11526 *J. Am. Chem. Soc.* **1998,** *120,* 11526−11527

Stable Aminooxy- and Aminothiocarbenes

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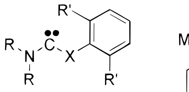
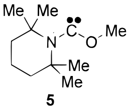
Received June 3, 1998
Revised Manuscript Received September 10, 1998

We report the first observation of isolable carbenes stabilized by one dialkylamino group and an alkoxy, aryloxy, or thioaryloxy group, **1**−**5**. Since the observation of an imidazol-2-ylidene by the Arduengo group in1991,[1] a widening range of diaminocarbenes have been observed,[2,3] including the first air stable carbene, **6**.[4] Previously reported imidazol-2-ylidenes are thermodynamically stable to dimerization,[5,6] but dihydroimidazol-2-ylidenes,[7,8] and acyclic diaminocarbenes with appropriate steric hindrance, like bis(diisopropylamino)carbene **7**,[9] can also be isolated. Unhindered examples such as bis(dimethylamino)carbene **8**, generated by deprotonation of amidinium salts with lithium amide bases, dimerize slowly at ambient temperatures,[10] although the effect of Li$^+$ complexation on carbene stability is uncertain. Stable carbenes with adjacent heteroatoms other than nitrogen are restricted to a thiazol-2-ylidene,[11] **9**, related to the thiamine intermediate,[12] and the unique phosphinocarbenes,[13,14] e.g., **10**.



1, X=O, R=*i*-Pr, R'=*t*-Bu
2, X=O, R=Me, R'=*t*-Bu
3, X=O, R=*i*-Pr, R'=Me
4, X=S, R=*i*-Pr, R'=Me



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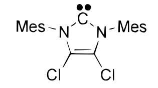
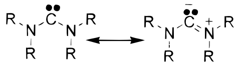
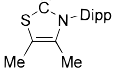


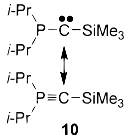
6, Mes=
2,4,6-trimethylphenyl



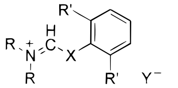
7, R=*i*-Pr
8, R=Me



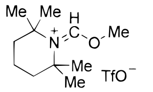
9, Dipp=
2,6-diisopropylphenyl



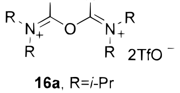
10



11, X=O, R=*i*-Pr, R'=*t*-Bu, Y=OTf
12, X=O, R=Me, R'=*t*-Bu, Y=OTf
13, X=O, R=*i*-Pr, R'=Me, Y=BF$_4$
14, X=S, R=*i*-Pr, R'=Me, Y=BF$_4$



15



16a, R=*i*-Pr
16b, R=Me

Stabilization in most cases arises from π-electron donation symbolized by contributions from ylidic resonance, as shown for **7**. Oxygen is the next best candidate, after nitrogen, phosphorus, and sulfur, to provide good π-electron stabilization, and extensive studies[15] demonstrated the nucleophilic character of dialkoxycarbenes as reactive intermediates. Aminooxycarbenes have been much less studied,[16,17] although their role as intermediates in exchange of the methine proton of HC(OMe)$_2$NMe$_2$ was recognized many years ago.[18] Warkentin developed a convenient route to aminooxycarbenes through thermolysis of Δ^3-1,3,4-oxadiazolines, and has examined their reactivity.[16,17] We set out to see if aminooxy- and aminothiocarbenes could be observed as stable species. We sought examples where $C_{carbene}$−N bond rotation could be observed, since this should provide some evidence concerning the degree of π-electron stabilization. In addition, when the N−$C_{carbene}$−O unit is not part of a ring, it may be expected that the O (or S) substituent would adopt a conformation in which it would provide some steric protection for the carbene center.

