gel (1 g, 25% ethyl acetate/hexane) afforded **45** (23.1 mg, 73%): IR (neat) 2975, 2925, 1720, 1700, 1600, 1460, 1440, 250, 1180, 1040, 760, 690; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.92 (s, 3 H, CCH_3), 1.21 (d, J = 7.3 Hz, 3 H, CHCH_3), 1.31 (t, J = 7.1 Hz, 6 H, two OCH$_2$CH_3), 4.13–4.50 (m, 5 H, two OCH_2CH$_3$, CHCH$_3$), 6.35 (s, 1 H, olefinic CH), 7.43–7.53 (m, 3 H, phenyl CH), 7.56–7.67 (m, 2 H, phenyl CH). Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.54; H, 6.60.

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Electronic Stabilization of Nucleophilic Carbenes[1]

Anthony J. Arduengo, III,* H. V. Rasika Dias, Richard L. Harlow, and Michael Kline

Contribution No. 6107 from Du Pont Central Research, Experimental Station, Wilmington, Delaware 19880-0328. *Received January 14, 1992*

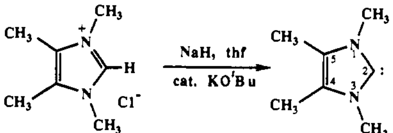
Abstract: Four new stable nucleophilic carbenes have been synthesized and structurally characterized. The remarkable ability of the imidazole nucleus to stabilize a carbene center at the C-2 position is demonstrated by the isolation of 1,3,4,5-tetramethylimidazol-2-ylidene. The isolation of three imidazol-2-ylidenes that bear aryl substituents is counter to speculations based on previous reports.

Introduction

Carbenes[2] are two-coordinate carbon compounds that have two nonbonding electrons and no *formal charge*[3] on the carbon. These types of two-coordinate carbon compounds essentially represent carbon in an oxidation state of II. Oxidation state II is well represented in carbon chemistry by stable monocoordinated carbon centers such as those in carbon monoxide (C═O) and isonitriles (R—N═C). In biochemistry, structures such as thiamine-derived intermediates can be formulated as either zwitterions (ylides) or carbenes.[4] However, in the absence of isolable model compounds, the best characterization for these important intermediates remains a matter for speculation. Stable compounds in the carbene category have been made only recently, and definite structural and electronic information is now available.[5–7] Apparently, the stability of these carbenes is derived from a combination of steric and electronic factors. These factors achieve the stability necessary for isolation. We now describe the syntheses and structures of four new stable carbenes. Structural features of these new carbenes suggest that steric factors are unimportant in contributing to the stability of the imidazol-2-ylidenes.

Results and Discussion

Most remarkably, carbene **2** (1,3,4,5-tetramethylimidazol-2-ylidene) is obtained in 89% yield when 1,3,4,5-tetramethylimidazolium chloride (**1**) is treated with 1 equiv of sodium hydride and 5 mol % potassium *tert*-butoxide in tetrahydrofuran (thf) (eq 1). Carbene **2** is a colorless crystalline solid melting at 109–110 °C. A previously melted sample of **2** showed no depression of the melting point upon remelting. Samples of **2** could be purified by recrystallization from toluene or vacuum sublimation. The ^{1}H NMR spectrum (thf-d_8) shows only two resonances of equal area at 2.01 and 3.48 for the methyls on carbon and nitrogen. The ^{13}C NMR spectrum has a resonance at δ 213.7 similar to the value of 211.4 found for the carbene center of **3** (Table I).



1 **2** (1)

Cooling a toluene solution of **2** gave crystals suitable for X-ray diffraction studies. The resulting structure for **2** is shown in Figure 1. Selected bond lengths and angles are given in Table II. The molecule sits on a crystallographic 2-fold axis. The five ring atoms are planar by symmetry, and the methyl carbons at nitrogen and carbon deviate by 0.023 and 0.049 Å, respectively, from the molecular plane.

The KANVAS[8] drawing in Figure 1 illustrates the unencumbered geometry of the carbene center in **2**. The lack of significant steric hindrance in **2** starkly contrasts the previously synthesized stable carbene, 1,3-di(1-adamantyl)imidazol-2-ylidene (**3**).[5] The structures of **2** and **3** are quite similar, but there are some slight differences that are noteworthy. The valence angle at the carbene center in **2** is 0.7° smaller than the same angle in **3**. The ring internal angle at nitrogen is 1.3° larger for **2** compared to **3**. The $N_{1(3)}$—C_2 bond distance is 0.7 pm shorter in **2** than in **3**. The $N_{1(3)}$—$C_{5(4)}$ bond distance is 1.2 pm longer and the ring C═C distance is 1.4 pm longer in **2** than in **3**. These differences bring the experimental structure of **2** very close to the calculated structure for the unsubstituted imidazol-2-ylidene.[9] This result supports our earlier assumption[9] that small differences in the calculated structure for the unsubstituted imidazol-2-ylidene and the experimental structure of **3** are the result of steric influences of the 1-adamantyl substituent on the imidazole ring. Very similar trends can be seen among the structures observed for the 1,3-di(1-adamantyl)imidazolium and 1,3-dimethylimidazolium ions and the structure calculated for the unsubstituted imidazolium ion.

