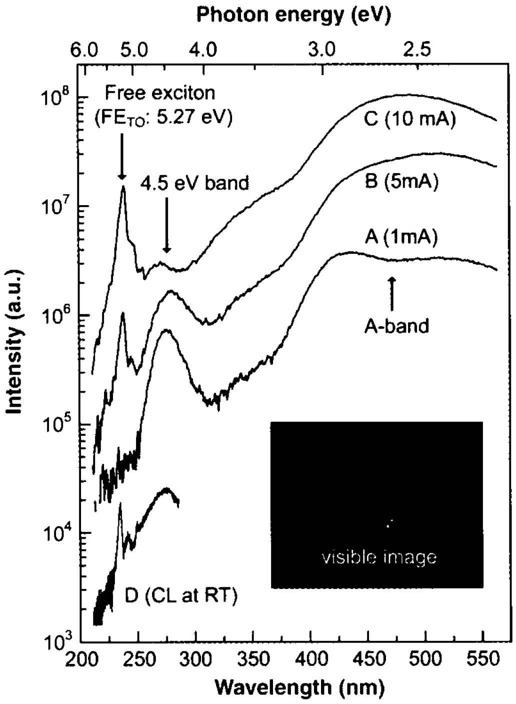

Fig. 3. Optical emission spectra of the pn junction operated with forward current of (**A**) 1, (**B**) 5, and (**C**) 10 mA. A representative CL spectrum of P-doped diamond thin film taken at room temperature is shown in (**D**). The inset is a representative optical image of the diamond LED with light emission. The circular-shaped electrodes (diameter, 150 μm) are formed by the separating each other by 150 μm. Light emission can be seen around the electrode located at the center of the image.

increase of the voltage in a reverse voltage region, confirming the existence of a depletion layer and its narrowing according to the voltage increase.

For forward currents exceeding 0.1 mA, light emission was observed. In the present structure of the samples, light emission was observed around the electrode of the sample because the pn junction and the light-emitting area exist behind the electrode and because the driving voltage is applied perpendicular to the sample surface (Fig. 3 inset). As we increased the forward current, we observed the UV light emission in the spectrum (Fig. 3). The driving voltages were 20 V for 1 mA, 21.5 V for 5 mA, and 23 V for 10 mA. For the present sample, over 5 mA, we saw a sharp emission peak located at 235 nm (5.27 eV), which is attributed to free exciton recombination luminescence coupled with TO phonon (FE$_{TO}$) (Fig. 3, B and C). The small peak (shoulder) located at around 243 nm (5.10 eV) is attributed to the phonon replica of FE$_{TO}$ peak. Also observed were broadband emissions at an UV region with peak energy located at 4.5 eV and a broadband emission in the visible region. The origin of a 4.5-eV band emission is not very clear yet, but it is often observed for B- and P-doped CVD diamond thin films by CL and PL analysis (*3*, *4*). The band emission in the visible region is attributed to A-band emission that is often observed by CL and PL from CVD diamond thin films. The intensity ratio of the free exciton peak against the A band was 1:7 for a forward current of 10 mA (Fig. 3C). The appearances of the free exciton and the 4.5-eV band emissions are very consistent with room temperature CL spectrum observed from P-doped diamond thin film (Fig. 3D). This result supports high crystalline perfection of the P-doped layer prepared here. In our series of B-doping experiments for {111} diamond thin films, the quality of the B-doped layer was not so good, such that the exciton peak bound to boron was negligibly weak, even at 110 K. The visible lights such as A-band luminescence observed in the spectrum are most likely emitted from B-doped layer. By further improving the crystalline quality of the B-doped layer, the A-band emission will be suppressed and a diamond light-emitting diode (LED) that exclusively emits monochromatic UV light of 235 nm will be feasible.

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(Amino)(Aryl)Carbenes: Stable Singlet Carbenes Featuring a Spectator Substituent

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Didier Bourissou,[1] Guy Bertrand[1]*

Several (amino)(aryl)carbenes have been shown to be stable at room temperature in solution and in the solid state. Electroneutrality of the carbene center is ensured by the amino group, which has both π-donor and σ-acceptor electronic character. The aryl group remains a spectator substituent, as shown by single-crystal x-ray analysis and by its chemical behavior. Because only one electron-active substituent is needed, numerous stable carbenes will become accessible, which will open the way for new synthetic developments and applications in various fields.