Carbenes **1**−**5** were generated by deprotonation of alkoxyiminium salts **11**−**15** with lithium 2,2,6,6,-tetramethylpiperidide or sodium or potassium salts of hexamethyldisilylazane. Alkoxyiminium salt **15** was prepared by alkylation of *N*-formyl-2,2,6,6-tetramethylpiperidine with methyl triflate. The salts **11**−**14** were prepared by reaction of the appropriate phenoxide or thiophenoxide ion with **16a** or **16b**, which were themselves made by reaction of *N*,*N*-diisopropylformamide or DMF with triflic anhydride.[19] Reaction of **11**−**15** with the amide bases was carried out in THF, and ^{1}H and ^{13}C NMR spectra of **1**−**5** were obtained in benzene-d_6 or tetrahydrofuran-d_8. The two outstanding features of the NMR spectra of **1**−**5** are (a) the ^{13}C chemical shifts of the carbene carbons and (b) the clear evidence for slow rotation about the bond between nitrogen and the carbene carbon. The carbene carbons of **1**−**5** resonate at 267.3, 263.8, 262.8, 296.6, and 277.8 ppm, respectively. ^{13}C chemical shifts of imidazol-2-ylidenes occur at around 200−220 ppm, while those for other diaminocarbenes range from 230 to 260 ppm. In **9**, C-2 resonated at 254.3 ppm.

Crystals of **1** suitable for X-ray structure determination were obtained by slow cooling of a saturated toluene solution to −20 °C under N$_2$, while crystals of **11** were grown by slow diffusion of ether into a chloroform solution at room temperature. The structures[20,21] are shown in Figure 1, and selected geometrical data are given in Table 1. Carbene **1** and cation **11** adopt similar conformations, each minimizing nonbonding interactions among the isopropyl and *tert*-butyl groups. In this geometry, there is

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[14] λ^3-Phosphinocarbenes such as **10** can also be regarded as λ^5-phosphaacetylenes, and related sulfur species are normally shown this way: Pötter, B.; Seppelt, K.; Simon, A.; Peters, E.-M.; Hettich, B. *J. Am. Chem. Soc.* **1985**, *107*, 980.

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[20] Crystal data for **1**: $C_{21}H_{35}N_O$, *M* 317.5, monoclinic, $a = 6.848(2)$ Å, $b = 17.966(5)$ Å, $c = 16.589(4)$ Å, $b = 90.78(3)°$, $V = 2040.8(9)$ Å^3 (by least squares refinement of 125 reflections), $\lambda = 0.71073$ Å, $T = 173$ K, space group $P2_1/n$, $Z = 4$, $D_x = 1.033$ g cm^{-3}, colorless rectangular rod 0.65 × 0.16 × 0.12 mm, μ(Mo Kα) = 0.062 mm^{-1}. R_1 (obs) = 0.0581, $S = 0.961$. The near 90° β gave rise to pseudomerohedral twinning (pseudoorthorhombic, twin law (1 0 0, 0 −1 0, 0 0 −1)) in the crystal. The twin component refined to 0.154(3). Due to the weak diffraction of the crystal, data with $2\theta > 48°$ were omitted from the least squares refinement.

10.1021/ja9819312 CCC: $15.00

Table 1. Selected Geometrical Data for **1** and **11**

	1	**11**		**1**	**11**
		bond lengths			
C(1)−N(2)	1.319(5)	1.283(5)	N(2)−C(3)	1.503(5)	1.501(5)
C(1)−O(1)	1.379(5)	1.321(4)	O(1)−C(4)	1.415(5)	1.427(4)
N(2)−C(2)	1.488(6)	1.493(5)			
		bond angles			
N(2)−C(1)−O(1)	109.3(3)	118.8(3)	C(1)−N(2)−C(3)	126.8(4)	121.5(3)
C(1)−N(2)−C(2)	116.1(3)	119.0(3)	C(1)−O(1)−C(4)	112.6(3)	118.5(3)
		torsion angles			
C(2)−N(2)−C(1)−O(1)	−179.8(4)	−179.3(3)	C(1)−O(1)−C(4)−C(5)	−84.8(5)	−95.5(4)
C(3)−N(2)−C(1)−O(1)	0.6(7)	−0.5(5)	C(1)−O(1)−C(4)−C(9)	97.8(4)	91.9(4)