We also have observed another sterically unencumbered carbene, 1,3-dimethylimidazol-2-ylidene (**4**), in solution. Although

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[1] Dedicated to Dr. H. E. Simmons, Jr. on the occasion of his retirement.

[2] The term "carbene" was first used in connection with this type of structure in a Chicago taxi; see: Doering, W. v E.; Knox, L. H. *J. Am. Chem. Soc.* **1956**, *78*, 4947 footnote 9.

[3] The *formal charge* at an atom is determined by its valence bond representation. The significance of *formal charges* has been discussed elsewhere: Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 8 and 9 and references therein.

[4] For a recent paper on the generation of thiamine-related intermediates, see: Bordwell, F. G.; Satish, A. V. *J. Am. Chem. Soc.* **1991**, *113*, 985. For a more comprehensive review, see: Kluger, R. *Chem. Rev.* **1987**, *87*, 863.

[5] Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

[6] Bertrand et al. have reported a stable compound than can be characterized either as a λ^3-phosphinocarbene or as λ^5-phosphaacetylene structures; see: Igau, A.; Grutzmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463 and Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 621. Recent theoretical models suggest that the best description is as a λ^5-phosphaacetylene; see: Dixon, D. A.; Dobbs, K. D.; Arduengo, A. J., III; Bertrand, G. *J. Am. Chem. Soc.* **1991**, *113*, 8782.

[7] Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 674.

[8] These drawings were 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 (Du Pont Central Research, 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.

[9] Dixon, D. A.; Arduengo, A. J., III *J. Phys. Chem.* **1991**, *95*, 4180.

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Table I. Selected NMR Chemical Shifts (ppm) in **2**–**4** and **7**–**9**[a,b]

nucleus	**2**	**3**	**4**	**7**	**8**	**9**
$^{13}C_2$	213.7	211.4[c]	215.2	219.7	215.8	216.3
$^{13}C_{4(5)}$	123.1	113.9[c]	120.5	121.3	118.8	119.2
$^{1}H_{4(5)}$		7.02 (6.91[c])	6.92	7.04 (6.48[c])	7.64 (6.96[c])	7.76 (6.68)[c]
$^{15}N_{1(3)}$	−198.5	−160.5[c]	−197.3	−178.9		
$^{14}N_{1(3)}$	−198	−161[c]	−197.5	−180	−171	−174

[a] The numbering scheme for all compounds is as indicated for **2**. [b] In thf-d_8 solution. References are tetramethylsilane or $NH_4^+NO_3^-$. [c] In benzene–d_6 solution.

Table II. Selected Bond Lengths (pm) and Angles (deg) in **2**, **3**, and **7**–**9**[a]

property	**2**	**3**	**7**	**8**	**9**
$r(C_2–N_{1(3)})$	136.3 (1)	136.7 (2), 137.3 (2)	136.5 (4), 137.1 (4)	137.1 (2), 137.5 (2)	136.8 (2), 136.8 (2)
$r(C_4–C_5)$	135.2 (2)	133.8 (3)	133.1 (5)	133.4 (2)	133.9 (2)
$r(N_{1(3)}–C_{5(4)})$	139.4 (1)	138.2 (2), 138.6 (2)	138.1 (4), 137.8 (4)	139.2 (2), 139.4 (2)	139.1 (2), 139.2 (2)
$r(N_{1(3)}–\text{subst})$	145.4 (1)	148.2 (2), 148.5 (2)	144.1 (4), 144.2 (4)	143.0 (2), 143.0 (2)	143.0 (2), 143.0 (2)
$r(C_{4(5)}–\text{subst})$	149.0 (1)	96.8 (20), 95.9 (22)	88.5 (36), 95.1 (48)	95.6 (16), 96.5 (19)	92.2 (17), 94.8 (16)
$\theta(N_1–C_2–N_3)$	101.5 (1)	102.2 (2)	101.4 (2)	101.2 (1)	101.7 (1)
$\theta(C_{5(4)}–N_{1(3)}–C_2)$	113.47 (8)	112.1 (2), 112.3 (2)	112.8 (3), 112.8 (3)	112.9 (1), 113.0 (1)	112.8 (1), 112.8 (1)
$\theta(N_{1(3)}–C_{5(4)}–C_{4(5)})$	105.78 (5)	107.2 (2), 106.2 (2)	106.5 (3), 106.5 (3)	106.6 (2), 106.2 (1)	106.4 (1), 106.3 (1)
$\theta(C_2–N_{1(3)}–\text{subst})$	122.9 (1)	123.4 (2), 122.1 (2)	121.8 (2), 122.6 (2)	123.1 (1), 122.9 (1)	122.6 (1), 122.0 (1)
$\theta(N_{1(3)}–C_{5(4)}–\text{subst})$	122.8 (1)	124 (1), 123 (1)	125 (3), 125 (2)	124 (1), 123 (1)	123 (1), 124 (1)

[a] The numbering scheme for all compounds is as indicated for **2**.

