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CO Fixation to Stable Acyclic and Cyclic Alkyl Amino Carbenes: Stable Amino Ketenes with a Small HOMO–LUMO Gap**

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Keywords

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Reactive intermediates play a central role in modern chemistry.[1] Since 1900, and the discovery by Gomberg of a stable radical,[2] many species that were thought to be too short-lived for observation have been isolated. The availability of stable versions of reactive intermediates has allowed for a superior control of their reactivity and a better understanding of the mechanism of chemical reactions. Even more importantly, new applications of these species have been found, for example, the successful use of stable carbenes as ligands for transition-metal catalysts,[3] and even as organic catalysts.[4]

There are still several families of synthetically important reactive intermediates, the preparation of which has been impeded by the belief that they are incapable of existence, or has eluded the synthetic skills of investigators. Because of their very high reactivity, ketenes are key intermediates in synthetic organic chemistry, and have even found industrial applications.[5–7] Despite the isolation of diphenylketene as early as the beginning of the 20th century,[8] most ketenes are intrinsically unstable and cannot be isolated.[5] Calculations have predicted that σ -electron-withdrawing substituents, as well as π -donor groups destabilize ketenes.[9] Accordingly, alkoxy ketenes have only been characterized at low temperature or by fast-spectroscopic methods,[10] whereas amino ketenes have never been observed.[11]

Transient triplet carbenes, such as methylene, react with CO to give the corresponding ketenes.[12] In contrast, although the carbonylation of singlet carbenes is spin-allowed, there are very few examples of ketene formation using this route.[13] In 1994 it was claimed that the imidazol-2-ylidene **1a** reacts with carbon monoxide to give the stable diamino ketene **2a** (Scheme 1).[14] However, a year later Arduengo et al.[15] were not able to duplicate these experimental results. They demonstrated computationally that the parent compound **2b** is not even a transition state, and found that there is no stable structure associated with the combination of **1b** and CO, other than “a non-bonded weakly interacting (van der Waals) complex” **3b** (scheme 1). Moreover, the calculations showed that the CO addition leading to **2b** is not favored thermodynamically [$\Delta H(298\text{ K}) = +15.9\text{ kcalmol}^{-1}$].[15]

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Herein we report that, in marked contrast with cyclic diamino carbenes **1**, stable acyclic **4a** [16] and **4b**, and cyclic alkyl amino carbenes (CAACs) **6**[17] react with CO to afford amino ketenes **5a,b** and **7**, respectively (see Scheme 2), which are indefinitely stable at room temperature both in solution and in the solid state. We show that the ring structure forces the planarization of the amino fragment of **7**, and therefore causes the destabilizing n- π donation from the amino group. Consequently, the HOMO of the ketene **7** is raised and the singlet-triplet gap considerably reduced, which induces unusual optical and NMR spectroscopic properties.

According to calculations,[16] the singlet-triplet gap (26.7 kcalmol⁻¹) and the HOMO (-4.3 eV) for acyclic alkyl amino carbenes **4** are much smaller and higher in energy, respectively, than for NHCs **1** (79.6 kcalmol⁻¹ and -5.4 eV).[18] Consequently, carbenes **4** are more nucleophilic but also more electrophilic than NHCs **1**, and are therefore better candidates for a carbonylation reaction. Indeed, when carbon monoxide was bubbled at room temperature through a THF solution of acyclic carbene **4a**, a clean reaction occurred, and after evaporation of the solvent under vacuum, ketene **5a** was obtained in good yield as a pale yellow oil (Scheme 2). The IR spectrum of **5a** shows a very strong C=C=O stretching vibration at 2066 cm⁻¹, and the ¹³C NMR signals for the ketene group appear at δ = 213.95 (CCO) and 60.90 (CCO) ppm; all these values are expected for a ketene bearing a σ -electron-withdrawing group.[9] Only one set of NMR signals was observed for the isopropyl substituents, which suggests free rotation around the N-CCO bond.

