

Persistent (Amino)(Silyl)Carbenes

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The stable singlet carbenes¹ can be classified in three categories. Push–pull carbenes **A** are quasilinear. The interaction of the D substituent lone pair and the W substituent vacant orbital with the p_y and p_x orbitals of the carbene, respectively, gives rise to a polarized allene-type system; the most representative carbenes of this type are the (phosphino)(silyl)carbenes² (Figure 1). Push–push carbenes **B** are bent, and the π -donation of the D substituent lone pair results in a polarized four-electron three-center π -system; the archetypical carbenes of this type are the diaminocarbenes.³ Last, carbenes **C** represented by (amino)- and (phosphino)(alkyl)carbenes have only a single electron-active substituent (a strong π -donor) and are also bent due to the presence of an heteroatom–carbon double bond.² On the basis of this classification, (amino)(silyl)carbenes should be of type **A**, and since (phosphino)(silyl)carbenes have been known for more than 15 years,⁴ it is rather surprising that thus far none of these compounds have been described. Here we report that in fact (amino)(silyl)carbenes are bent and, surprisingly, are not very stable.

(Phosphino)(silyl)carbenes are usually prepared by photolysis or thermolysis of the corresponding diazo compounds, whereas aminocarbenes are classically obtained by deprotonation of iminium salts. None of these methods can be extrapolated to the synthesis of (amino)(silyl)carbenes since neither amino-substituted diazo derivatives nor silyl-substituted iminium salts are known; both of these compounds are probably unstable. Therefore, we turn our attention to our recently published synthesis of carbenes by substitution reactions at a carbene center.⁵ Treatment of Alder's dimer **1a**⁶ with 1 equiv of di(*tert*-butyl)phenylphosphine, followed by deprotonation with sodium *t*-butoxide cleanly led to the carbene precursor **3a**. Then, addition of the lithium salt of *t*-butyldiphenylsilane quantitatively afforded (according to multinuclear NMR) the (amino)(silyl)carbene **4a**, along with di-*tert*-butylphenylphosphine (Scheme 1).

Carbene **4a** has a half-life of about 12 h at 0 °C, but quantitatively decomposes into the corresponding (*E*)-imine **5** and propene within a few minutes at room temperature. This rearrangement is similar to that observed for the (*t*-butyl)(di-*i*-propylamino)carbene.⁷ In the hope of increasing the stability of such carbenes, we replaced the *i*-propyl at nitrogen by bulkier *c*-hexyl groups. Carbene **4b** is stable for a few days at 0 °C and has even a half-lifetime of about 1 h at room temperature. The ¹³C NMR signals for the carbene carbon of **4a** (+377 ppm) and **4b** (381 ppm) are shifted downfield by more than 200 ppm compared to that for (phosphino)(silyl)carbenes. This is a good indication that carbenes **4** do not belong to the family of push–pull carbenes **A**. Indeed, these signals are even at lower field than those for aryl-, alkyl- and even phosphino-amino carbenes (300–350 ppm), which are of type **C**. All attempts to obtain crystals of carbenes **4** failed. It is noteworthy that, despite numerous

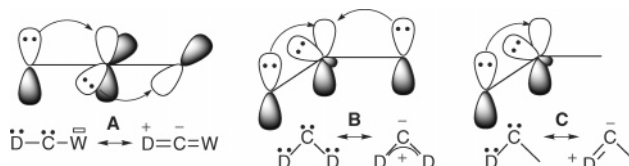


Figure 1. Electronic effects of the substituents for push–pull carbenes **A**, push–push carbenes **B**, and carbenes **C** with a single electron-active group.