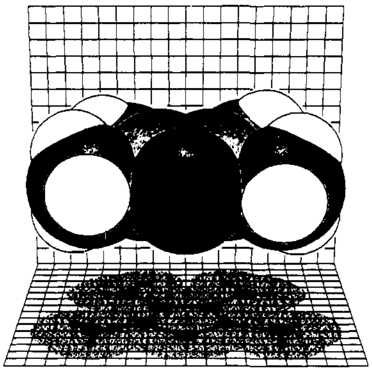
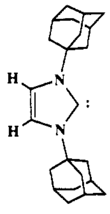
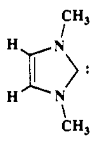


Figure 1. KANVAS[8] drawing of **2**.

4 persists in solution for days without decomposition, it is an unstable oily liquid when pure. The imidazole ring protons at $C_{4(5)}$ in **4** exhibit a resonance at δ 6.92 in the ^1H NMR spectrum (thf-d_8). In the ^{13}C NMR spectrum a resonance is found at δ 215.2 for the carbene center. The multitude of decomposition products from **4** have not been characterized.



3

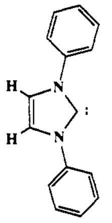


4

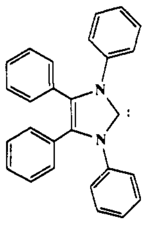
The stability of **3** was attributed to a combination of steric and electronic factors.[5,9] The electronic factors operate in both the π- and σ-framework. In the π-framework, electron donation into the carbene out-of-plane p-orbital by the electron-rich system ($\ddot{N}—C{=}C—\ddot{N}$) leads to a moderation of the typical electrophilic reactivity of carbenes. In the σ-framework, additional stability for the carbene electron pair may be gained from the σ-electron-withdrawal effects on the carbene center by the more electronegative nitrogens. This σ-effect would serve to moderate the nucleophilic reactivity of a 1A′ carbene. The combination of these σ- and π-effects serves to increase the singlet–triplet gap and stabilize the singlet carbene over the more reactive triplet state.[9,10]

The final stabilizing feature of **3** is the steric effect of the two adamantyl substituents. This steric effect should hinder reaction of the carbene center with external reagents. Prior to our discovery of **2**, it has not been possible to evaluate the relative importance of the steric and electronic factors.

The only previous evidence which has bearing on the relative importance of steric and electronic factors in stabilizing imidazol-2-ylidenes is supplied by H.-W. Wanzlick,[11] who recognized the potential for an imidazole ring to stabilize a carbene center at the 2-position. Wanzlick studied two specific imidazole derivatives, **5**[12] and **6**.[13]

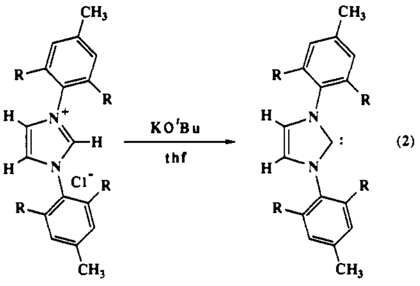


5



6

In light of the stability of **2**, it is puzzling that **5** and **6** were not isolated as stable solids. Both **5** and **6** are expected to be solids, so that their stability and isolation seem assured. It is possible that there is some subtle electronic effect of the phenyl rings that prevents the imidazole nitrogens from sufficiently stabilizing the adjacent carbene center. To separate the σ- and π-effects of the N-aryl substituents, we decided to attempt the synthesis of two aryl-substituted carbenes **7** and **8**.



(2)

7 R = CH$_3$
8 R = H

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(10) More recently this "push-pull" synergistic effect has been invoked for halocarbenes: Irikura, K. K.; Goddard, W. A., III; Beauchamp, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 48.

(11) Wanzlick, H.-W. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 75.

(12) Schönherr, H.; Wanzlick, H. *Chem. Ber.* **1970**, *103*, 1037.

(13) Wanzlick, H.; Schönherr, H. *Justus Liebigs Ann. Chem.* **1970**, *731*, 176.

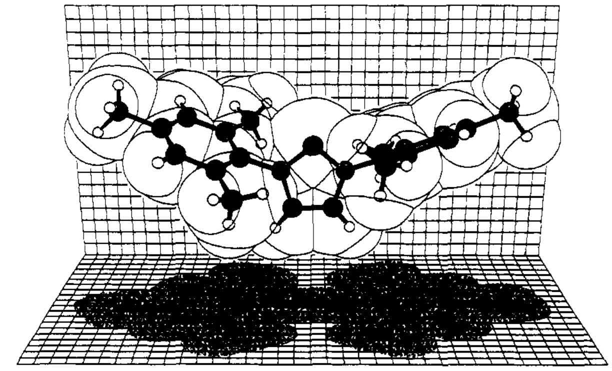


Figure 2. KANVAS[8] drawing of **7**.