Starting from carbene **4b**, which has cyclohexyl instead of isopropyl groups, ketene **5b** was isolated as pale yellow crystals (m.p.: <20°C) suitable for X-ray diffraction (Figure 1).[19] Interestingly, the N-C1 bond (ca. 1.43 Å) is much longer than in carbene **4a** (1.30 Å), suggesting again the absence of interaction between the nitrogen lone pair and the CCO fragment. Indeed, molecule **5b** escapes the destabilizing n- π donation, by pyramidalization of the amino group (sum of the angles: 347.7°), and by directing the nitrogen lone pair 180° away from the CCO moiety. Consequently, the observed geometric parameters of the CCO fragment of **5b** are very similar to those calculated for the parent ketene H₂CCO (Table 1).[20]

The next challenge was to synthesize an amino ketene in which the nitrogen lone pair would be forced to stay parallel to the C=C π system. We have recently shown that despite the reluctance of phosphorus to be planar (inversion barrier 35 kcalmol⁻¹ for PH₃ compared to 5 kcalmol⁻¹ for NH₃), its incorporation into a ring, in addition to the use of bulky substituents, allowed us to force its planarization.[21,22] Applying the same concept, the CAAC **6** (Scheme 2) appeared to be the ideal precursor. As soon as carbon monoxide was bubbled at room temperature through a THF solution of CAAC **6**, a very deep blue color appeared. After evaporation of the solvent under vacuum, ketene **7** crystallizes from hexane at -20°C as blue crystals (65%, m.p.: 95-97°C) suitable for X-ray diffraction (Figure 2).[19] As expected, the nitrogen atom is in a planar environment (sum of the angles: 357.3°), and the lone pair is coplanar with the C=C π system. Although the N1a-C1 bond (ca. 1.40 Å) is much longer than that of carbene **6** (1.31 Å), it is similar to that observed for ketene **5b**. Similarly, in the IR spectrum, the C=C=O stretching vibration for **7** is at 2073 cm⁻¹, very close to that observed for **5** ($\Delta\nu$ = 7 cm⁻¹). These results suggest only a weak interaction between the nitrogen lone pair and the CCO fragment. However, compared to other ketenes, a dramatic red-shifted UV absorption is observed (very intense band from 500 to 700 nm, λ_{\max} 598 nm), as well as a spectacular downfield shift of the ¹³C NMR signal of the CCO carbon of **7** (δ \approx 278 ppm; Table 1).

To gain further insight into the electronic structure of amino ketenes **5** and **7**, density functional theory (DFT) calculations at triple-zeta basis set quality[20] were performed on the parent acyclic amino ketenes **5c_{pyr}** and **5c_{pla}** (Scheme 3), which feature a nitrogen atom in a pyramidal

(pyr) and planar (pla) environment, respectively. The calculated geometry and NMR chemical shifts for **5c_{pyr}** are similar to those observed experimentally for **5a,b** (Table 1). Of particular interest, the lone pair of **5c_{pyr}** is also directed 180° away from the CCO fragment. Forcing the nitrogen to be in a planar geometry, with the lone pair parallel to the C=C π system, costs 6.8 kcalmol⁻¹, and **5c_{pla}** is not even an energy minimum on the electronic hypersurface. In **5c_{pla}** the π-conjugation of the amino group with the adjacent C=C π bond has a drastic effect on the frontier orbitals. It raises the HOMO (π-C=C) while the LUMO (π*-C=O), is not affected. The resulting smaller HOMO–LUMO gap is in line with the smaller value of the adiabatic singlet–triplet energy separation, which decreases from 23.9 for **5c_{pyr}** to 17.0 kcalmol⁻¹ for **5c_{pla}**. In other words, forcing the π-conjugation with the adjacent amino substituent, as in the calculated **5c_{pla}** and observed ketenes **7**, induces a biradical character. The reduction of the HOMO–LUMO energy gap readily explains the red-shift of the π(C=C)→π*(C=O) optical transition. The small singlet–triplet energy gap leads to the enhancement of the paramagnetic term, and therefore the downfield shift of the ¹³C NMR signal of the CO carbon of **5c_{pla}** and **7**.