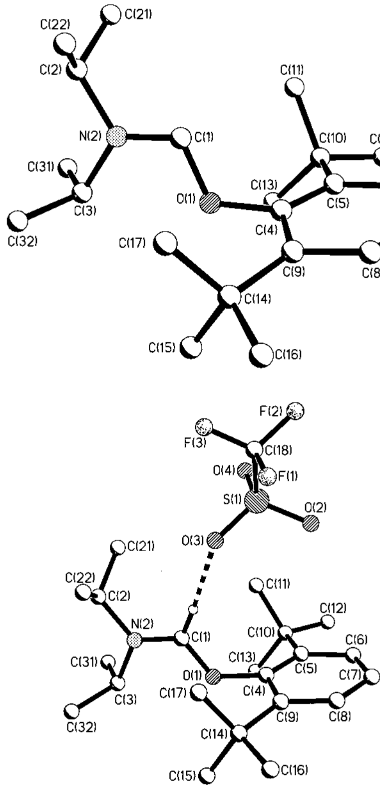

Figure 1. Structure of (a, top) carbene **1** and (b, bottom) alkoxyiminium salt **11**. The H(1)−O(3) distance is 2.19 Å.

no overlap between the aromatic ring π-orbitals and the oxygen p-type lone pair, and this is reflected in the lengths of the O−C$_{\text{aryl}}$ bonds in **1** and **11**. The C$_{\text{carbene}}$−O bond lengthens much more than the C$_{\text{carbene}}$−N bond on going from cation **11** to carbene **1**, and it probably has very little π-character in **1**. The length of the C$_{\text{carbene}}$−N bond is typical of iminium ions in **11**, and while it does lengthen in **1**, it is still short enough to suggest strong π-bonding and ylidic character; note that the nitrogen atom is flat ($\sum$(C−N−C) 360.000). The structural data for **1** plainly indicate that electron donation from the nitrogen lone pair is more important than from that on oxygen.

Carbenes **1**−**5** all show separate, sharp ^{1}H and ^{13}C absorptions for the two different alkyl substituents on the nitrogen atoms at ambient temperatures, indicating slow rotation about the C$_{\text{carbene}}$−N bond; this is also observed for the precursor iminium ions. Inspection of models of **1** (and **11**) shows that serious nonbonded interactions between the isopropyl and *tert*-butyl groups are likely in the transition state for rotation about the C$_{\text{carbene}}$−N bond, but these interactions appear to be absent for the other cases such as **2**. At 105 °C in toluene-d_8, the line widths for the ^{1}H NMR signals of the methyl groups in **2** are not detectably dynamically broadened, leading to a rate constant of <5 s^{-1}, and a lower limit of 88 kJ mol^{-1} for the barrier to rotation about the C$_{\text{carbene}}$−N bond. Thus, the barrier is much higher than the 53 kJ mol^{-1} barrier observed for **7**. While steric effects, including destabilization of the ground state in **7**, will complicate any detailed comparison, the extra demand for π-electron donation being made on the single nitrogen in **2** probably contributes to this increased barrier.

Carbenes **1**−**5** do not dimerize at ambient temperatures. Carbenes **1**−**3** are also stable in toluene-d_8 at 100 °C, showing no sign of dimerization or of 1,2-aryl shift to give amides. The unexpectedly long life of simple diaminocarbenes such as **8** in solution suggests that less sterically hindered examples of alkoxydialkylaminocarbenes should be observable, and this is currently under study.

Acknowledgment. We thank EPSRC for financial support of this work (Grant GR/K76160) and Professor G. R. Weisman for NMR simulations and helpful discussions.

Supporting Information Available: Preparative procedures and spectroscopic data for **1**−**5** and **11**−**15**, details of X-ray diffraction experiments, structural information, and ORTEP plots for **1** and **11** (17 pages, print/PDF). An X-ray crystallographic file, in CIF format, is available through the Internet only. See any current masthead page for ordering information and Web access instructions.

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(21) Crystal data for **11**: $C_{22}H_{36}F_3NO_4S$, $M = 467.58$, orthorhombic, $a = 9.717(3)$ Å, $b = 15.133(5)$ Å, $c = 17.025(6)$ Å, $V = 2503.6(14)$ Å^3 (by least squares refinement of 57 reflections), $\lambda = 0.71073$ Å, $T = 173$ K, space group $P2_12_12_1$, $Z = 4$, $D_x = 1.240$ g cm^{-3}, colorless rectangular block $0.70 \times 0.41 \times 0.39$ mm, μ(Mo Kα) = 0.178 mm^{-1}. R_1 (obs) = 0.0701, $S = 0.905$.