Attempts to prepare the parent carbene (CH_2) by dehydration of methanol were reported as early as the 1830s (*1*). At that time, the tetravalency of carbon had not been established, and therefore the existence of stable carbenes was considered to be quite reasonable. Carbenes were only recognized as reactive intermediates some 50 years later (*2*, *3*), at which time it quickly became clear that their six-valence-electron shell, which defied the octet rule, was responsible for their fugacity. Thus, the quest for stable carbenes became an unreasonable target and remained so for quite some time, although these transient species found numerous applications in synthetic chemistry (*4*–*7*).

In the last 15 years, the preparation of persistent triplet carbenes **I** (*8*) and the isolation at room temperature of singlet carbenes **II** and **III** (Fig. 1) represent spectacular achievements (*9–11*). In all of these compounds, the carbene center strongly interacts with both of its substituents. For triplet diarylcarbenes **I**, the spin density is partly shifted over the ring, as shown by resonance forms **I′** and **I″** (*12*). Singlet push-push carbenes **II** [di(amino)carbenes **IIa** (*13*) and related compounds **IIb,c** (*14*)] have two π-donor substituents and are thus best described by the superposition of the two ylidic structures **II′** and **II″** resulting in a four–π-electron three-center system **II‴**. In singlet push-pull carbenes **III**, such as (phosphino)(silyl)carbenes **IIIa** (*15*), the carbon bears both a π-donating and a π-withdrawing substituents, resulting in the unsaturated ylidic structure **III′** with some participation of the cumulenic structure **III″** (*16*). This stabilization mode has recently allowed for the isolation of the first monoheteroatom-substituted carbene **IIIb** (*17*), for which the cumulenic structure **III″** is the most representative.

The question that remains is to what extent the degree of carbene perturbation can be decreased without precluding isolation at room temperature. Herein we report that a single electron-active substituent is sufficient. The second one can be a spectator that merely affords some steric protection to the system.

The push-pull carbenes **III** follow Pauling's prediction (*18*), with two substituents of opposite electronic properties being capable of stabilizing singlet carbenes by preserving the electroneutrality of the carbene center. It was thus tempting to use a single substituent, which on its own would be both an electron donor and an electron acceptor. The amino group was the obvious choice.

We initially prepared the iminium salt **1a**, bearing a bulky *tert*-butyl group at nitrogen and a 2,4,6-tri-*tert*-butylphenyl group at carbon (Scheme 1). Subsequently, **1a** was deprotonated with potassium hydride at −78°C in tetrahydrofuran (all manipulations were performed under argon), which cleanly led to the formation of (amino)(aryl)carbene **2a** (*19, 20*). The signal observed at $\delta = 314.2$ ppm in the ^{13}C nuclear magnetic resonance (NMR) spectrum is the most deshielded signal reported for a carbene center (*11*). Compound **2a** is stable for days in solution at −50°C but undergoes a C-H insertion reaction at room temperature; within a few hours, the 4,6-di-*tert*-butyl-1,1-dimethyl-3-(methyl-*tert*-butylamino)indan **3a** (*19*) is obtained as the major product. This reaction, which is typical of transient singlet and triplet carbenes (*21*), has never been observed for push-push carbenes of type **II** (*22*). This striking difference demonstrates the less perturbed character of carbene **2a**.

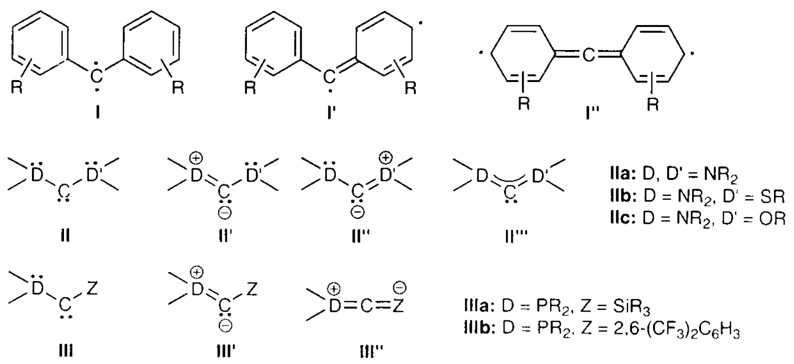


Fig. 1. Structure of the persistent triplet carbenes **I** and stable singlet carbenes **II** and **III**.

