

Borylated Methylene phosphonium Salts: Precursors of Elusive Boryl(phosphino)carbenes

Florie Lavigne,[†] Eddy Maerten,[†] Gilles Alcaraz,[‡] Nathalie Saffon-Merceron,[§] Carles Acosta-Silva,^{||} Vicenç Branchadell,^{||} and Antoine Baceiredo^{*,†}

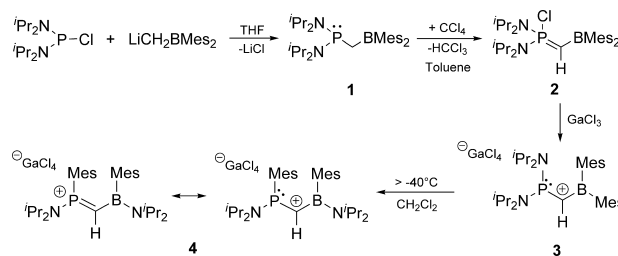
Université de Toulouse, UPS, and CNRS, LHFA, 118 route de Narbonne, F-31062 Toulouse, France, LCC, UPR CNRS 8241, 205 route de Narbonne, F-31077 Toulouse, France, Structure Fédérative de Chimie, FR 2599, 118 route de Narbonne, F-31062 Toulouse, France, and Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

Received April 29, 2010; E-mail: baceired@chimie.ups-tlse.fr

Since the first stable carbenes were isolated by Bertrand and co-workers^{1a} in 1988 and by Arduengo et al.^{1b} in 1991, tremendous developments and substantial efforts have been devoted to understanding their stabilization and tuning their reactivity.^{1c} The stabilization and chemical behavior of these species result from the degree of carbene perturbation, which is directly dependent on the substitution pattern at the electron-deficient carbon center.² With the exception of the cyclopropenylidene synthesis,³ all of the examples reported to date involve one amino or phosphino π -donating (or *push*) substituent attached to the carbenic center, defining the two main families of stabilized carbenes. The second substituent determines the nature of the carbene: *push–push*, *push–pull*, or *push–spectator*. The carbene synthetic strategy depends strongly on the push group. The deprotonation route of imidazolium salts initially developed by Arduengo et al. and later extended to iminium compounds allowed general access to aminocarbenes.⁴ The synthetic approaches involving the weaker- π -donor phosphino group are more limited, the syntheses being mostly⁵ restricted to the decomposition of phosphino diazomethane precursors.⁶ The challenging introduction of an electron-withdrawing group such as a boryl substituent at the carbenic center should produce the best model of a push–pull carbene version profiting from the ability of boron to stabilize a lone pair in an adjacent position.⁷

As part of our program involving group-13-substituted electron-deficient species, we report here the synthesis and characterization of a new class of boryl(phosphino)carbenes that provide a synthetic entry to novel and stable boryl(phosphino)carbenes.

Since boryl(phosphino)diazomethane species remain an elusive class of diazo derivatives,⁸ we focused our attention on the possible deprotonation of boryl-substituted methylene phosphonium derivatives, the phosphorus analogues of iminium salts.⁹ Phosphino(boryl)methane **1** was synthesized by reaction of (lithiomethyl)dimesitylborane with bis(diisopropylamino)chlorophosphine in tetrahydrofuran (THF). Subsequent reaction of **1** with carbon tetrachloride in toluene afforded the expected ylide **2** in 66% overall yield. A stoichiometric amount of gallium trichloride was then used to abstract the chloride from **2** in dichloromethane solution, generating methylenephosphonium salt **3**.^{9b,c} Monitoring of the reaction by ³¹P NMR spectroscopy revealed the complete formation of **3** (³¹P: 147 ppm), which appeared to be stable only below –40 °C. Above this temperature, we observed the gradual consumption of **3** with the concomitant formation of a new compound exhibiting a signal at 153 ppm. After evaporation of the solvent and workup, the methylenephosphonium isomer **4** resulting from an exchange of substituents between the boron and phosphorus centers

Scheme 1. Synthesis of Ylide **2** and Methylene phosphonium Salts **3** and **4**

was isolated in 73% yield (Scheme 1).¹⁰ The identity of isomer **4** was unambiguously confirmed by NMR spectroscopy and X-ray diffraction techniques (Figure 1).

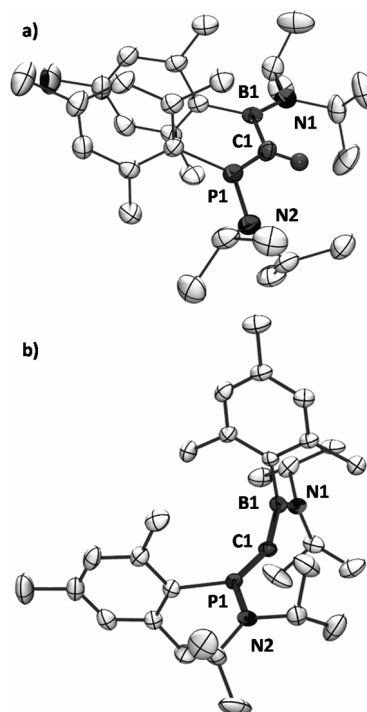


Figure 1. Molecular structures of (a) methylenephosphonium salt **4** and (b) boryl(phosphino)carbene **5**.

Deprotonation of **4** was carried out in THF at –80 °C using a stoichiometric amount of potassium hexamethyldisilazane (KHMDs) (Scheme 2). After evaporation of the solvent and workup, the stable boryl(phosphino)carbene **5** was isolated as yellow crystals from a cold

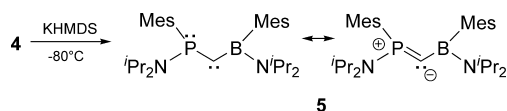
[†] Université de Toulouse, UPS, and CNRS, LHFA.

