A Stable Diaminocarbene[†]

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We have previously reported the synthesis and isolation of a series of stable carbenes (imidazol-2-ylidenes).[1] These carbenes are stable at room temperature under an inert atmosphere and can be kept under these conditions indefinitely. A number of detailed theoretical and physical studies on these unusual molecules have been completed.[2] Several of these studies, both theoretical and physical, have concluded that while π-interactions (cyclic delocalization and/or resonance) in the imidazole ring may contribute somewhat to the stability of these carbenes, they do not appear to be a dominant feature and may not be required at all.[2] On the other hand, the saturated analogs of the imidazol-2-ylidenes (*i.e.*, imidazolin-2-ylidenes) have been extensively studied by Wanzlick and others and no stable, isolable, carbenes have been reported.[3−5] Also noteworthy is the observation that dimers of the imidazolin-2-ylidenes (C2−C2′ olefins) are well-characterized compounds[3,5] while the corresponding dimers of the unsaturated imidazol-2-ylidenes are unknown. We now report the isolation and characterization of a stable carbene in the saturated imidazolin-2-ylidene series. This structure is closely related to an imidazol-2-ylidene previously reported from our laboratory and differs only in the absence of the C4−C5 double bond in the imidazole ring. This result conclusively demonstrates that unsaturation in the imidazole ring is *not* required to produce a stable nitrogen-substituted carbene.

When 1,3-dimesitylimidazolinium chloride (**1**) reacts with potassium hydride in tetrahydrofuran (thf) at room temperature, the stable carbene 1,3-dimesitylimidazolin-2-ylidene (**2**) is formed through the elimination of KCl and H_2 (eq 1).[6] Potassium chloride precipitate is removed from the reaction mixture by filtration, and thf is evaporated *in vacuo*. The residue is recrystallized from hexane to afford pure carbene **2** (72%). The saturated carbene **2** is remarkably stable in the absence of oxygen and moisture and will even tolerate boiling hexane (69 °C). Pure **2** is a colorless crystalline solid that melts at 107−109 °C without decomposition.

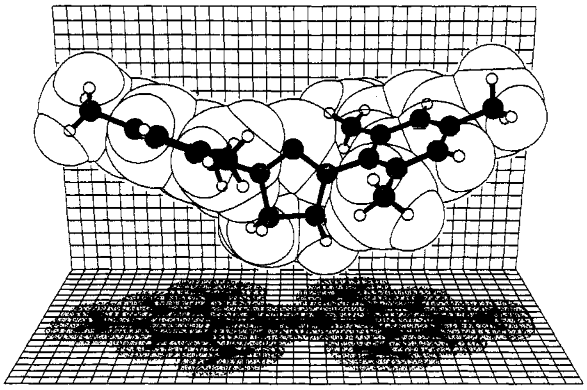
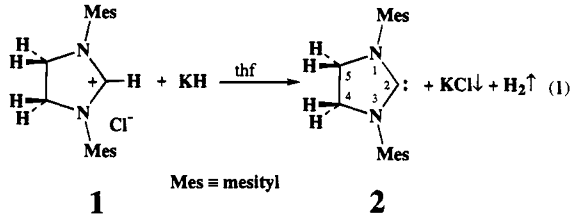


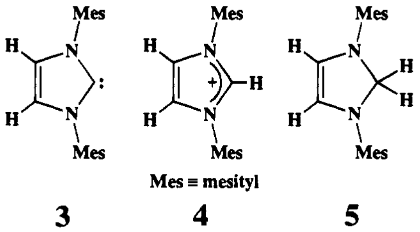
Figure 1. Space-filling KANVAS[7] drawing of the X-ray structure of **2**.



1 **2**

The ^{13}C NMR spectrum of **2** in thf-d_8 reveals a resonance at δ 244.5 that clearly identifies the compound as a carbene (*vide infra*). The high-resolution mass spectrum (EI/70 eV) gives the molecular ion at *m/z* 306.2093 (calcd 306.2095) and fragments for M^+ − ethylene at 278 and M^+ − mesityl isocyanide at 161).

A single crystal suitable for X-ray diffraction studies was grown by cooling a hexane solution of **2**. Interestingly, the structure of the saturated carbene (**2**) is isomorphic with the original unsaturated carbene structure (**3**). The X-ray crystal structure of **2** is depicted in Figure 1.[7] Selected bond lengths and angles are given in Table 1 along with related structural parameters from the carbenium ion **1**, the unsaturated carbene (1,3-dimesitylimidazol-2-ylidene, **3**) and the carbenium ion **4** derived from protonation of **3**. The final *R* factors for **2** were $R = 0.053$ and $R_w = 0.040$.