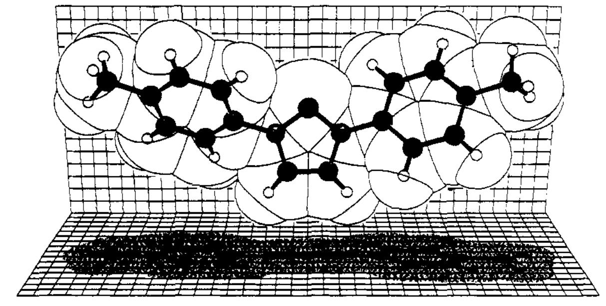


Figure 3. KANVAS[8] drawing of **8**.

The mesityl substituents of carbene **7** provide an opportunity to observe the σ-effect of an aryl substituent since the *o*-methyls will prevent conjugation between the phenyl rings and the nitrogen centers. On the other hand, the *p*-tolyl substituents of **8** will allow a π-effect because the rings can assume a planar (conjugating) arrangement.

Carbene **7** (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) is obtained in 84% yield when 1,3-bis(2,4,6-trimethylphenyl)-imidazolium chloride is treated with 1 equiv of potassium *tert*-butoxide in thf. Carbene **7** is a colorless crystalline solid melting at 150–155 °C dec. Samples of **7** can be purified by recrystallization from hexane. The ^{1}H NMR spectrum (thf-d_8) of **7** shows a resonance for the imidazole ring protons at C$_{4(5)}$ of 7.04, which is quite similar to the values in **3** (7.02 in thf-d_8) and **4** (6.92 in thf-d_8). The ^{13}C NMR spectrum of **7** reveals the carbene resonance at δ 219.69, similar to the carbene centers in **2–4** (Table I).

Cooling a hexane solution of **7** gave crystals suitable for X-ray diffraction studies. The X-ray crystal structure of **7** is depicted in Figure 2. Selected bond lengths and angles are given in Table II. The imidazole ring is essentially planar, with no atom deviating from the best plane by more than 0.005 Å. Substituent atoms at both nitrogens are also essentially coplanar with deviations of 0.059 and 0.030 Å. The two mesityl substituents are substantially twisted with respect to the imidazole plane with interplane angles of 80° and 71°. The orientation of the mesityl substituents is conrotatory, such that there is a pseudo 2-fold axis passing through the carbene center.

The twists of the mesityl substituents in **7** prevent conjugation with the imidazole ring. The mesityl substituents substantially hinder the imidazole ring from above and below due to the four *o*-methyls. However, approach to the carbene center in the plane appears to be unencumbered as indicated in Figure 2. Carbene **7** does not survive melting at 150 °C but is sufficiently stable to allow isolation and easy manipulation. It does not appear that there is any special σ-effect of aryl substituents that detracts from imidazol-2-ylidene stability.

The general compatibility of the imidazol-2-ylidene moiety with simple aryl substituents is demonstrated by the synthesis and isolation of carbene **8**. Carbene **8**, 1,3-bis(4-methylphenyl)-imidazol-2-ylidene, is isolated in 45% yield from reaction of 1,3-bis(4-methylphenyl)imidazolium chloride with potassium *tert*-butoxide in thf (eq 2). Carbene **8** crystallizes from warm benzene as a colorless solid melting at 156–158 °C dec. The NMR spectra (thf-d_8) of **8** reveal the carbene center at δ 215.79 and the remaining imidazole ring protons at δ 7.64 (Table I). This chemical shift for the imidazole ring protons at C$_{4(5)}$ is substantially downfield of resonances for the same protons in **3**, **4**, and **7**. This shift difference is most likely the result of anisotropy of the aryl groups in **8** which can adopt a more nearly planar arrangement than in **7**. A similar chemical shift is observed for another aryl-substituted imidazol-2-ylidene, **9**, which bears no ortho substituents (vide infra).[14]

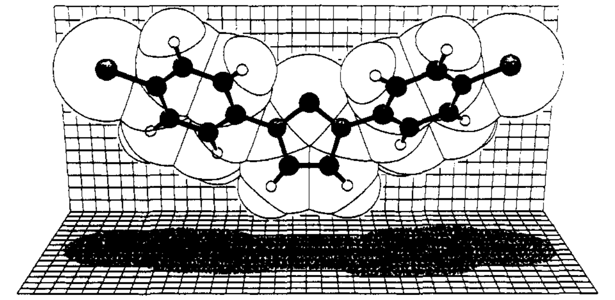
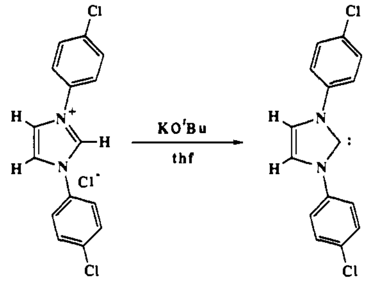


Figure 4. KANVAS[8] drawing of **9**.

Crystals of **8** were obtained by allowing a warm saturated benzene/diethyl ether solution to cool to room temperature. The X-ray crystal structure of **8** is depicted in Figure 3, and selected bond lengths and angles are given in Table II. As in **7**, the imidazole ring is essentially planar with no atom deviating from the best plane by more that 0.003 Å. Substituent atoms at both nitrogens are also essentially coplanar with deviations of 0.012 and 0.042 Å. The two tolyl substituents are more nearly planar with the imidazole ring than in **7**; however, they are still twisted with interplane angles of 31° and 34°. The twists of the tolyl substituents are in the same direction as found in **7**, so that again there is a pseudo 2-fold axis.

