively by refluxing a THF- d_6 solution (1 mL) of carbene **1** (72 mg, 0.15 mmol) for 1 h or by stirring the solution at

room temperature for 24 h. The product was spectroscopically characterized without any further purification. **¹H-NMR (400 MHz, THF-d₈)**: δ 0.80 (d, ³J_{HH} = 6.3 Hz, 12H, PNCHCH₃), 0.85 (d, ³J_{HH} = 6.9 Hz, 6H, BNCHCH₃), 1.09 (d, ³J_{HH} = 6.9 Hz, 6H, BNCHCH₃), 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, ³J_{HH} = 6.9 Hz, ³J_{HP} = 13.5 Hz, 2H, PNCHCH₃), 3.32 (sept, ³J_{HH} = 7.2 Hz, 2H, BNCHCH₃), 6.32 (s, 2H, CH_{Ar} Mes), 6.46 (s, 2H, CH_{Ar} B). **¹³C{¹H}-NMR (100 MHz, THF-d₈)**: δ 19.9 (s, CH_{3ortho} Mes), 20.2 (s, CH_{3para} Mes), 21.3 (s, CH_{3ortho} B), 22.0 (s, CH_{3para} B), 22.9 (s, BNCHCH₃), 23.0 (s, PNCHCH₃), 23.5 (s, BNCHCH₃), 47.1 (s, BNCHCH₃), 48.1 (d, ³J_{CP} = 3.1 Hz, PNCHCH₃), 126.3 (s, CH_{Ar} Mes), 127.4 (s, CH_{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 (d, ¹J_{CP} = 61.2 Hz, PCB). **³¹P{¹H}-NMR (162 MHz, THF-d₈)**: δ 231.7. **¹¹B{¹H}-NMR (128 MHz, THF-d₈)**: δ 42.6. **HRMS (ESI⁺)** (C₃₁H₅₀BN₂P) [M+H]⁺calcd : 493.3883, found 493.3872.

Phosphine oxide 3: At room temperature, water (2.5 μL, 0.14 mmol) was added to a pentane solution (2 mL) of boryl(phosphino)carbene **1** (70 mg, 0.14 mmol). 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. **HRMS (ESI⁺)** (C₃₁H₅₂BN₂OP) [M+H]⁺ calcd 511.3989, found 511.3991. **³¹P{¹H}-NMR (121.5 MHz, C₆D₆)**: δ 37.8 (s). **¹¹B{¹H}-NMR (96.3 MHz, C₆D₆)**: δ 43.4 (s). **¹H-NMR (300.1 MHz, C₆D₆)**: δ 0.79 (d, ³J_{HH} = 6.9 Hz, 3H, BNCHCH₃), 0.84 (d, ³J_{HH} = 6.6 Hz, 3H, BNCHCH₃), 1.04 (d, ³J_{HH} = 6.6 Hz, 6H, PNCHCH₃), 1.30 (d, ³J_{HH} = 6.9 Hz, 6H, PNCHCH₃), 1.36 (d, ³J_{HH} = 7.2 Hz, 3H, BNCHCH₃), 1.52 (d, ³J_{HH} = 6.9 Hz, 3H, BNCHCH₃), 2.03 (s, 3H, CH_{3ortho} P), 2.15 (s, 3H, CH_{3ortho} B), 2.18 (s, 3H, CH_{3ortho} B), 2.24 (s, 3H, CH_{3para} B), 2.31 (dd, ²J_{HH} = 14.1 Hz, ²J_{HP} = 16.2 Hz, 1H, PCH₂B), 2.37 (s, 3H, CH_{3para} P), 2.68 (dd, ²J_{HH} = 14.1 Hz, ²J_{HP} = 22.8 Hz, 1H, PCH₂B), 2.88 (s, 3H, CH_{3ortho} P), 3.25 (sept, ³J_{HH} = 7.5 Hz, 1H, BNCHCH₃), 3.42 (sept, ³J_{HH} = 6.9 Hz, 2H, PNCHCH₃), 3.60 (sept, ³J_{HH} = 6.9 Hz, 1H, BNCHCH₃), 6.44 (s, 1H, CH_{Ar} P), 6.50 (s, 1H, CH_{Ar} B), 6.59 (s, 1H, CH_{Ar} B), 6.64 (s, 1H, CH_{Ar} P). **¹³C{¹H}-NMR (75.1 MHz, C₆D₆)**: δ 20.9 (s, CH_{3ortho} P), 21.2 (s, CH_{3ortho} B), 22.0 (s, BNCHCH₃), 22.1 (s, BNCHCH₃), 22.6 (s, CH_{3ortho} B), 22.9 (s, CH_{3para} P), 23.2 (s, CH_{3para} B), 23.2 (d, ³J_{CP} = 2.2 Hz, PNCHCH₃), 23.6 (d, ³J_{CP} = 2.8 Hz, PNCHCH₃), 24.4 (s, CH_{3ortho} P), 24.9 (s, BNCHCH₃), 25.0 (s, BNCHCH₃), 28.6 (d, ¹J_{CP} = 82.5 Hz, PCH₂B), 47.4 (d, ²J_{CP} = 3.1 Hz, PNCHCH₃), 48.5 (s, BNCHCH₃), 50.4 (s, BNCHCH₃), 127.3 (s, CH_{Ar} B), 127.4 (s, CH_{Ar} B), 128.9 (d, ¹J_{CP} = 111.3 Hz, C_{ipso} P), 130.4 (d, ³J_{CP} = 11.7 Hz, CH_{Ar} P), 131.4 (d, ³J_{CP} = 12.9 Hz, CH_{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 (d, ²J_{CP} = 10.1 Hz, C_{ortho} P). The carbon *ipso* to boron was not observed.

Phosphorylalkene 4: At room temperature, benzaldehyde (58.2 μL, 0.57 mmol) was added to a pentane solution (3 mL) of boryl(phosphino)carbene **1** (200 mg, 0.41 mmol). Within 5 min, the solution turns 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. **HRMS (ESI⁺)** (C₃₈H₅₆BN₂OP) [M+Na]⁺ calcd: 621.4121, found 621.4132. **³¹P{¹H}-NMR (121.5 MHz, CDCl₃)**: δ 44.6 (s). **¹¹B{¹H}-NMR (96.3 MHz, CDCl₃)**: δ 45.1 (s). **¹H-NMR (300.1 MHz, CDCl₃)**: δ 0.95 (d, ³J_{HH} = 6.0 Hz, 3H, BNCHCH₃), 1.27 (d, ³J_{HH} = 6.9 Hz, 3H, PNCHCH₃), 1.33 (d, ³J_{HH} = 6.9 Hz, 3H, PNCHCH₃), 1.35 (d, ³J_{HH} = 7.5 Hz, 3H, PNCHCH₃), 1.36 (d, ³J_{HH} = 7.0 Hz, 3H, BNCHCH₃), 1.39 (d, ³J_{HH} = 6.5 Hz, 3H, BNCHCH₃), 1.59 (d, ³J_{HH} = 6.0 Hz, 3H, BNCHCH₃), 1.67 (d, ³J_{HH} = 7.2 Hz, 3H, PNCHCH₃), 1.89 (s, 3H, CH_{3ortho} P), 2.00 (s, 3H, CH_{3para} B), 2.06 (s, 3H, CH_{3ortho} B), 2.13 (s, 3H, CH_{3para} P), 2.22 (s, 3H, CH_{3ortho} B), 2.80 (s, 3H, CH_{3ortho} P), 3.39 (m, 1H, BNCHCH₃), 3.65 (m, 1H, BNCHCH₃), 4.00 (sept, ³J_{HH} = 7.5 Hz, 1H, PNCHCH₃), 4.33 (sept, ³J_{HH} = 7.0 Hz, 1H, PNCHCH₃), 6.06 (s, 1H, CH_{Ar} B), 6.07 (s, 1H, CH_{Ar} P), 6.44 (s, 1H, CH_{Ar} P), 6.69 (s, 1H, CH_{Ar} B), 7.39 (m, 3H, CH_{Ar} Ph), 7.40 (d, ³J_{PH} = 44.5 Hz, 1H, PC=CHPh), 7.89 (m, 2H, CH_{Ar} Ph). **¹³C{¹H}-NMR (75.1 MHz, CDCl₃)**: δ 20.8 (d, ⁵J_{CP} = 4.5 Hz, CH_{3para} P), 20.9 (s, CH_{3ortho} B), 22.1 (s, BNCHCH₃), 22.5 (s, PNCHCH₃), 23.0 (s, CH_{3ortho} B), 23.1 (s, PNCHCH₃), 23.3 (s, BNCHCH₃), 23.9 (d, ³J_{CP} = 4.1 Hz, CH_{3ortho} P), 24.0 (s, BNCHCH₃), 24.1 (d, ³J_{CP} = 3.7 Hz, CH_{3ortho} P), 25.0 (s, CH_{3para} B), 25.7 (s, PNCHCH₃), 26.8 (s, BNCHCH₃), 26.9 (s, PNCHCH₃), 46.6 (s, BNCHCH₃), 48.4 (s, BNCHCH₃), 51.3 (s, PNCHCH₃), 51.4 (s, PNCHCH₃), 126.5 (s, CH_{Ar} P), 127.1 (s, CH_{Ar} P), 127.9 (s, CH_{Ar} Ph), 128.0 (d, ¹J_{CP} = 111.4 Hz, C_{ipso} P), 128.9 (s, CH_{Ar} B), 129.7 (s, CH_{Ar} B), 130.7 (d, ⁴J_{CP} = 1.4 Hz, CH_{Ar} Ph), 135.3 (s, C_{ortho} B), 137.2 (d, ¹J_{CP} = 25.6 Hz, PCB), 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 (d, ²J_{CP} = 2.4 Hz, PC=CH). The carbon *ipso* to boron was not observed.

Cyclopropane syn and anti 5: 2-chloroacrylonitrile (3 eq., 48.7 μL, 0.60 mmol) was slowly added to a pentane solution of carbene **1** (100 mg, 0.20 mmol) at -80 °C. The solution was warmed up to -30 °C, stirred at this temperature for 24h, filtered and the solvent was removed under vacuum. Extraction with pentane (2 x 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 77/23 ratio, as indicated by ³¹P NMR (64 mg, 55 % yield). White crystals of **5** in a 55/45 ratio (estimated by ³¹P NMR analysis) could be obtained from a saturated pentane solution at -40 °C. **IR (THF)**: ν = 2305 cm⁻¹. **Major diastereomer**: **³¹P{¹H}-NMR (121.5 MHz, C₆D₆)**: δ 49.0 (s). **¹¹B{¹H}-NMR (96.3 MHz, C₆D₆)**: δ 42.6 (s). **¹H-NMR (300.1 MHz, C₆D₆)**: δ 0.31 (m, 3H, BNCHCH₃), 1.00 (d, ³J_{HH} = 6.9 Hz, 3H, BNCHCH₃), 1.01 (d, ³J_{HH} = 6.9 Hz, 3H, BNCHCH₃), 1.09 (d, ³J_{HH} = 7.2 Hz, 3H, PNCHCH₃), 1.18 (d, ³J_{HH} = 7.2 Hz, 3H,

PNCHCH₃), 1.26 (s, 3H, CH_{3ortho} B), 1.46 (m, 3H, BNCHCH₃), 1.69 (d, ³J_{HH} = 6.6 Hz, 3H, PNCHCH₃), 1.74 (s, 3H, CH_{3ortho} P), 1.78 (d, ³J_{HH} = 7.2 Hz, 3H, PNCHCH₃), 1.79 (m, 1H, CH_{2cycle}), 2.08 (s, 3H, CH_{3para} P), 2.13 (s, 3H, CH_{3para} B), 2.38 (dd, ²J_{HH} = 3.3 Hz, ³J_{HP} = 6.0 Hz, 1H, CH_{2cycle}), 2.45 (s, 3H, CH_{3ortho} B), 2.81 (d, ⁴J_{HP} = 3.6 Hz, 3H, CH_{3ortho} P), 3.13 (m, 1H, BNCHCH₃), 3.61 (m, 1H, BNCHCH₃), 3.82 (sept, ³J_{HH} = 7.2 Hz, 1H, PNCHCH₃), 5.19 (sept d, ³J_{HH} = 6.6 Hz, ³J_{HP} = 2.7 Hz, 1H, PNCHCH₃), 6.44 (s, 1H, CH_{Ar} B), 6.54 (m, 1H, CH_{Ar} P), 6.69 (s, 1H, CH_{Ar} B), 6.76 (d, ⁴J_{HP} = 6.3 Hz, 1H, CH_{Ar} P). **¹³C{¹H}-NMR (75.1 MHz, C₆D₆)**: δ 20.4 (s, BNCHCH₃), 20.8 (s, CH_{3para} P), 21.0 (s, CH_{3para} B), 22.2 (s, CH_{3ortho} B), 23.3 (m, CH_{3ortho} P), 23.4 (s, PNCHCH₃), 23.5 (s, PNCHCH₃), 24.5 (s, CH_{3ortho} P), 25.0 (s, BNCHCH₃), 25.2 (s, CH_{3ortho} B), 25.5 (s, BNCHCH₃), 25.6 (s, PNCHCH₃), 26.1 (s, BNCHCH₃), 29.1 (d, ³J_{CP} = 8.9 