3 **4** **5**

Several noteworthy features are evident in the X-ray structure of **2**. One is the N−C−N angle at the carbene center. This

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[†] In memory of Frederick N. Tebbe, 1935−1995.

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(6) Under dry nitrogen at 25 °C a suspension of 381 mg (1 mmol) of **1** in 20 mL of thf was added to 150 mg of a 35% suspension of potassium hydride in mineral oil (corresponding to 1.3 mmol of KH). Immediately a moderate evolution of gas began. The mixture was stirred for 3 h at 25 °C. The mixture was filtered through a glass frit covered with filter aid, and the filtrate evaporated to give a light yellow solid. The crude product was recrystallized from hexane to give 220 mg (72%) of pure **2**: ^1H NMR (thf-d_8) δ 2.26 (s, *o*- + *p*-C*H*$_3$, 18 H), 3.71 (s, NC*H*$_2$, 4 H), 6.89 (s, *m*-*H*, 4 H); ^{13}C NMR [^1H] (thf-d_8) δ 18.26 (s, *o*-*C*H$_3$), 21.04 (s, *p*-*C*H$_3$), 51.36 (s, N*C*H$_2$), 129.55 (s, *m*-*C*), 136.64 (s, *p*-*C*), 136.78 (s, *o*-*C*), 140.21 (s, *ipso*-*C*), 244.5 (s, N*C*N); ^{14}N NMR (thf-d_8) δ −234; ^{15}N NMR [^1H] (thf-d_8) δ −236.7 (ref NH_4NO_3). Elemental anal. Found for **2**: C, 82.11; H, 8.99; N, 9.10 (theory: C, 82.31; H, 8.55; N, 9.14).

(7) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institute der Universitat Freiburg, Germany), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid, and the lighting source is at infinity so that shadow size is meaningful.

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Table 1. Selected Bond Lengths (pm) and Angles (deg) in **1**, **2**, **3**, and **4**

property	**2**	**1**	**3**[b]	**4**[c]
$r(C_2{-}N_{1(3)})$	135.2(5), 134.5(5)	132.7(5), 131.0(5)	136.5(4), 137.1(4)	133.2(5), 131.9(5)
$r(C_4{-}C_5)$	150.5(6)	151.8(7)	133.3(5)	135.3(6)
$r(N_{1(3)}{-}C_{5(4)})$	147.5(5), 148.7(5)	149.8(6), 148.7(6)	138.1(4), 137.8(4)	138.5(5), 138.2(5)
$r(N_{1(3)}{-}C_{mes})$	142.7(5), 143.7(5)	143.2(5), 143.7(6)	144.1(4), 144.2(4)	145.6(5), 144.5(5)
$\theta(N_1{-}C_2{-}N_3)$	104.7(3)	113.1(4)	101.4(2)	108.7(4)
$\theta(C_{5(4)}{-}N_{1(3)}{-}C_2)$	115.0(3), 114.6(3)	109.7(4), 110.6(4)	112.8(3), 112.8(3)	109.0(4), 108.7(4)
$\theta(N_{1(3)}{-}C_{5(4)}{-}C_{4(5)})$	101.6(4), 101.9(4)	103.0(4), 103.3(4)	106.5(3), 106.5(3)	106.1(4), 107.5(4)
$\theta(C_2{-}N_{1(3)}{-}C_{mes})$	122.9(3), 122.5(3)	127.0(4), 126.2(4)	121.8(2), 122.6(2)	125.8(4), 127.1(4)

[a] The numbering scheme for all compounds is as indicated for **2**. [b] Reference 1b. [c] Reference 10.