There does not seem to be any strong sensitivity of imidazol-2-ylidene stability to the electronic character of *N*-aryl substituents. The substituent constant, σ_p, for a 4-methyl group is −0.170.[15] For a 4-chloro substituent σ_p is 0.277.[15] The pK_a's of the corresponding anilinium ions for *p*-toluidine and *p*-chloroaniline are 5.08 and 4.15, respectively.[16] In spite of this difference of almost 1 order of magnitude in nitrogen basicity, the carbene with *N*-*p*-chlorophenyl substituents is as easily prepared and isolated as is **8**.



(3)

9

Carbene **9**, 1,3-bis(*p*-chlorophenyl)imidazol-2-ylidene, is obtained in 43% isolated yield when 1,3-bis(*p*-chlorophenyl)-imidazolium chloride reacts with potassium *tert*-butoxide in thf (eq 3). Carbene **9** crystallizes from warm benzene as a colorless solid melting at 153–155 °C dec. Similar to **8**, the NMR spectra (thf-d_8) of **9** reveal the carbene center at δ 216.28 and the re-

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(14) A related set of chemical shift variations can be seen for the *Z* β-proton in styrene (δ 5.59), 2,4,6-trimethylstyrene (δ 5.21), and 3,3-dimethyl-1-butene (δ 4.78). These latter shifts were observed in CCl$_4$: Sadtler Proton NMR Spectra, Sadtler Research Laboratories, spectra no.'s 6408, 8899, and 5318, respectively. It should be noted that 2,4,6-trimethylstyrene probably has more rotational freedom than **7** due to the absence of a second α-substituent.

(15) Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

(16) *CRC Handbook of Chemistry and Physics*; Chemical Rubber Publishing Company: Boca Raton, FL, 1986–1987; pp D159–160.

maining imidazole ring protons at δ 7.76 (Table I). The imidazole ring protons again show a downfield shift due to the anisotropic effects of the unhindered aryl substituents.

Crystals of **9** were obtained by allowing a warm saturated benzene solution to cool to room temperature. The X-ray crystal structure of **9** is depicted in Figure 4, and selected bond lengths and angles are given in Table II. As in the previous structures, the imidazole ring is essentially planar with no atom deviating from the best plane by more than 0.003 Å. Substituent atoms at both nitrogens are also essentially coplanar with deviations of 0.072 and 0.049 Å. The two *p*-chlorophenyl substituents have inclinations with respect to the central imidazole ring similar to those in **8** (interplane angles of 28° and 39°). However, the twists of the *p*-chlorophenyl substituents are in an orientation opposite (disrotatory) that found in **7** and **8**, so that there is no pseudo 2-fold axis but rather a pseudo mirror plane which is normal to the imidazole ring.

We have previously shown that theoretical models of the imidazol-2-ylidenes exhibit a small valence angle at the carbene center as well as the long carbene–substituent bond distances which are characteristic of 1A′ states for carbenes like $:CH_2$ and $:CF_2$.[9] The structures of these four new stable carbenes all possess these same geometric features. The structures of the imidazol-2-ylidenes show consistent differences from the structures of imidazolium ions, as we have previously discussed.[5] Typically, imidazolium ions have N–C–N angles in range the 108.3–109.7°, and the lengths of the C_2–$N_{1(3)}$ bonds range from 131.5 to 133.5 pm.[17] These differences between imidazolium (carbenium) ions and imidazol-2-ylidenes show that the imidazol-2-ylidenes respond to protonation as would be expected for 1A′ carbenes.

The exceptional stability observed for the adamantyl-substituted carbene (**3**) is at least partially derived from the steric hindrance offered by the adamantyl substituents. However, the electronic stabilization of the carbene center in imidazol-2-ylidenes is sufficient to provide stable, easily isolable carbenes even in the absence of steric protection, as demonstrated by the isolation of **2**, **8**, and **9**.

Conclusions

All four new carbene structures show the small valence angle at the carbene center which is characteristic of 1A′ carbenes. The long C_2–$N_{1(3)}$ bond distance is also typical for imidazol-2-ylidenes. Five substituent groups from alkyl (methyl and 1-adamantyl) to aryl (mesityl, *p*-tolyl, and *p*-chlorophenyl) have been shown to yield stable imidazol-2-ylidenes. In spite of the large variatioin in steric bulk and electronic character, the imidazol-2-ylidene moiety does not show any large structural variations. Contrary to the results of Wanzlick et al., the isolation of stable carbenes **7**–**9** demonstrates that aryl substituents can be tolerated on the imidazol-2-ylidene nucleus without severely affecting the stability. It is interesting to note that all three of the aryl-substituted carbenes have melting points of approximately 155 °C with decomposition. Possibly all of the aryl-substituted imidazol-2-ylidenes undergo decomposition with similar activation energies. The stability of the aryl-substituted imidazol-2-ylidenes is not as great as that observed for the adamantyl-substituted compound **3**.