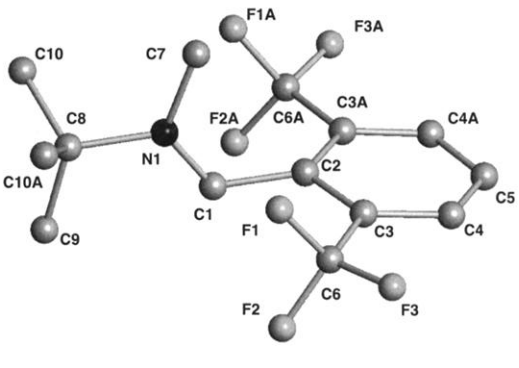
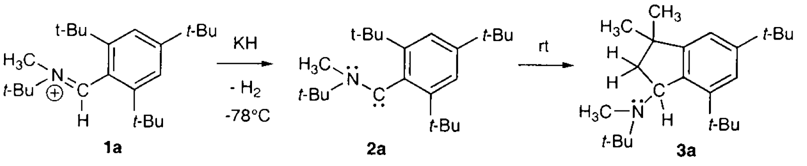
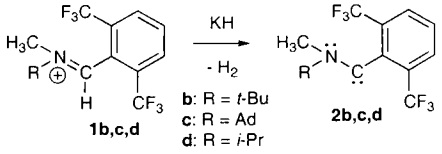


Fig. 2. Molecular view of **2b** in the solid state. Selected bond lengths: N1-C1, 1.283 ± 0.003 Å; C1-C2, 1.453 ± 0.003 Å; C2-C3, 1.419 ± 0.002 Å; C3-C4, 1.385 ± 0.003 Å; C4-C5, 1.375 ± 0.003 Å; N1-C7, 1.484 ± 0.003 Å; and N1-C8, 1.517 ± 0.003 Å. Selected angles: N1-C1-C2, 121.0° ± 0.2°; C8-N1-C7, 115.1° ± 0.2°; C8-N1-C1, 120.7° ± 0.2°; and C1-N1-C7, 124.2° ± 0.2°.



Scheme 1.

Because C-F bonds are inert toward insertion of any type of carbene (*23, 24*), we then replaced the ortho-*tert*-butyl groups of the aryl ring by trifluoromethyl substituents. Following the same procedure as described above, the (amino)(aryl)carbenes **2b–d** were prepared from the corresponding iminium salts **1b–d** (Scheme 2). Because the insertion reaction is no longer possible and the dimerization is precluded on steric grounds, carbenes **2b–d** could be isolated at room temperature in almost quantitative yields (*19*). The ^{13}C NMR resonances for the carbene carbons have similar chemical shifts (299 to 303 ppm) to that of **2a**, suggesting analogous electronic structure. Extremely air-sensitive pale yellow crystals of **2b** (melting point 16°C), suitable for x-ray study (*25*), were obtained by recrystallization from pentane at −55°C.



Scheme 2.

It is interesting to compare the molecular structure of **2b** (Fig. 2) with those of the push-push di(amino)carbenes **IIa** (*10, 11*) and push-pull (phosphino)(aryl)carbene **IIIb** (*17*). The nitrogen atom is in a planar environment and the N1-C1 bond length (1.283 ± 0.003 Å) is shorter than that observed for di(amino)carbenes **IIa** (1.32 to 1.37 Å), which indicates a stronger donation of the nitrogen lone pair into the vacant carbene orbital. In marked contrast with the cumulenic system **IIIb**, the C1-C2 bond distance is long (**2b**: 1.453 ± 0.003 Å; **IIIb**: 1.390 ± 0.004 Å) and the carbene bond angle acute (**2b**: 121.0° ± 0.2°; **IIIb**: 162.1° ± 0.3°) (*26*). These data clearly indicate that the potentially π-accepting 2,6-bis(trifluoromethyl)phenyl group does not interact with the carbene lone pair of **2b** and is therefore a spectator, as shown in Fig. 3.

The spectator role of the aryl substituent is well illustrated by the reactivity of carbenes

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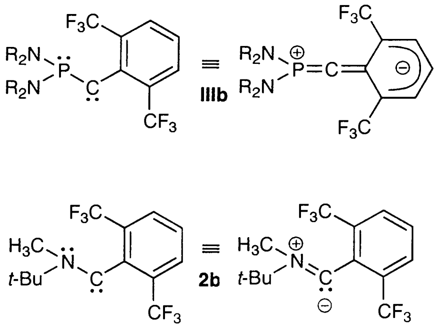
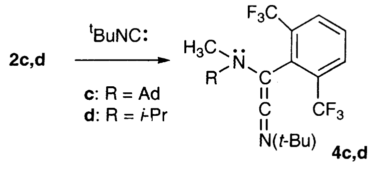


Fig. 3. Best representations for the (phosphino)-(aryl)carbene **IIIb** and the (amino)(aryl)-carbene **2b**.