In conclusion, cumulenes **5** and **7** are the first ketenes prepared from CO fixation to stable carbenes. When compared to the parent ketene (H₂CCO), the presence of a pyramidal amino group as in **5** reduces the singlet–triplet energy gap by about 50%, and the planarization of the amino group as in **7** induces another 30% reduction to reach 17 kcalmol⁻¹. The small HOMO–LUMO energy gap induces unusual optical and NMR spectroscopic properties.[26] The design of ketenes featuring an even more pronounced diradical character is under active investigation.

Experimental Section

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ¹H and ¹³C NMR spectra were recorded on Varian Inova 300, 500, and Bruker Avance 300 spectrometers.

5a,b and **7**: Carbon monoxide was bubbled (30 min) at room temperature through a THF solution (20 mL) of the appropriate carbene **4a,b** and **6** (4.7 mmol). After evaporation of the solvent under vacuum and extraction with hexane (10 mL), ketene **5a** was obtained as a yellow oil (82% yield), whereas **5b** and **7** were isolated by crystallization in hexane at –20°C as yellow (80% yield) and blue crystals (65% yield), respectively. **5a**: ¹H NMR (C₆D₆, 300 MHz, 25 °C): δ = 3.08 (sept, 2H, CHCH₃, J = 6.7 Hz), 1.01 (s, 9H, C(CH₃)₃), 0.99 ppm (d, 12H, CHCH₃, J = 6.7 Hz); ¹³C NMR ([D₈]THF, 100 MHz, 25 °C): δ = 213.95 (CCO), 60.90 (CCO), 53.02, 30.71, 29.00, 21.99 ppm; IR (CH₂Cl₂): ν (CO) 2066 cm⁻¹; UV (hexane): λ_{max} 381 nm; DCI-MS *m/z* 170 [carbene + H⁺]. **5b**: m.p. <20°C; ¹H NMR (C₆D₆, 500 MHz, 25 °C): δ = 2.71 (m, 2H, CH), 1.02–1.90 (m, 20H, CH₂), 1.05 ppm (s, 9H, C(CH₃)₃); ¹³C NMR (C₆D₆, 125 MHz, 25 °C): 214.68 (CCO), 63.64, 62.26 (CCO), 34.31, 31.80, 29.92, 27.38, 26.61 ppm; IR (CH₂Cl₂): ν (CO) 2066 cm⁻¹; UV (hexane): λ_{max} 380 nm. **7**: m.p. 95–97°C; ¹H NMR (C₆D₆, 500 MHz, 25 °C): δ = 7.25–7.35 (m, 3H, H_{ar}), 3.92 (sept, 1H, CHCH₃, J = 7.0 Hz), 3.88 (sept, 1H, CHCH₃, J = 6.5 Hz), 2.74 (d, 1H, J = 13.0 Hz), 2.56 (d, 2H, J = 13.0 Hz), 1.58–1.78 (m, 4H), 1.47 (d, 3H, CHCH₃, J = 6.5 Hz), 1.46 (d, 3H, CHCH₃, J = 7.0 Hz), 1.44 (3H, CHCH₃, J = 6.5 Hz), 1.35–1.42 (m, 12H), 1.24 (d, 3H, CHCH₃, J = 7.0 Hz), 1.16 (d, 3H, CHCH₃, J = 7.5 Hz), 1.07 (d, 3H, CHCH₃, J = 6.5 Hz), 0.94 ppm (m, 1H); ¹³C NMR (C₆D₆, 125 MHz, 25 °C): 277.96 (CCO), 152.27, 151.97, 134.57, 128.93, 125.01, 124.94, 81.40 (CCO), 64.55, 55.04, 53.76, 49.89, 49.79, 35.17, 31.49, 30.99, 30.66, 29.17, 29.11, 28.36, 27.13, 26.49, 25.71, 24.87, 24.21, 23.80, 23.02, 18.65 ppm; IR (CH₂Cl₂): ν (CO) 2073 cm⁻¹; UV (hexane): λ_{max} 598 nm; DCI-MS *m/z* 383 [carbene + H⁺].