The amazing stability of **2** proves that electronic stabilization of the carbene center in imidazol-2-ylidene is sufficient to produce stable species without the need of steric hindrance. Although **2**, **3**, and **7**–**9** have indefinite stability in the solid state, **8** and **9** decompose slowly in solution over a period of several days. We could not identify the dimer (olefin) among the decomposition products. Why Wanzlick did not isolate carbenes **5** and **6** as stable solids is not known, but we found that the imidazolium salts used as precursors in our work were difficult to dry. Wanzlick has noted a decomposition pathway for imidazol-2-ylidenes involving water.[12]

We are continuing to explore the chemistry of these stable nucleophilic carbenes.[18] The range of substituents that can be tolerated in the para positions of the *N*-arylimidazol-2-ylidenes is also under study.

Experimental Section

Reactions and manipulations were carried out under an atmosphere of dry nitrogen, either in a Vacuum Atmospheres dry box or using standard Schlenk techniques. Solvents were dried (using standard procedures),[19] distilled, and deoxygenated prior to use, unless otherwise indicated. Glassware was oven-dried at 160 °C overnight. ^1H NMR spectra were recorded on a General Electric QE-300 spectrometer. ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded on a GE Omega 300 MHz WB spectrometer. NMR references are $(CH_3)_4Si$ (^1H, ^{13}C) and $NH_4{}^+NO_3{}^-$ (^{14}N, ^{15}N). Melting points were obtained on a Thomas-Hoover capillary apparatus and were not corrected. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

1,3,4,5-Tetramethylimidazol-2-ylidene (2). A 50-mL round-bottom flask was charged with 1,3,4,5-tetramethylimidazolium chloride (**1**)[20] (5.25 g, 32.7 mmol), a stir bar, and 15 mL of thf. To this suspension was added oil-free sodium hydride (863 mg, 35.9 mmol) in a single portion. The suspension was stirred for 3 min to insure good mixing, and 184 mg (1.64 mmol, 5 mol %) of potassium *tert*-butoxide in 5 mL of thf was added as a single portion. The flask was capped with a septum, and the rate of hydrogen evolution was monitored by piercing the septum with a hypodermic needle connected to an oil-filled bubbler. After 4 h the reaction mixture was filtered through Celite, and the filtercake was washed with thf (2 × 25 mL). The combined filtrate and washes were concentrated under vacuum to give 3.46 g (89%) of **2** as a light yellow solid. 1,3,4,5-Tetramethylimidazol-2-ylidene could be further purified by recrystallization from thf or toluene to afford colorless crystals with mp 109–110 °C: ^1H NMR (thf-d_8) δ 2.01 (s, CCH_3, 6 H), 3.48 (s, NCH_3, 6 H); ^{13}C NMR δ 8.98 (s, CCH_3), 35.24 (bs, NCH_3), 123.05 (s, NCC), 213.73 (s, NCN); ^{15}N NMR δ −198.52 (reference $NH_4{}^{15}NO_3$). A sublimed sample of **2** gave satisfactory (±0.4%) C, H, and N analyses.

1,3-Dimethylimidazol-2-ylidene (4). A 300-mL round-bottom flask was charged with 1,3-dimethylimidazolium chloride[20] (10.28 g, 77.57 mmol), 2.05 g (85.4 mmol) of oil-free sodium hydride, a stir bar, and 150 mL of thf. The suspension was stirred for 3 min to insure good mixing, and 400 mg (3.6 mmol, 5 mol %) of potassium *tert*-butoxide in 10 mL of thf was added as a single portion. The flask was capped with a septum, and the rate of hydrogen evolution was monitored by piercing the septum with a hypodermic needle connected to an oil-filled bubbler. After 4.25 h the reaction mixture was filtered through Celitie, and the filtercake was washed with thf (2 × 20 mL). The combined filtrate and washes were concentrated under vacuum to give a light yellow viscous liquid. The oily liquid was transferred to a short-path distillation apparatus and flash distilled to give **4** as a mobile clear liquid. Approximately half of the material remained in the distillation pot as a dark, extremely viscous oil. The fresh distillate of **4** gave the following NMR spectra (thf-d_8): ^1H, δ 3.63 (s, CH_3, 3 H), 6.92 (s, NCH, 2 H); ^{13}C, δ 36.1 (s, CH_3), 120.5 (s, NCC), 215.2 (s, NCN); ^{15}N, δ −197.28 (reference $NH_4{}^{15}NO_3$). In thf solution the oily liquid **4** is somewhat stable and can be stored for several days at −30 °C without substantial decomposition. However, as a neat liquid **4** darkens and becomes extremely viscous even at low temperatures. There appears to be a multitude of decomposition products from **4**, and they have not been identified. It was not possible to identify NMR resonances for any material that might be the dimer.