Scheme 3.

2. Despite the steric protection of the carbene carbon atom, **2c,d** undergo coupling reactions with *tert*-butyl isocyanide at room temperature and afford the corresponding ketenimines **4c,d** in good yields (Scheme 3). Because this reaction, which is typical of transient singlet carbenes (*27*), is not observed for push-push carbenes **II**, we concluded that the isocyanide acts here as a Lewis base toward carbenes **2**. This result demonstrates that, in contrast with **II**, the vacant carbene orbital of **2** remains accessible.

Up to now, the number and variety of stable carbenes have been limited by the perceived necessity for two strongly interacting substituents. Despite this perceived limitation, these species have found applications (*9*, *28–33*) even on a large scale. This work establishes that only a single electron-active substituent is necessary to isolate a carbene. Therefore, a broad range of these species will soon be readily available, which will open the way for new synthetic developments and applications in various fields.

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22. For di(amino)carbenes, the reported C-H insertion reactions initially involve the protonation of the carbene center and thus only occur with strongly polarized C-H bonds [A. J. Arduengo III *et al.*, *Helv. Chim. Acta* **82**, 2348 (1999)].
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25. Crystal data for **2b**: Cell constants and an orientation matrix for data collection correspond to the orthorhombic space group *Pbcm*, with a = 6.0039(4) Å, b = 19.6483(13) Å, c = 12.4792(8) Å, and V (cell volume) = 1472.1(2) Å^3. A half molecule of $C_{14}H_{15}F_6N$ per asymmetric unit (number of formula units per cell = 4), giving a formula weight of 311.27 and a calculated density (D_c) of 1.404 Mg m^{-3}. The data of the structure were collected on a Bruker-AXS CCD 1000 diffractometer at a temperature of 173(2) K with graphite-monochromated Mo Kα radiation (wavelength = 0.71073 Å) by using phi- and omega-scans. We solved the structure by direct methods, using SHELXS-97 [G. M. Sheldrick, *Acta Crystallogr.* **A46**, 467 (1990)]. The linear absorption coefficient, μ, for Mo K radiation is 0.136 mm^{-1}. The structure was refined with all data on F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_{obs}^2) + (g1\cdot P)^2 + (g2\cdot P)$ with $P = (F_{obs}^2 + 2F_{calc}^2)/3$ using *SHELXL-97* [G. M. Sheldrick, *Program for Crystal Structure Refinement* (Universität Göttingen, Göttingen, 1997)] [g is the weighting factor (g_1 = 0.051400 and g_2 = 0.755700) and F_{obs} and F_{calc} are the observed and calculated structure factors, respectively]. All non-H atoms were treated anisotropically. The H atoms were located by difference Fourier maps and refined with a riding model. The final cycle of full-matrix least square refinement was based on 11,530 measured (1472 unique) reflections and 108 variable parameters and converged with the unweighted agreement factor equal to R_1 [$I > 2\sigma(I)$ = 0.0424 (where I is the observed reflection intensity) and the weighted factor wR_2 = 0.1198 for all data. Crystallographic details may be obtained from the corresponding author or from the Cambridge Crystallographic Data Centre, by quoting the full literature citation. Crystallographic details are available at *Science* Online (*34*).
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Microbial Genes in the Human Genome: Lateral Transfer or Gene Loss?

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The human genome was analyzed for evidence that genes had been laterally transferred into the genome from prokaryotic organisms. Protein sequence comparisons of the proteomes of human, fruit fly, nematode worm, yeast, mustard weed, eukaryotic parasites, and all completed prokaryote genomes were performed, and all genes shared between human and each of the other groups of organisms were collected. About 40 genes were found to be exclusively shared by humans and bacteria and are candidate examples of horizontal transfer from bacteria to vertebrates. Gene loss combined with sample size effects and evolutionary rate variation provide an alternative, more biologically plausible explanation.

Studies of the evolution of species long assumed that gene flow between species is a minor contributor to genetic makeup, generally thought to only occur between closely related species. This picture changed when researchers began to study the genetics of microorganisms. Genes, including those encoding antibiotic resistance, can be exchanged between even distantly related bacterial species (horizontal or lateral gene transfer). A growing body of evidence suggests that lateral gene transfer may be a much more important force in prokaryotic evolution than was previously