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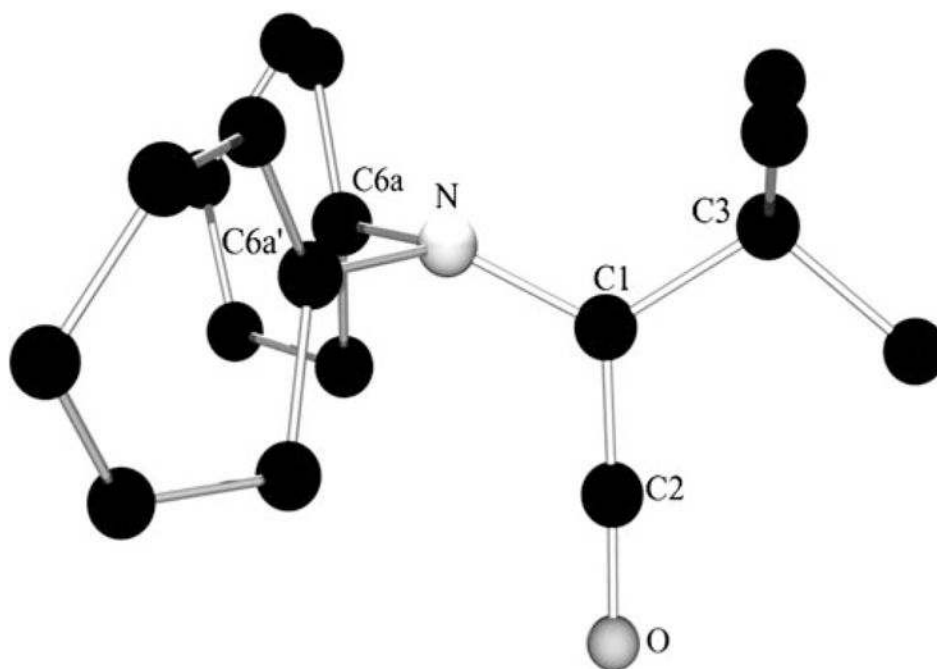


Figure 1. Molecular view of the crystal structure of **5 b**. Selected bond lengths [\AA] and angles [$^\circ$]: N–C1 1.426(4), C1–C2 1.310(5), C2–O 1.174(4), C1–C3 1.517(4), N–C6a 1.417(7); N–C1–C3 122.6(3), C3–C1–C2 119.2(3), N–C1–C2 118.2(3), C6a–N–C1 127.7(3), C6a'–N–C1 127.7(3), C6a'–N–C6a 92.3(5).