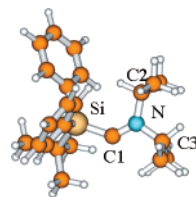
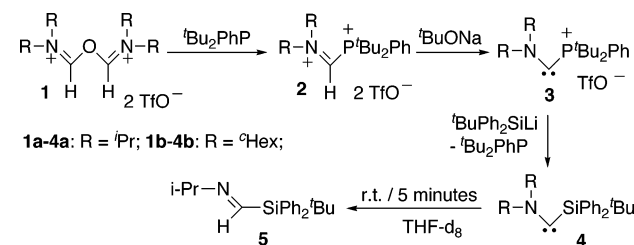


Figure 2. B3LYP/6-31g* optimized geometry of **4a**. Selected bond distances (Å) and angles (deg): N–C1 129.3, C1–Si 186.6, N–C1–Si 133.1, C1–N–C2 118.0, C1–N–C3 127.2, C2–N–C3 114.8.

Scheme 1



examples of stable (phosphino)(silyl)carbenes, only one single-crystal X-ray diffraction study has been reported.⁸

We performed ab initio calculations at the B3LYP/6-31g* level⁹ on the experimentally observed carbene **4a** (Figure 2) and on related (amino)(silyl)-**4c–f**, (amino)(germyl)-**6**, (amino)(alkyl)-**7**, and (phosphino)(silyl)-**8a,b** carbenes (Table 1).

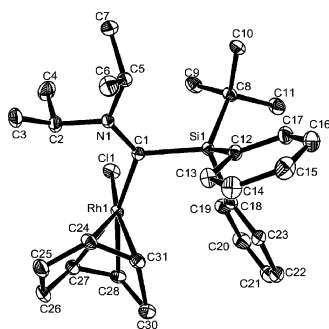
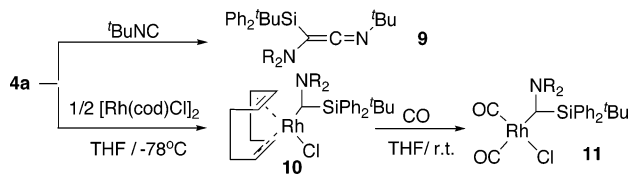
The singlet–triplet energy separation for the parent amino-carbenes **4c**, **6**, and **7** increases with the electronegativity of the second carbene substituent as predicted relatively early on for non-amino carbenes.¹⁰ More importantly, the singlet–triplet gap is much larger for the parent (amino)- (**4c**: 20.9 kcal/mol) than that for the (phosphino)(silyl)carbene (**8a**: 4.2 kcal/mol). This is in line with the better π -donor ability of the amino group. The values of the carbene bond angle (**4c**: 116.8; **8a**: 133.7; **8b**: 151.1°) coupled with the carbon–silicon bond lengths (**4c**: 188.3; **8a**: 183.8; **8b**: 180.5 pm) indicate a stronger interaction of the silyl group with the carbene center for the phosphino carbenes **8**. In fact, carbenes **4** are much more similar to the (alkyl)(amino)carbenes **7** (type **C**) than to the push–pull (phosphino)(silyl)carbenes **8** (type **A**). In other words, for **4** there is a very weak, if any, interaction between the carbene lone pair and the vacant σ^* -orbitals at silicon. This is a further demonstration that the stabilizing effect of an amino group toward a carbene center is so efficient, that a second electronically

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Table 1. Calculated Geometric Parameters and Singlet/Triplet Energy Separation for Carbenes **4** and **6–8**

	carbene	S/T gap (kcal/mol)	carbene angle (deg)	C–Si (pm)
4a	$^i\text{Pr}_2\text{N}-\text{C}-\text{SiPh}_2^t\text{Bu}$	20.3	133.1	186.6
4c	$\text{H}_2\text{N}-\text{C}-\text{SiH}_3$	20.9	116.8	188.3
4d	$\text{Me}_2\text{N}-\text{C}-\text{SiH}_3$	22.3	126.6	186.6
4e	$\text{Me}_2\text{N}-\text{C}-\text{SiMe}_3$	20.5	129.8	187.0
4f	$^i\text{Pr}_2\text{N}-\text{C}-\text{SiMe}_3$	22.2	132.0	186.5
6	$\text{H}_2\text{N}-\text{C}-\text{GeH}_3$	23.4	112.3	
7	$\text{H}_2\text{N}-\text{C}-\text{CH}_3$	33.3	111.0	
8a	$\text{H}_2\text{P}-\text{C}-\text{SiH}_3$	4.2	133.7	183.8
8b ^{12c}	$(\text{H}_2\text{N})\text{P}-\text{C}-\text{SiH}_3$	11.1	151.1	180.5