1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (7). A 200-mL round-bottom flask equipped with a stir bar was charged with 10.0 g (29.3 mmol) of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride[20] and 80 mL of thf. The resulting suspension was stirred for 15 min. Solid potassium *tert*-butoxide (3.5 g, 31.2 mmol) was added to the suspension at room temperature in a single portion. A dark gray solution was obtained immediately. The mixture was stirred for 20 min, and volatiles were removed under vacuum. The residue was extracted into warm toluene (2 × 50 mL) and filtered through Celite, and the solvent was removed in vacuo to provide small crystals of carbene **7** (7.55 g, 84%).

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(17) For structures of representative imidazolium ions, see: (a) 1,3-dimethylimidazolium chloride (supplementary material, this work). (b) 1,3-di(1-adamantyl)imidazolium tetraphenylborate (ref 5, supplementary material). (c) Langer, V.; Huml, K.; Reck, G. *Acta Crystallogr., Sect. B* **1982**, *38*, 298. (d) Luger, P.; Ruban, G. *Z. Kristallogr.* **1975**, *142*, 177. (e) Abdul-Sada, A. K.; Greenway, A. M.; Hitchcock, P. B.; Mohammed, T. J.; Seddon, K. R.; Zora, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1753.

(18) Arduengo, A. J., III; Kline, M.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1991**, *113*, 9704.

(19) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: New York, 1985.

(20) These 1,3-disubstituted imidazolium chlorides are available by established procedures: Arduengo, A. J., III U.S. Patent 5 077 414, 1991. 1,3-Dimethylimidazolium chlorides are also available by alkylation of the appropriately substituted imidazole with 1.1 equiv of methyl chloride in thf at room temperature (sealed bomb).

Crude **7** was recrystallized from hexane to obtain colorless crystals: mp 150–155 °C dec; ^{1}H NMR (thf-d_8) δ 2.02 (s, 2,6-CH_3, 12 H), 2.30 (s, 4-CH_3, 6 H), 6.94 (s, ArH, 4 H), 7.04 (s, NC*H*, 2 H); ^{13}C NMR δ 18.04 (s, 2,6-*C*H$_3$), 21.04 (s, 4-*C*H$_3$), 121.28 (s, N*C*C), 129.69 (s, Mes *C*-3,5), 135.73 (s, Mes *C*-2,6), 137.55 (s, Mes *C*-4), 139.73 (s, Mes *C*-1), 219.69 (s, N*C*N); ^{15}N NMR δ −178.85 (reference NH$_4$^{15}*N*O$_3$). A recrystallized sample of **7** gave satisfactory (±0.4%) C, H, and N analyses.

1,3-Bis(4-methylphenyl)imidazol-2-ylidene (8). A 100-mL round-bottom flask equipped with a stir bar was charged with 1.61 g (5.65 mmol) of 1,3-bis(4-methylphenyl)imidazolium chloride[20] and 50 mL of thf. The resulting suspension was stirred for 15 min. Potassium *tert*-butoxide (0.650 g, 5.76 mmol) in 5 mL of thf was added to the suspension at room temperature in a single portion. The mixture was stirred for 20 min. The volatiles were removed under reduced pressure, and the residue was extracted into warm benzene (50 mL). The benzene solution was filtered through Celite. The filtrate was concentrated in vacuo and diluted with hexane to induce crystallization. The crystalline product was collected by filtration and rinsed with diethyl ether (2 × 1 mL) then hexane (2 mL) and dried under vacuum to afford 0.640 g (45%) of **8**. Crystals of **8** began to soften at 152 °C and melted at 156–158 °C dec: ^{1}H NMR (thf-d_8) δ 2.34 (s, CH_3, 6 H), 7.20 (dm, J_{HH} = 8.74 Hz, *m*-C*H*, 4 H), 7.64 (s, NC*H*, 2 H), 7.79 (dm, J_{HH} = 8.48 Hz, *o*-C*H*, 4 H); ^{13}C NMR δ 20.87 (s, *C*H$_3$), 118.78 (s, N*C*C), 121.06 (s, Ar *C*-3,5), 130.19 (s, Ar *C*-2,6), 136.12 (s, Ar *C*-4), 140.98 (s, Ar *C*-1), 215.79 (br s, N*C*N); ^{14}N NMR δ −171 (reference NH$_4$^{14}*N*O$_3$). Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.49; N, 11.28. Found: C, 82.24; H, 6.49; N, 10.77.

1,3-Bis(4-chlorophenyl)imidazol-2-ylidene (9). A 100-mL round-bottom flask equipped with a stir bar was charged with 0.500 g (1.53 mmol) of 1,3-bis(4-chlorophenyl)imidazolium chloride[20] and 20 mL of thf. The resulting suspension was stirred for 15 min. Potassium *tert*-butoxide (0.189 g, 1.68 mmol) in 5 mL of thf was added to the suspension at room temperature in a single portioin. The mixture was stirred for 20 min. The volatiles were removed under reduced pressure, and the residue was extracted into warm benzene (50 mL). The benzene solution was filtered through Celite. The filtrate was concentrated in vacuo and diluted with hexane to induce crystallization. The crystalline product was collected by filtration and rinsed with diethyl ether (2 × 1 mL) then hexane (2 mL) and dried under vacuum to afford 0.190 g (43%) of **9** (softened at 150 °C, melted with decomposition at 153–155 °C): ^{1}H NMR (thf-d_8) δ 7.42 (dm, J_{HH} = 9.12 Hz, *m*-C*H*, 4 H), 7.76 (s, NC*H*, 2 H), 7.93 (dm, J_{HH} = 8.85 Hz, *o*-C*H*, 4 H); ^{13}C NMR δ 119.24 (s, N*C*C), 122.54 (s, Ar *C*-3,5), 129.89 (s, Ar *C*-2,6), 132.22 (s, Ar *C*-4), 141.69 (s, Ar *C*-1), 216.28 (br s, N*C*N); ^{14}N NMR δ −174. A sample of **9** gave satisfactory (±0.4%) C, H, and N analyses.