Hz, PNCHCH₃), 29.7 (d, ²J_{CP} = 5.5 Hz, CH_{2cycle}), 39.2 (d, ¹J_{CP} = 7.5 Hz, PCB), 50.1 (s, BNCHCH₃), 51.8 (s, BNCHCH₃), 52.0 (s, PNCHCH₃), 52.3 (s, PNCHCH₃), 119.9 (s, CN), 128.2 (s, CH_{Ar} B), 128.3 (s, CH_{Ar} B), 129.8 (s, CH_{Ar} P), 131.9 (s, CH_{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 (m, C_{ortho} P). The bridgehead carbon atom *alpha* to the nitrile was not observed. **Minor Diastereomer**: **³¹P{¹H}-NMR (121.5 MHz, C₆D₆)**: δ 47.3 (s).

Bicyclo[1.1.0]phosphetanium salt 6: A CH₂Cl₂ solution (1 mL) of silver triflate (57 mg, 0.22 mmol) was added to a CH₂Cl₂ solution (2 mL) of cyclopropane **5** (130 mg, 0.22 mmol) at -80 °C. The solution was slowly warmed up to room temperature (4h) and filtered. After removal of the solvent, crude **6** was washed with pentane (3 x 3mL). **6** was obtained as a white powder containing two diastereoisomers in a 67/33 ratio. (85 mg, 55 % yield). **HRMS (ESI⁺)** (C₃₄H₅₂BClN₃P) [M+H]⁺ calcd : 580.3759, found 580.3763. The counter anion was found to be chlorine by HRMS. **Major diastereomer (67 %)**: **IR (THF)**: ν = 2150 cm⁻¹. **³¹P{¹H}-NMR (121.5 MHz, CDCl₃)**: δ 15.7 (s). **¹¹B{¹H}-NMR (128.4 MHz, CDCl₃)**: δ 40.4 (s). **¹H-NMR (400.1 MHz, CDCl₃)**: δ 1.15 (d, ³J_{HH} = 6.8 Hz, 3H, BNCHCH₃), 1.21 (d, ³J_{HH} = 7.2 Hz, 3H, BNCHCH₃), 1.22 (d, ³J_{HH} = 7.2 Hz, 6H, PNCHCH₃), 1.24 (s, 3H, CH_{3ortho} B), 1.38 (d, ³J_{HH} = 6.8 Hz, 6H, PNCHCH₃), 1.51 (d, ³J_{HH} = 7.2 Hz, 3H, BNCHCH₃), 1.52 (d, ³J_{HH} = 6.8 Hz, 3H, BNCHCH₃), 2.14 (s, 3H, CH_{3para} B), 2.28 (s, 3H, CH_{3ortho} B), 2.44 (s, 3H, CH_{3para} P), 2.76 (s, 3H, CH_{3ortho} P), 2.89 (s, 3H, CH_{3ortho} B), 2.99 (dd, ²J_{HH} = 5.2 Hz, ³J_{HP} = 53.7 Hz, 1H, CH_{2cycle}), 3.11 (dd, ²J_{HH} = 5.2 Hz, ³J_{HP} = 27.6 Hz, 1H, CH_{2cycle}), 3.72 (sept d, ³J_{HH} = 6.4 Hz, ³J_{HP} = 13.2 Hz, 2H, PNCHCH₃), 3.77 (sept, ³J_{HH} = 6.8 Hz, 1H, BNCHCH₃), 4.47 (sept, ³J_{HH} = 7.2 Hz, 1H, BNCHCH₃), 6.54 (s, 1H, CH_{Ar} B), 6.73 (s, 1H, CH_{Ar} B), 7.23 (d, ⁴J_{PH} = 6.4 Hz, 1H, CH_{Ar} P), 7.24 (d, ⁴J_{PH} = 6.0 Hz, 1H, CH_{Ar} P). **¹³C{¹H}-NMR (100.1 MHz, CDCl₃)**: δ 20.9 (s, CH_{3para} B), 21.6 (s, CH_{3para} P), 21.7 (s, BNCHCH₃), 22.6 (s, CH_{3ortho} B), 22.9 (s, CH_{3ortho} P), 23.0 (s, PNCHCH₃), 23.1 (s, PNCHCH₃), 23.2 (s, BNCHCH₃), 23.3 (s, CH_{3ortho} B), 24.0 (s, CH_{3ortho} P), 24.7 (s, BNCHCH₃), 25.6 (s, BNCHCH₃), 