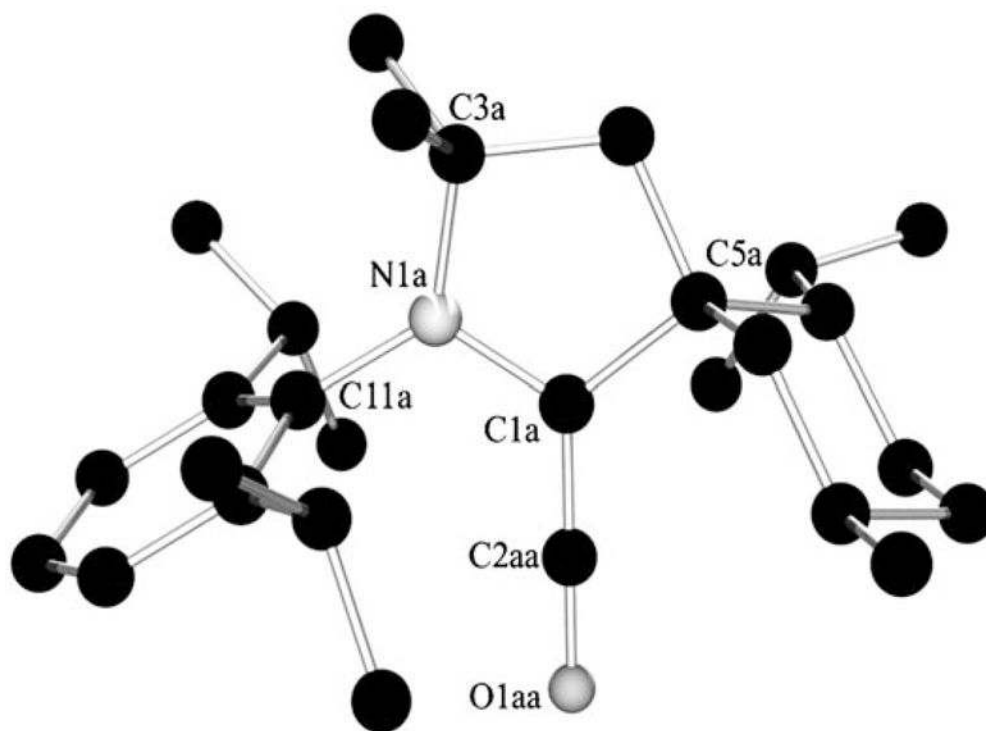
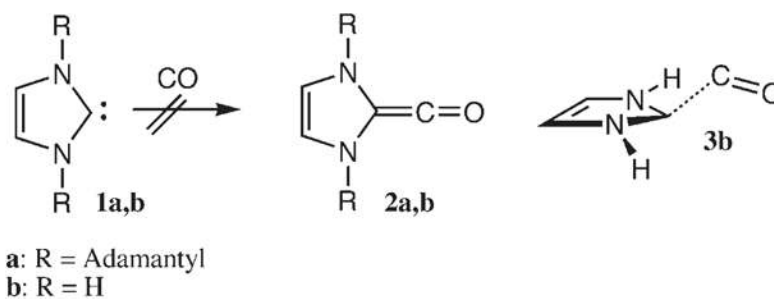
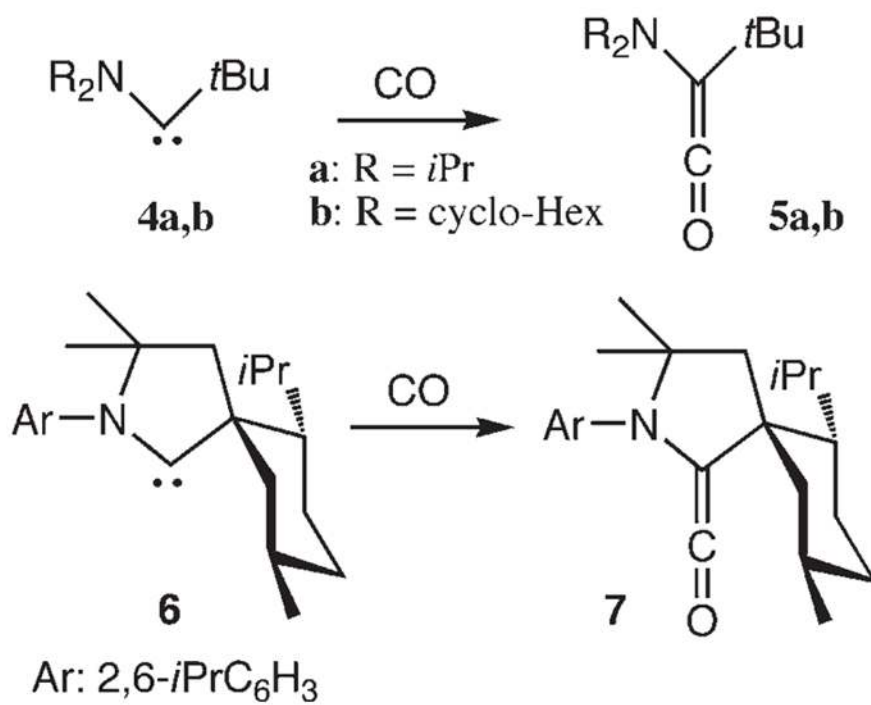