Crystal Data for 2 at −100 °C with Mo Kα radiation: a = 977.7 (2), b = 692.9 (2), c = 1060.5 (2) pm; β = 94.00 (2)°; monoclinic, $C2/c$; Z = 4; μ(Mo) = 0.66 cm^{-1}; 758 unique reflections with $I > 3\sigma(I)$. The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares on F. Carbons and nitrogen were refined with anisotropic thermal parameters. Hydrogens were refined with isotropic thermal parameters. The largest residual electron density in the final difference Fourier map was 0.23 e/Å^3 near C-4(5). The data/parameter ratio was 11.45. The final R factors were R = 0.040 and R_w = 0.044. Further details of the crystal structure are available in the supplementary material.

Crystal data for 7 at −100 °C with Mo Kα radiation: a = 835.1 (2), b = 1301.2 (3), c = 880.0 (2) pm; β = 109.39 (1)°; monoclinic, $P2_1$; Z = 2; μ(Mo) = 0.61 cm^{-1}; 1542 unique reflections with $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares on F. Carbons and nitrogens were refined with anisotropic thermal parameters. Hydrogens were refined with isotropic thermal parameters. The largest residual electron density in the final difference Fourier map was 0.16 e/Å^3. The data/parameter ratio was 5.08. The final R factors were R = 0.049 and R_w = 0.039. Further details of the crystal structure are available in the supplementary material.

Crystal data for 8 at −85 °C with Mo Kα radiation: a = 785.9 (2), b = 941.9 (2), c = 1879.7 (4) pm; β = 100.45 (2)°; monoclinic, $P2_1/n$; Z = 4; μ(Mo) = 0.67 cm^{-1}; 1745 unique reflections with $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares on F. Carbons and nitrogens were refined with anisotropic thermal parameters. Hydrogens were refined with an isotropic thermal parameter. The largest residual electron density in the final difference Fourier map was 0.16 e/Å^3 near the carbene center. The data/parameter ratio was 7.02. The methyl group on the phenyl attached to N-3 was refined with a 2-fold rotational disorder and a 0.5 occupancy for each conformer. The final R factors were R = 0.038 and R_w = 0.033. Further details of the crystal structure are available in the supplementary material.

Crystal data for 9 at −70 °C with Mo Kα radiation: a = 2539.9 (5), b = 891.6 (3), c = 1143.2 (2) pm; β = 97.62 (1)°; monoclinic, $C2/c$; Z = 8; μ(Mo) = 4.91 cm^{-1}; 2262 unique reflections with $I > 3\sigma(I)$. The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares on F. Carbons, chlorines, and nitrogens were refined with anisotropic thermal parameters. Hydrogens were refined with an isotropic thermal parameter. The largest residual electron density in the final difference Fourier map was 0.23 e/Å^3 near one of the meta carbons of a *p*-chlorophenyl substituent. The data/parameter ratio was 10.65. The final R factors were R = 0.030 and R_w = 0.030. Further details of the crystal structure are available in the supplementary material.

Crystal data for 1,3-dimethylimidazolium chloride at −70 °C with Mo Kα radiation: a = 865.2 (6), b = 785.8 (2), c = 1053.9 (8) pm; β = 106.34 (3)°; monoclinic, $P2_1/n$; Z = 4; μ(Mo) = 4.54 cm^{-1}; 1212 unique reflections with $I > 3\sigma(I)$. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on F. Carbons, chlorines, and nitrogens were refined with anisotropic thermal parameters. Hydrogens were refined with an isotropic thermal parameter. The largest residual electron density in the final difference Fourier map was 0.15 e/Å^3 near one of the ring carbons. The data/parameter ratio was 11.12. The final R factors were R = 0.029 and R_w = 0.035. Further details of the crystal structure are available in the supplementary material.

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Supplementary Material Available: A complete description of the X-ray crystallographic structure determinations on 1,3,4,5-tetramethylimidazol-2-ylidene (**2**), 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (**7**), 1,3-di(*p*-tolyl)imidazol-2-ylidene (**8**), 1,3-di(*p*-chlorophenyl)imidazol-2-ylidene (**9**), and 1,3-dimethylimidazolium chloride including experimental procedures, tables of data, and ORTEP structure drawings (21 pages). Ordering information is given on any current masthead page.