

## An Air Stable Carbene and Mixed Carbene “Dimers”

Anthony J. Arduengo, III,\* Frederic Davidson, H. V. R. Dias,<sup>1</sup> Jens R. Goerlich,<sup>2</sup> Dilip Khasnis,<sup>3</sup> William J. Marshall, and T. K. Prakasha

Contribution No. 7604 from the DuPont Science and Engineering Laboratory, Experimental Station, Wilmington, Delaware 19880-0328

Received September 15, 1997<sup>⊗</sup>

**Abstract:** The air-stable crystalline carbene 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene (**2**) is produced from the chlorination of 1,3-dimesitylimidazol-2-ylidene (**1**) by 2 equiv of carbon tetrachloride. The physical and spectroscopic properties of the carbene are reported. The features which contribute to the exceptional stability of the carbene are discussed. Further reaction of **2** with carbon tetrachloride leads to reduction of CCl<sub>4</sub> to dichlorocarbene. The formation of the mixed carbene “dimers” (olefins) from *in situ* generated dichlorocarbene and various imidazol(in)-2-ylidenes is also reported. The tellurones derived from **1** and **2** are synthesized and compared.

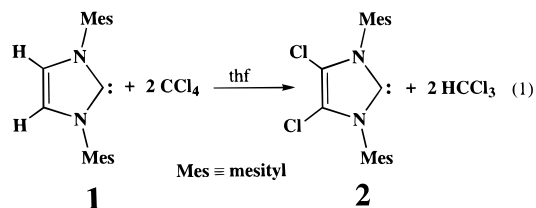
## Introduction

We have previously reported the synthesis and isolation of a series of stable carbenes, imidazol-2-ylidenes.<sup>4,5</sup> These carbenes are stable at room temperature under a nitrogen atmosphere and can be kept under these conditions indefinitely. They are however quite sensitive to moist air. The source of the remarkable stability of these carbenes has been the focus of several previous theoretical studies.<sup>6–14</sup> The large singlet–triplet gap in imidazol-2-ylidenes (~80 kcal/mol), along with  $\pi$ -interactions in the imidazole ring, electronegativity effects from the nitrogens, steric effects, and kinetic factors, have all been offered as explanations of the enhanced stability of these carbenes. Although all of these effects undoubtedly contribute somewhat to the stability of these carbenes, it is difficult to assign one dominant feature that is primarily responsible for their stability. The role of steric effects seems to be largely unimportant because a number of sterically unencumbered imidazol-2-ylidenes have now been prepared. Kinetic factors are important, but their origin lies primarily with entropy effects that tend to favor the monomeric imidazol-2-ylidene over the corresponding dimer (olefin). A stable saturated imidazolin-2-ylidene carbene<sup>15</sup> and even an acyclic diaminocarbene<sup>16</sup> have been reported which shows that the C4–C5 double bond is not

essential to produce a stable carbene in this series. Very recently, we were able to synthesize a stable thiazol-2-ylidene, demonstrating that substituents other than nitrogen can be tolerated on the carbene center.<sup>17</sup> In this paper we now show that the electronic features of a  $\sigma$ -electronegativity effect and  $\pi$ -interactions can be used in concert to further enhance the stability of the imidazol-2-ylidenes.<sup>18</sup>

## Results and Discussion

The carbene 1,3-dimesitylimidazol-2-ylidene<sup>4b</sup> (**1**) reacts rapidly with carbon tetrachloride in tetrahydrofuran (thf) at room temperature to produce 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene (**2**) and chloroform (eq 1). This reaction can be easily



followed by <sup>1</sup>H NMR where the disappearance of **1** and the formation of **2** and chloroform is observed. The reaction is complete in about 20 min at room temperature. The enhanced stability of **2** over **1** is immediately evident since the carbene **1** is such a strong base that it cannot tolerate prolonged exposure to such acidic solvents as chloroform while **2** is easily isolated from a reaction mixture that contains chloroform.

Remarkably carbene **2** is even *stable to air* for limited exposure times. A solid sample of **2** that was left in a laboratory hood exposed to air for two days showed no reaction or decomposition. A benzene solution of **2** that was also exposed to air overnight showed (by NMR) no evidence for decomposition. Pure **2** is a slightly off-white solid that melts at 180–2 °C with decomposition. The <sup>1</sup>H NMR spectrum of **2** in benzene-*d*<sub>6</sub> shows resonances at  $\delta$  2.09, 2.12, and 6.75 for the *p*- and *o*-methyls and the aromatic ring proton of the mesityl groups, respectively. The <sup>13</sup>C NMR spectrum in benzene-*d*<sub>6</sub> shows a resonance at  $\delta$  219.9 for the carbene center. This carbene resonance is typical of imidazol-2-ylidenes and is very

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, December 15, 1997.