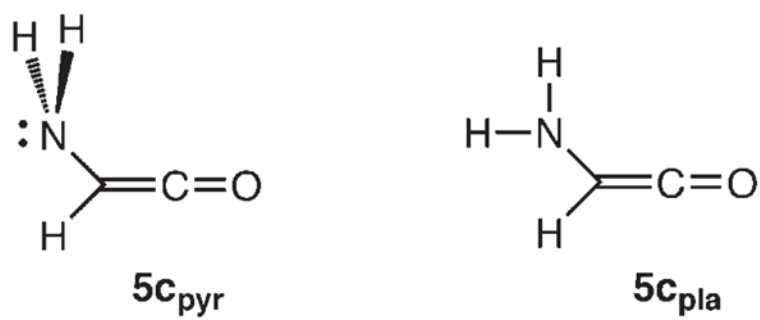
Figure 2. Molecular view of the crystal structure of **7**. Selected bond lengths [\AA] and angles [$^\circ$]: N1a–C1a 1.405(2), C1a–C2aa 1.334(5), C2aa–O1aa 1.186(5) C1a–C5a 1.524(2), N1a–C11a 1.437(2); N1a–C1a–C5a 110.80(14), C5a–C1a–C2aa 125.6(2), N1a–C1a–C2aa 122.8(2), C11a–N1a–C1a 119.27(13), C11a–N1a–C3a 125.63(14), C3a–N1a–C1a 112.41(13).

**Scheme 1.**

N-heterocyclic carbenes (NHCs) do not react with CO; the structure of van der Waals complex **3 b**.



Scheme 2.
Addition of CO to carbenes **4 a,b** and **6**.



Scheme 3.
Schematic representations of the calculated parent amino ketenes **5 c_{pyr}** and **5 c_{pla}**.

Table 1

Comparison of the spectroscopic data, geometric parameters, and singlet-triplet (S/T) energy gap for ketenes.

| Ketene | ^{13}C CCO [ppm] | ^{13}C CCO [ppm] | IR $\nu_{\text{C=O}}$ [cm^{-1}] | UV λ_{max} [nm] | Σ_N^a [$^\circ$] | N-C1 [\AA] | C1-C2 [\AA] | C2-O [\AA] | S/T gap [Kcalmol^{-1}] |
|--------------------------------|---------------------------|---------------------------|--|--------------------------------|---------------------------|-----------------------|------------------------|-----------------------|-----------------------------------|
| H ₂ CCO | 194.0[23] | 2.5[23] | 2151[24] | 329[20] | | | 1.315[20] | 1.173[20] | 51.8[20] |
| Ph ₂ CCO | 201.2[23] | 47.6[23] | 2105[25] | 405[25] | | | | | |
| 5 a | 213.9 | 60.9 | 2066 | 381 | | | | | |
| 5 b | 214.7 | 62.3 | 2066 | 380 | 347.7 | 1.426 | 1.310 | 1.174 | |
| 5 C _{pyr} [20] | 209.1 | 35.6 | | 370 | 336.4 | 1.443 | 1.326 | 1.176 | 23.9 |
| 5 C _{pld} [20] | 288.1 | 53.7 | | 673 | 360 | 1.409 | 1.322 | 1.186 | 17.0 |
| 7 | 278.0 | 81.4 | 2073 | 598 | 357.3 | 1.405 | 1.334 | 1.186 | |