[‡] LCC, UPR CNRS 8241.

[§] Structure Fédérative de Chimie, FR 2599.

^{||} Universitat Autònoma de Barcelona.

Scheme 2. Synthesis of Boryl(phosphino)carbene 5



(−40 °C) saturated pentane solution (52% yield) and fully characterized by NMR spectroscopy and X-ray crystallography (Figure 1).

The ^{31}P NMR spectrum of **5** shows a signal at high field (−36.7 ppm) that is typical for phosphinocarbenes.^{2b} The ^{13}C NMR chemical shift for the carbene center appears as a well-resolved doublet at relatively low field (174.6 ppm, $^1J_{\text{PC}} = 208.9$ Hz), and the large coupling constant is indicative of direct P–C connectivity. The X-ray structures of **4** and **5** were determined at −80 °C (Figure 1 and Table 1). The phosphorus and boron atoms are both in planar environments, and these planes are almost perpendicular for **5** ($\text{N2}–\text{P}–\text{B}–\text{N1} = 103.1^\circ$) and coplanar for **4** ($\text{N1}–\text{B}–\text{C1}–\text{P} = 172.6^\circ$ and $\text{N2}–\text{P}–\text{C1}–\text{B} = 163.2^\circ$). In carbene **5**, the P–C1 distance [1.563(13) Å] is shorter than that in **4** [1.634(3) Å], and the value is consistent with those reported in the previous phosphinocarbenes (1.53–1.56 Å).^{6a,c,d} The B–C1 bond undergoes a small shortening in going from **4** [1.568(4) Å] to **5** [1.54(2) Å] but remains long for a B=C double bond.¹¹ This corresponds to a slightly elongated N1–B bond in **5** [1.43(3) Å vs 1.406(3) Å in **4**], indicative of a competition between the carbene and nitrogen lone pairs to fill the vacant boron orbital. The large value of the P–C1–B angle, which is wider in **5** [$151.6(13)^\circ$] than in **4** [$128.6(2)^\circ$], is reminiscent of that in phosphino(silyl)carbenes.¹²

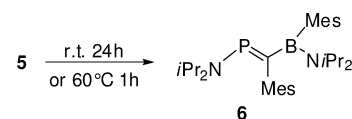
Table 1. Selected Geometrical Parameters for Experimental and Optimized Structures of **4** and **5** (Distances in Å, Angles in deg)

	5	5 _{calcd}	4	4 _{calcd}
P–C1	1.563(13)	1.569	1.634(3)	1.634
B–C1	1.54(2)	1.498	1.568(4)	1.593
P–C1–B	151.6(13)	160.2	128.6(2)	124.4

The geometries of phosphino(boryl)carbene **5** and methylenephosphonium **4** were optimized at the M05-2X/6-31G(d) level (see the Supporting Information). Except for the too-large P–C1–B angle computed for **5**, as in the case of other P–C–Si carbene analogues,¹³ the other geometrical parameters were reproduced accurately, and the optimized geometries of **4** and **5** are in good agreement with the experimental structures (see Table 1). The bonding nature can be rationalized using natural bond order (NBO) analysis. For carbene **5**, the analysis shows a P=C triple bond, with the π orbital in the P–C1–B plane (π') strongly polarized to C1 (88% C vs 12% P). As expected, the perpendicular 2p atomic orbital at boron [$\text{LP}^*(\text{B})$] in **4** and **5** has a relatively large occupancy resulting from π donation of the nitrogen lone pair (0.429e in **5** and 0.396e in **4**), with a slight increase upon deprotonation despite the more-localized lone pair at the N1 atom (1.706e in **5** vs 1.623e in **4**). Indeed, the analysis of the donor–acceptor interactions in the NBO basis estimated from second-order perturbation theory shows that in the case of carbene **5**, the donations $\text{LP}(\text{N1})$ and $\pi'(\text{C1}–\text{P})$ to $\text{LP}^*(\text{B})$ are of comparable magnitude. This feature is illustrated in **5** by a rotation of the boron plane that favors the interaction between the carbene lone pair [$\pi'(\text{C1}–\text{P})$] and the vacant $\text{LP}^*(\text{B})$ orbital at boron. Finally, the variations of the Wiberg bond indices around the carbenic center in going from **4** to **5** (P–C1, +0.33; C1–B, +0.25) confirm that **5** can be classified as a push–pull carbene. As expected for this type of carbene, the singlet–triplet energy gap was predicted to be relatively small (17.7 kcal/mol).^{2b}

Carbene **5** is perfectly stable in the solid state and slowly rearranges in solution into the corresponding phosphalkene **6**

Scheme 3. Synthesis of Phosphaalkene 6



through a 1,2-migration of the mesityl group from the phosphorus to the central carbon atom (Scheme 3).

More than 20 years after the isolation of the first stable carbene, the existence of a stable boryl(phosphino)carbene has been clearly demonstrated. An original synthetic pathway starting from boryl-substituted methylenephosphonium derivatives has been developed and should provide a promising alternative to the classical phosphinodiazomethane precursors. Developments of new models allowing a more complete understanding of this new family of carbenes are under active investigation.

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Supporting Information Available: Experimental procedures, selected NMR data, X-ray crystallographic files for **4** and **5** (CIF), and computational details and Cartesian coordinates for the calculated structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) Species **3** and **4** can be regarded as electron-deficient α -boryl carbocations. Calculations at the M05-2X/6-31G(d) level revealed that isomer **4** is 29.9 kcal/mol more stable than isomer **3**, suggesting increased stabilization due to π donation from $\text{LP}(\text{N1})$ to $\text{LP}^*(\text{B})$ in **4**.
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