27.6 (d, ¹J_{CP} = 48.5 Hz, PCB), 34.8 (d, ²J_{CP} = 2.2 Hz, CH_{2cycle}), 50.5 (s, BNCHCH₃), 52.9 (s, PNCHCH₃), 54.0 (s, BNCHCH₃), 110.8 (s, CN), 116.7 (d, ¹J_{CP} = 125.4 Hz, C_{ipso} P), 127.7 (s, CH_{Ar} B), 127.9 (s, CH_{Ar} B), 130.6 (d, ¹J_{CP} = 14.0 Hz, CH_{Ar} P), 131.7 (d, ³J_{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, ²J_{CP} = 12.3 Hz, C_{ortho} P), 143.6 (d, ²J_{CP} = 12.0 Hz, C_{ortho} P), 148.4 (d, ⁴J_{CP} = 2.6 Hz, C_{para} P). The bridgehead carbon atom *alpha* to the nitrile was not observed. **Minor diastereomer (33 %)**: Product not isolated, NMR were deduced from analysis of the mixture. **³¹P{¹H}-NMR (161.9 MHz, CDCl₃)**: δ 7.6 (s). **¹¹B{¹H}-NMR (128.4 MHz, CDCl₃)**: δ 41.2 (s). **¹H-NMR (400.1 MHz, CDCl₃)**: δ 1.13 (d, ³J_{HH} = 6.8 Hz, 3H, BNCHCH₃), 1.17 (d, ³J_{HH} = 6.8 Hz, 3H, BNCHCH₃), 1.38 (d, ³J_{HH} = 6.8 Hz, 6H, PNCHCH₃), 1.39 (d, ³J_{HH} = 6.8 Hz, 6H, PNCHCH₃), 1.42 (d, ³J_{HH} = 6.8 Hz, 3H, BNCHCH₃), 1.50 (d, ³J_{HH} = 6.4 Hz, 3H, BNCHCH₃), 2.21 (m, 2H, CH_{2cycle}), 2.24 (s, 3H, CH_{3ortho} B), 2.25 (s, 3H, CH_{3ortho} B), 2.31 (s, 3H, CH_{3para} B), 2.38 (s, 3H, CH_{3ortho} P), 2.39 (s, 3H, CH_{3para} P), 2.58 (s, 3H, CH_{3ortho} P), 3.71 (m, 1H, BNCHCH₃), 3.99 (sept d, ³J_{HH} = 6.8 Hz, ³J_{HP} = 13.6 Hz, 2H, PNCHCH₃), 4.38 (sept, ³J_{HH} = 6.8 Hz, 1H, BNCHCH₃), 6.81 (s, 1H, CH_{Ar} B), 6.84 (s, 1H, CH_{Ar} B), 7.15 (d, ⁴J_{PH} = 6.4 Hz, 2H, CH_{Ar} P). **¹³C-NMR (100.1 MHz, CDCl₃)**: δ 6.9 (d, ¹J_{CP} = 63.2 Hz, PCB), 21.0 (s, CH_{3ortho} B), 21.6 (s, CH_{3para} P), 21.7 (s, CH_{3ortho} P), 21.8 (s, BNCHCH₃), 22.1 (d, ²J_{CP} = 13.1 Hz, CH_{2cycle}), 22.6 (s, BNCHCH₃), 23.6 (s, PNCHCH₃), 23.8 (s, CH_{3ortho} B), 23.9 (s, CH_{3para} B), 24.0 (s, CH_{3ortho} P), 24.1 (s, BNCHCH₃), 24.2 (s, PNCHCH₃), 24.3 (s, BNCHCH₃), 49.8 (s, BNCHCH₃), 51.8 (d, ²J_{CP} = 2.8 Hz, PNCHCH₃), 53.7 (s, BNCHCH₃), 106.9 (d, ¹J_{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, ³J_{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, ²J_{CP} = 13.7 Hz, C_{ortho} P), 144.8 (d, ²J_{CP} = 9.9 Hz, C_{ortho} P), 148.9 (d, ²J_{CP} = 2.8 Hz, C_{para} P). The bridgehead carbon atom *alpha* to the nitrile was not observed. Alternative procedure for synthesis of bicyclo[1.1.0]phosphetanium salt **6**: Methylene phosphonium **7** (645 mg, 0.92 mmol) was dissolved in THF (6 mL). The solution was cooled at -80 °C and a THF solution (2 mL) of KHMDS was added dropwise (185 mg, 0.92 mmol). After 30 minutes at -80 °C, excess of 2-chloroacrylonitrile was added, then the solution was warmed up at room temperature and stirred overnight. A brown precipitate appeared. The solvent was evaporated under vacuum and the crude was washed with pentane (4 x 5 mL). **6** was isolated as a light brown powder (417 mg, 60% yield) in a 55/45 diastereoisomeric ratio (³¹P NMR). White crystals of the major isomer were obtained, at -30 °C, as from a saturated toluene solution. **Major diastereomer (55 %)**: **³¹P{¹H}-NMR (121.5 MHz, CDCl₃)**: δ 15.7 (s). **Minor diastereomer (45 %)**: **³¹P{¹H}-NMR (121.5 MHz, CDCl₃)**: δ 7.6 (s).

Fluorophosphine 8 and borylcyclopropane 9: A THF-d₈ solution (0.5 mL) of KF (5 mg, 0.09 mmol) was added to a THF-d₈ solution (0.6 mL) of **6** (30 mg, 0.04 mmol,

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67/33 mixture). The solution was stirred for 48 h at room temperature to afford fluorophosphine **8** and borylcyclopropene **9**, quantitatively. **Fluorophosphine 8: HRMS (ESI⁺)** (C₁₃H₂₅NFP) [M+H]⁺: calcd: 270.1787, found: 270.1756. ³¹P{¹H} NMR (202.5 MHz, THF-d₈): δ 151.2 (d, ¹J_{PF} = 984.2 Hz). ¹⁹F NMR (282.4 MHz, THF-d₈): δ -113.8 (d, ¹J_{PF} = 984.2 Hz). ¹H NMR (500.3 MHz, THF-d₈): δ 1.01 (d, ³J_{HH} = 10.0 Hz, 12H, NCHCH₃), 2.27 (s, 3H, CH_{3para}), 2.44 (d, ⁴J_{HP} = 2.5 Hz, 6H, CH_{3ortho}), 2.91 (sept, ³J_{HH} = 5.0 Hz, 2H, NCHCH₃), 6.86 (d, ⁴J_{HH} = 1.6 Hz, 2H, CH_{Ar}). ¹³C{¹H} NMR (125.8 MHz, THF-d₈): δ 20.0 (s, CH_{3para}), 21.1 (s, CH_{3ortho}), 22.7 (s, NCHCH₃), 45.0 (s, NCHCH₃), 129.9 (m, CH_{Ar}), 138.8 (s, C_{para}), 140.7 (d, ²J_{CP} = 21.3 Hz, C_{ortho}). *Ips*o carbon could not be observed. **Borylcyclopropene 9: HRMS (ESI⁺)** (C₁₉H₂₇BN₂) [M+H]⁺: calcd: 295.2346, found: 295.2345. **IR(THF)** : ν = 2236 cm⁻¹ (CN). ¹¹B{¹H} NMR (160.5 MHz, THF-d₈): δ 38.5 (s). ¹H NMR (500.3 MHz, THF-d₈): δ 1.16 (d, ³J_{HH} = 10.0 Hz, 6H, NCHCH₃), 1.34 (d, ³J_{HH} = 10.0 Hz, 6H, NCHCH₃), 1.50 (s, 2H, CH_{2cycle}), 2.24 (s, 3H, CH_{3para}), 2.29 (s, 6H, CH_{3ortho}), 3.60 (m, 1H, NCHCH₃), 3.74 (sept, 1H, ³J_{HH} = 10.0 Hz, NCHCH₃), 6.78 (s, 2H, CH_{Ar}). ¹³C{¹H} NMR (125.8 MHz, THF-d₈): δ 12.7 (s, CH_{2cycle}), 20.2 (s, CH_{3para}), 20.7 (s, NCHCH₃), 21.1 (s, CH_{3ortho}), 24.5 (m, NCHCH₃), 45.3 (s, NCHCH₃), 51.8 (s, NCHCH₃), 96.2 (s, CCN), 112.1 (s, CN), 127.1 (s, CH_{Ar}), 136.8 (s, C_{para}), 137.9 (s, C_{ortho}). The carbon *ipso* to boron and the bridgehead carbon atom *alpha* to the boron were not observed.

