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Stable (Amino)(phosphino)carbenes: Difunctional Molecules

Nathalie Merceron,[†] Karinne Miqueu,[†] Antoine Baceiredo,[†] and Guy Bertrand*,[†,‡]

Laboratoire d'Hétérochimie Fondamentale et Appliquée, UMR 5069, Université Paul Sabatier,
118 route de Narbonne, F-31062 Toulouse Cédex 04, France, and UCR-CNRS Joint Research Chemistry
Laboratory, UMR 2282, Department of Chemistry, University of California, Riverside, California 92521-0403

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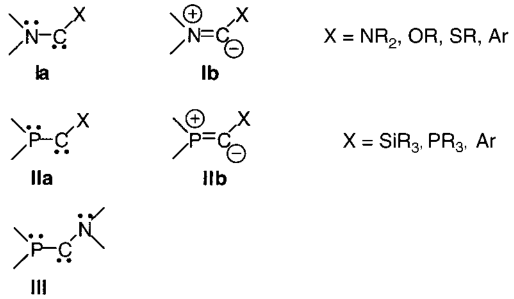
All known stable singlet carbenes feature either an amino (type **I**) or a phosphino (type **II**) substituent.[1] It is now well-established that the unusual stability of both of these species is mainly due to electron donation from the heteroatom lone pair into the formally empty p_π orbital of the carbenic center.[2,3] This is apparent from the planarity of the heteroatom and by the short heteroatom−carbene bond lengths (ylide forms **Ib** and **IIb**).[4,5] The isolation of phosphinocarbenes **II** requires a second electronically active substituent, namely an electron-withdrawing group, which gives rise to push−pull carbenes.[6] In contrast, we have recently shown that for amino carbenes **I**, the second substituent can play a spectator role.[7] Therefore, the next question to answer was whether the spectator substituent could be used as a second functional group. In other words, would it be possible to perform chemical transformations at the periphery of these types of molecule without affecting what has been considered for many years to be the prototype of reactive intermediates, namely the carbene center. Here we report the synthesis, structure, stability, and reactivity of (amino)-(phosphino)carbenes **III** (Chart 1).

Chart 1



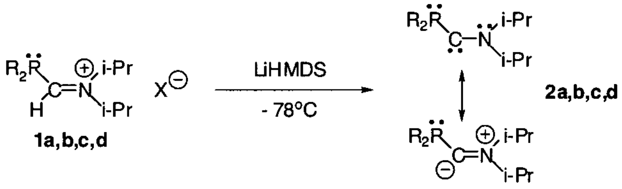
Ia **Ib** X = NR_2, OR, SR, Ar

IIa **IIb** X = SiR_3, PR_3, Ar

III

Carbenes **2a−d** were generated cleanly at −78 °C by deprotonation of the corresponding phosphinoiminium salts **1a−d**[8] with the lithium salt of hexamethyldisilylazane (Scheme 1) and were characterized by multinuclear NMR spectroscopy at −30 °C. The main feature of the NMR spectra of **2a−d** is the very low field values of the ^{13}C chemical shifts of the carbene carbon atoms (δ 320−348 ppm, J_{PC} 22−101 Hz). These signals are even further downfield than those observed for the other known aminocarbenes **I** (210−300 ppm) and in a totally different region from those for phosphinocarbenes **II** (100-145 ppm).[1,7] In all cases the ^{1}H NMR spectra highlighted the presence of two different isopropyl groups on the nitrogen atom bound to the carbene center, which indicates the absence of free rotation about the C−N bond.[9] All these NMR data strongly suggest that only the amino substituent interacts with the carbene center, the phosphino group remaining merely a spectator substituent.