angle (104.7°) is opened somewhat relative to the unsaturated analog **3** (101.4°).[1b] The larger N−C−N angle relative to **3** may reflect strain introduced by the longer $C_4{-}C_5$ and $C_{4(5)}{-}N_{3(1)}$ bonds that result from reduction of the double bond. The average length of the $C_2{-}N_{1(3)}$ bonds in **2** (134.9 pm) increases only 3 pm from the average value of 131.9 pm found in the imidazolinium salt **1**, and a similar but slightly larger trend is observed in the unsaturated series.[1b] The nitrogen bonds to the carbene center in **2** are very slightly shorter than those found in the unsaturated compound **3** ($\Delta\bar{r}$ = 1.9 pm).[1b] It is tempting to attribute this difference to increased π-interactions at the carbene center, but σ-effects from the increase in the N−C−N angle will also shorten these bonds. The lengths of the $N_1{-}C_5$, $N_3{-}C_4$, and $C_4{-}C_5$ bonds clearly identify these as single bonds and are very similar in **1** and **2**. The imidazoline ring in **2** is not perfectly planar. The C_4 and C_5 centers respectively deviate 90 pm above and 148 pm below the plane of the other three imidazoline ring atoms. The two nitrogens are also very slightly pyramidal so that the *ipso* carbons of the mesityl substituents lie 89 pm below (at N_1) and 82 pm above (at N_3) the N−C−N plane in the imidazoline ring.

The bulky mesityl groups at nitrogen in **2** probably provide some measure of kinetic stability by hindering the dimerization of carbene centers along a non-least-motion pathway.[8] Examination of the precise role of steric factors in stabilizing **2** will have to await the synthesis of imidazolin-2-ylidenes with other substituents.

The chemical shift of the carbene center in **2** at δ 244.5 is appromixately 25 ppm downfield of the carbene resonance in the corresponding unsaturated carbene, **3**.[1b] This downfield shift is consistent with expectations based on previously reported anaylsis of the carbene shielding tensors in imidazol-2-ylidenes, ^{1}:CF_2 and ^{1}:CH_2.[2c] In the ^{1}H NMR spectrum, the *o*-methyls of the mesityl groups provide additional information on the changes in the saturated carbene **2** relative to the unsaturated analog **3**. The *o*-methyls in **2** (thf-d_8) resonate 0.24 ppm downfield of their resonance in **3** (δ 2.02).[1b] It is interesting also to consider the *o*-methyls in compound **5**, in which the carbene center of **3** has been replaced by a CH_2 group. This could disrupt potential delocalization in the imidazole ring of **3** at the 2-position.[9] The *o*-methyls in **5** (thf-d_8) resonate at δ 2.32, 0.30 ppm downfield of the *o*-methyl resonance in the unsaturated imidazol-2-ylidene **3**. If the protons in the 4- and 5-positions of the imidazole ring are considered, the resonance in **5** (δ 5.60) is upfield of that in **3** (δ 7.04) by 1.44 ppm. Similar shift trends are also seen for **2**, **3**, and **5** in benzene-d_6. Since the *o*-methyls in these compounds are positioned above (and below) the imidazole ring, they could be shielded by "ring current" effects in **3**. The position of the C_4 and C_5 protons in the plane of the imidazole ring would subject them to deshielding by anisotropy in the ring. The observed shift trends in both the *o*-methyls and $H_{4\&5}$ are consistent with some degree of aromatic π-character in **3** although other sources of anisotropy cannot be discounted. The ^{13}C NMR shifts of the *o*-methyls in **2** (δ 21.04), **3** (δ 18.04), and **5** (δ 18.98) suggest a similar trend, but the small downfield shift of the resonance in **5** relative to **3** is puzzling and suggests that other sources of anisotropy need to be carefully considered.

The existence and remarkable stability of the saturated carbene **2** demonstrate that the $C_4{-}C_5$ double bond is not critical to construction of a stable diaminocarbene. Clearly, Wanzlick's original hypothesis of stable carbenes in the imidazoline system was correct.[3a] The small structural changes at the carbene center of **2** relative to the unsaturated analog **3** can be attributed to σ-effects from an increase in the N−C−N angle that is a result of the longer bonds to the sp^3 centers at C_4 and C_5. However, some increase in $C_2{-}N_{1(3)}$ π-interactions cannot be ruled out. NMR comparisons of **2**, **3**, and **5** suggest some role for π-interactions in **3**. These interactions (which are not apparent in experimental electron density maps[2b]) do not appear to be dominant in determining the stability of imidazol-2-ylidenes and imidazolin-2-ylidenes although they undoubtedly enhance the stability of the unsaturated compounds over their saturated analogs. Additionally, one should consider that the unsaturation in **3** provides opportunities for chemistry not available in the saturated analogs and thus could lower the apparent stability of the unsaturated compounds under some circumstances. For example, consider the extended hydrogen-bonding networks that are seen in the imidazol-2-ylidene series.[10]

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Supporting Information Available: Complete description of the X-ray crystallographic determinations on **1** and **2**, including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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