**Figure 3.** Thermal ellipsoid diagram (50% probability) of **10** (H atoms are omitted). Selected bond distances (Å) and angles (deg): N1–C1 1.3163(15), C1–Rh1 1.9935(11), C1–Si1 1.9275(12), Rh1–C24 2.1076(13), Rh1–C31 2.1331(11), Rh1–C27 2.2405(10), Rh1–C28 2.2375(13), N1–C1–Si1 124.03(8), N1–C1–Rh1 123.67(8), Si1–C1–Rh1 112.30(6).**Scheme 2**

active substituent is useless.^{7,11} Note that the calculated carbene bond angle for **4a** (133.1°) is rather large, but this is due to the steric bulk of the substituents, as already observed for (amino)-(alkyl)carbenes (**7**: 111.0; $^t\text{BuCN}^i\text{Pr}_2$: 120.5°).

Except diaminocarbenes (**B**), stable carbenes readily react with isocyanides, and indeed addition of $t\text{-BuNC}$ at -40°C to **4a** cleanly leads to keteneimine **9** (Scheme 2). In contrast to carbenes **B** and **C**, push–pull carbenes **A** are reluctant to act as ligands for transition metals.¹² Therefore, it was of primary interest to evaluate the ligand properties of **4**. Addition of carbene **4a** to $[\text{RhCl}(\text{cod})]_2$ in THF at -78°C afforded carbene complex **10**, which was isolated by column chromatography in 56% yield (based on dication **2a**) as highly thermally and air-stable single crystals (mp $150\text{--}152^\circ\text{C}$).

Compared to the known $[\text{RhCl}(\text{cod})(\text{NHC})]$ complexes,¹⁴ the ^{13}C NMR signal for the carbene center of **10** (306 ppm, d, $^1J_{\text{CRh}} = 33\text{ Hz}$) is more deshielded and the $\text{C}_{\text{carbene}}\text{--Rh}$ bond length (1.993 Å)¹³ is shorter (Figure 3). The carbonyl stretching frequencies of $\text{cis-}[\text{RhCl}(\text{CO})_2(\text{L})]$ complexes are recognized as an excellent measure of the σ -donor and π -acceptor properties of the ligand L.^{14a,b} Complex **11** was readily obtained by treatment of a THF solution of **10** with CO at room temperature. The substitution of the cod ligand by the stronger acceptor CO ligands shows the strong donor capability of carbene **4**.^{14c} The carbonyl stretching frequencies of **11** (2072 and 1989 cm^{-1}) fall between those observed for the analogous complexes featuring the very basic acyclic bis(diisopropylamino)carbene¹⁵ (2057 and 1984 cm^{-1}) and the saturated

NHCs (2081 and 1996 cm^{-1}),¹⁴ and are very similar to those observed with the (*tert*-butyl)(di-*i*-propylamino)carbene (2070 and 1989 cm^{-1}).⁷

These results show the usefulness of the substitution route for the synthesis of original stable carbenes. They demonstrate that (amino)(silyl)carbenes are not push–pull carbenes as their phosphino analogues and therefore are excellent ligands for metal centers. We are currently investigating cyclic versions of these species as well as the catalytic properties of the ensuing transition-metal complexes.