X-ray structural analysis: The data of the structures for **5** and **6** were collected on a Bruker-AXS Quazar APEX II diffractometer using a 30 W air-cooled microfocus source (ImS) with focusing multilayer optics (**5**) and on a Bruker-AXS SMART APEX II diffractometer (**6**) at a temperature of 193(2)K, with MoK α radiation (wavelength = 0.71073 Å) by using phi- and omega-scans. The details of data collection and crystal structures refinement are summarized in 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 using the least-squares method on F².^[25] All non-H atoms were treated anisotropically. All H atoms attached to C atoms were fixed geometrically and treated as riding on their parent atoms with C-H = 0.95 Å (aromatic), 0.98 Å (CH₃), 0.99 Å (CH₂) or 1.0 Å (CH) with U_{iso}(H) = 1.2U_{eq}(CH, CH₂) or U_{iso}(H) = 1.5U_{eq}(CH₃). Supplementary crystallographic data for CCDC-951086 (**5**) and CCDC-951087 (**6**) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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

	5	6
Empirical formula	C ₃₄ H ₅₂ BClN ₃ P	C ₄₈ H ₆₈ BCl ₄ GaN ₃ P
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_{calc} [g cm ⁻³]	1.127	1.225
μ (MoK α) [mm ⁻¹]	0.185	0.814
F(000)	1256	992
Crystal size (mm ³)	0.10 x 0.10 x 0.08	0.40 x 0.20 x 0.08
Reflections collected	38108	33382
Independent reflections	6881	10215
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	10215 / 397 / 648
Goodness-of-fit on F ²	1.057	1.050
R1 [I > 2 σ (I)]	0.0414	0.0568
wR2 [I > 2 σ (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

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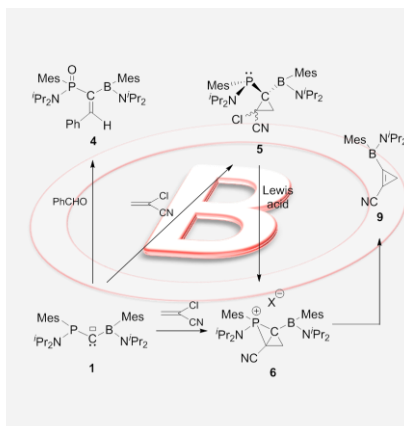
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Chemical Behaviour of Prototypical Boryl(phosphino)carbenes



The reactivity of stable boryl(phosphino)carbene **1** has been investigated showing the typical reactivity of transient singlet carbenes (1,2-migration and [2+1] cycloaddition) together with a marked α,β -ambiphilic character. Due to its specific electronic properties, **1** enabled the formation of original bicyclo[1.1.0]phosphetanium salts **6** and borylcyclopropene **9**.