Scheme 1



1a,b,c,d **2a,b,c,d**

a: R = c-Hex$_2$N, **b**: R = i-Pr$_2$N, **c**: R = Ph, **d**: R = t-Bu
X = CF_3SO_3

In the case of **2a** (R = *c*-Hex$_2$N), orange crystals suitable for an X-ray diffraction study[10] were obtained by cooling a saturated ether solution to −30 °C (Figure 1). The pyramidalization of the phosphorus atom (sum of bond angles = 304.5°) and the long P1−C1 bond length (1.856 Å), which is in the range associated with PC single bonds, demonstrate that the phosphino group is indeed a spectator substituent; this is confirmed by the orientation of the phosphorus lone pair, which is perpendicular to the (formally empty) p orbital on the carbene center. As expected, the nitrogen atom is in a planar environment (sum of bond angles = 359.6°), and the N1−C1 bond length (1.296 Å) is short. Finally, the carbene bond angle is acute (116.5°) as anticipated for aminocarbenes and in contrast with phosphinocarbenes.[1]

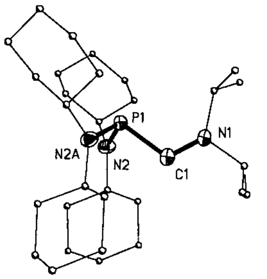


Figure 1. Molecular structure of **2a**. Selected bond lengths [Å] and angles [deg]: P1−C1 1.856(3), N1−C1 1.296(4), P1−N2 1.698(2), P1−N2A 1.698(2), N1−C1−P1 116.5(2), N2−P1−N2A 111.5(1), N2−P1−C1 96.48(9), N2A−P1−C1 96.48(9).

The stability of carbenes **2a−d** is dependent on the nature of the substituents at phosphorus. All compounds are stable for days at $T < -20$ °C. However, at room temperature, **2c** (R = Ph) quickly decomposes, giving a complex mixture, while carbenes **2a** and **2b** undergo a clean C−H insertion, involving the phosphorus substituents, affording four-membered rings **3a,b** (Scheme 2).[8] The most stable carbene is **2d** (R = *t*-Bu), which can be stored in solution for a few days at 0 °C. At 40 °C, an unusual reaction was observed, namely the elimination of propene from the nitrogen substituent with formation of the corresponding *C*-phosphino(imine) **4**.

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* To whom correspondence should be addressed. E-mail: gbertran@mail.ucr.edu.
[†] Laboratoire d'Hétérochimie Fondamentale et Appliquée, UMR 5069, Université Paul Sabatier.
[‡] UCR-CNRS Joint Research Chemistry Laboratory, UMR 2282, Department of Chemistry, University of California.

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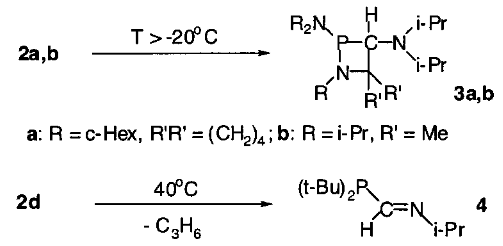
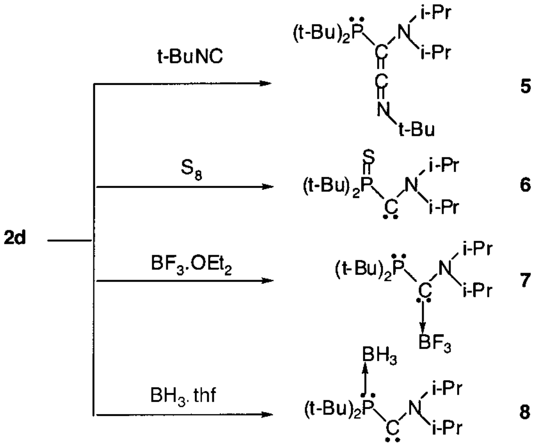
Scheme 2



Scheme 3



Isocyanides do not react with phosphines but are known to react with both phosphinocarbenes and aminoarylcarbenes.[1,7] Carbene **2d** slowly reacts (24 h at 20 °C, THF) with *tert*-butyl isocyanide affording the corresponding keteneimine **5** in near quantitative yield (IR 1972 and 1957 cm^{-1}; $^{13}\mathrm{C}$ 94.0 and 189.5 ppm) (Scheme 3).