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Supporting Information Available: Full experimental and computational details, spectroscopic data (PDF), and X-ray crystallographic data for **10** and **11** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) For reviews on stable singlet carbenes, see: (a) Kirmse, W. *Angew. Chem., Int. Ed.* **2004**, *43*, 1767. (b) Bertrand, G. In *Reactive Intermediates Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley: New York, 2004; pp 329–374. (c) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.
- (2) For reviews on carbenes of types **A** and **C**, see: (a) Canac, Y.; Soleilhavoup, M.; Conejero, S.; Bertrand, G. *J. Organomet. Chem.* **2004**, *689*, 3857. (b) Bourissou, D.; Bertrand, G. *Adv. Organomet. Chem.* **1999**, *44*, 175.
- (3) For reviews on carbenes of type **B**, see: (a) Alder, R. W.; Blake, M. E.; Chaker, M. E.; Harvey, J. N.; Paolini, F.; Schutz, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5896. (b) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239. (c) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247. (d) César, V.; Bellemin-Lapont, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619. (e) Enders, D.; Balensiefer, T. *Acc. Chem. Res.* **2004**, *37*, 534. (f) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951. (g) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181.
- (4) (a) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463. (b) Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 621.
- (5) (a) Merceron-Saffon, N.; Baceiredo, A.; Gornitzka, H.; Bertrand, G. *Science* **2003**, *301*, 1223. (b) Conejero, S.; Canac, Y.; Tham, F. S.; Bertrand, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 4089.
- (6) (a) Alder, R. W.; Blake, M. E.; Bufali, S.; Butts, C. P.; Orpen, A. G.; Schutz, J.; Williams, S. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1586. (b) Alder, R. W.; Butts, C. P.; Orpen, A. G. *J. Am. Chem. Soc.* **1998**, *120*, 11526.
- (7) Lavallo, V.; Mafhouz, J.; Canac, Y.; Donnadiou, B.; Schoeller, W. W.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 8670.
- (8) Kato, T.; Gornitzka, H.; Baceiredo, A.; Savin, A.; Bertrand, G. *J. Am. Chem. Soc.* **2000**, *122*, 998–999.
- (9) All quantum chemical calculations were performed with the Gaussian 98 set of programs: Frisch, M. J., et al. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (10) (a) Harrison, J. F. *J. Am. Chem. Soc.* **1971**, *93*, 4112. (b) Feller, B.; Borden, W. T.; Davidson, E. R. *Chem. Phys. Lett.* **1980**, *71*, 22. (c) Irikura, K. I.; Goddard, W. A., III; Beauchamp, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 48.
- (11) (a) Cattoen, X.; Gornitzka, H.; Bourissou, D.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 1342. (b) Merceron, N.; Miqueu, K.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **2002**, *124*, 6806. (c) Solé, S.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2001**, *292*, 1901.
- (12) The reluctance of push–pull carbenes to bind metals has been rationalized theoretically: (a) Schoeller, W. W.; Eisner, D.; Grigoleit, S.; Rozhenko, A. B.; Alijah, A. J. *Am. Chem. Soc.* **2000**, *122*, 10115. (b) Schoeller, W. W.; Rozhenko, A. B.; Alijah, A. J. *Organomet. Chem.* **2001**, *617*, 435. (c) Schoeller, W. W. *Eur. J. Inorg. Chem.* **2000**, 369.
- (13) Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-264588 (**10**), and 264589 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. Fax: (+44)1223-336-033. Email: deposit@ccdc.cam.ac.uk.
- (14) (a) Mayr, M.; Wurst, K.; Ongania, K.-H.; Buchmeiser, M. *Chem.–Eur. J.* **2004**, *10*, 1256. (b) Herrmann, W. A.; Ofèle, K.; Preysing, D. v.; Herdtweck, E. *J. Organomet. Chem.* **2003**, *684*, 235. (c) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219. (d) Enders, D.; Gielen, H.; Runsink, J.; Breuer, K.; Brode, S.; Boehn, K. *Eur. J. Inorg. Chem.* **1998**, 913. (e) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Chem.–Eur. J.* **1996**, *2*, 772. (f) Coleman, A. W.; Hitchcock, P. B.; Lappert, M. F.; Maskell, R. K.; Müller, J. H. J. *Organomet. Chem.* **1985**, 296, 173.
- (15) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1121.

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