Elemental sulfur reacts with both phosphines and aminocarbenes,[11] and therefore a competition could occur in the case of (amino)(phosphino)carbenes. Interestingly, at −30 °C a clean and quick reaction occurs when sulfur was added to a THF solution of **2d** affording the corresponding (amino)(thiophosphoranyl)carbene **6**, which is stable in solution at room temperature for a few days (Scheme 3). The carbenic structure of **6d** and the oxidation of the phosphorus center were apparent from the low field $^{13}\mathrm{C}$ signal at 322 ppm ($^{1}J_{\mathrm{PC}} = 108.1$ Hz) and the deshielding of the $^{31}\mathrm{P}$ NMR signal ($\Delta\delta = 54$ ppm), respectively.

Highly regioselective reactions were also observed, using Lewis acids. Treatment of a THF solution of **2d** with 1 equiv of $\mathrm{BF_3{\cdot}OEt_2}$ led to the quantitative formation of the carbene complex **7**,[12] which has been characterized by NMR spectroscopy. The $^{11}\mathrm{B}$ ($\delta = -14.6$) and $^{19}\mathrm{F}$ NMR ($\delta = -62.0$) signals appear as quartets ($^{1}J_{\mathrm{BF}} = 43$ Hz) without any coupling with phosphorus, demonstrating the selective interaction of $\mathrm{BF_3}$ with the carbene center. In contrast, the softer Lewis acid $\mathrm{BH_3}$ interacts selectively with the phosphorus lone pair to afford complex **8** (Scheme 3). The presence of boron directly bonded to the phosphorus atom was obvious from the $^{31}\mathrm{P}$ NMR spectrum which shows a broad quartet at $\delta = 29.2$ ($^{1}J_{\mathrm{BP}} = 47$ Hz). No interaction was observed with the carbene center as indicated by the $^{13}\mathrm{C}$ NMR signal at very low field ($\delta = 325$, $^{1}J_{\mathrm{PC}} = 79$ Hz). The structure of this new carbene **8**, which is perfectly stable at room temperature both in solution and in the solid state (mp 100−102 °C), was confirmed by an X-ray diffraction study.[10] Compared to **2d**, a wider carbene bond angle (123.0°) is observed, while the P1−C1 (1.831 Å) and C1−N1 (1.293 Å) bond lengths remain in the range expected for a single and double bond, respectively (Figure 2).

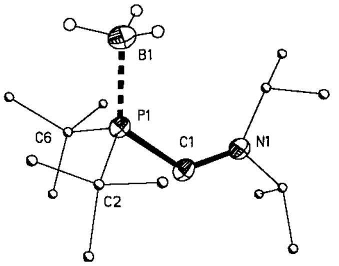


Figure 2. Molecular structure of **8**. Selected bond lengths [Å] and angles [deg]: P1−C1 1.831(1), N1−C1 1.293(2), P1−C2 1.874(1), P1−C6 1.874(1), P1−B1 1.954(2), N1−C1−P1 122.98(10), C1−P1−C2 98.85(6), C1−P1−C6 98.04(6), C2−P1−C6 115.34(6), C1−P1−B1 126.43(7), C2−P1−B1 12109.50(7), C6−P1−B1 108.60(7).

These results demonstrate that a carbene moiety has now to be considered as an ordinary functional group, readily tolerating chemical transformations at its periphery, without itself becoming involved. Moreover, the presence of a soft (phosphine) and a hard (carbene) center makes (amino)(phosphino)carbenes bidentate hybrid compounds, with potential application as ligands for transition metal complexes.[13]

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Supporting Information Available: Selected spectroscopic data for **2a−d**, **4**, **5**, **6**, **7**, and **8**, and crystal data for **2a** and **8** (PDF). X-ray crystallographic files for **2a** and **8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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