- (1) DuPont Visiting Research Scientist 1990–2.
- (2) DuPont Visiting Research Scientist 1995–7.
- (3) DuPont Visiting Research Scientist 1994. Deceased.
- (4) (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.
- (5) Arduengo, A. J., III; Krafczyk, R. *Chem. Unserer Zeit.*, in press.
- (6) Dixon, D. A.; Arduengo, A. J., III. *J. Phys. Chem.* **1991**, *95*, 4180.
- (7) Cioslowski, J. *Int. J. Quantum Chem., Quantum Chem Symp.* **1993**, *27*, 309.
- (8) Arduengo, A. J., III; Dias, H. V. R.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812.
- (9) Arduengo, A. J., III; Dixon, D. A.; Kumashiro, K. K.; Lee, C.; Power, W. P.; Zilm, K. W. *J. Am. Chem. Soc.* **1994**, *116*, 6361.
- (10) Arduengo, A. J., III; Bock, H.; Chen, H.; Dixon, D. A.; Green, J. C.; Herrmann, W. A.; Jones, N. L.; Wagner, M.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 6641.
- (11) Heinemann, C.; Thiel, W. *Chem. Phys. Lett.* **1994**, *217*, 11.
- (12) Sauer, R. R. *Tetrahedron Lett.* **1996**, *37*, 149.
- (13) Heinemann, A. E.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023.
- (14) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039.
- (15) Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027.
- (16) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem.* **1996**, *108*, 1211.

(17) Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *Liebigs Ann.* **1997**, 365.

(18) Arduengo, A. J.; Goerlich, J. R.; Khasnis, D. Appl. U.S. Patent Off.

similar to the chemical shift of the carbene center of **1** ( $\delta$  219.7 in  $\text{thf-d}_8$ ).<sup>4b</sup>

Crystals of **2** that were suitable for X-ray diffraction studies were grown by cooling a hexane solution. Carbene **2** crystallizes in the monoclinic space group  $C2/c$ . Molecules of **2** are positioned such that a 2-fold symmetry axis passes through the carbene center and bisects the  $C_4-C_5$  bond of the imidazole ring. This arrangement is similar to that observed for 1,3,4,5-tetramethylimidazol-2-ylidene.<sup>4b,8</sup> Selected bond lengths and angles for **2** and related structures are presented in Table 1. The solid state structure is depicted by the KANVAS drawing in Figure 1.<sup>19</sup> The imidazole ring in **2** is nearly planar, and only C4 and C5 deviate above and below the average plane of the imidazole ring by 0.1 pm. The nitrogen centers are almost planar. The *ipso*-carbons of the mesityl substituents deviate only 6.4 pm from the plane of the imidazole ring. The chlorine atoms lie almost in the plane of the imidazole ring and deviate by only 3.8 pm. The valence angle at the carbene center of **2** is 101.9° which is characteristic of singlet carbenes.<sup>4,6</sup> The geometry of the central imidazole ring of **2** is virtually identical to that of carbene **1** from which it is derived.<sup>4b</sup> As a result there are no structural differences between **1** and **2** that betoken the large difference in stability (reactivity) that is observed for these carbenes. Imidazolium salts are our usual precursors to imidazol-2-ylidene, and we have noted that there are characteristic changes between the imidazolium (carbenium) ions and their corresponding carbenes.<sup>4,15,17</sup> The carbenium ion (**2·HCl**) related to **2** can be prepared by the addition of the elements of HCl to **2**. The structural relationship between **2** and **2·HCl** is similar to those that we have previously observed with other imidazol-2-ylidenes and their corresponding carbenium ions (*cf.* the increase of the  $C_2-N_{1(3)}$  bond lengths and decrease of the  $N-C-N$  angle on going to the carbene, Table 1).

We believe that the chlorination of **1** by  $\text{CCl}_4$  to produce **2** proceeds according to Scheme 1. The process begins by the chlorination of the 2-position of the imidazole with the liberation of the trichloromethyl anion. The  $\text{Cl}_3\text{C}^-$  then reacts with the 2-chloro-1,3-dimesitylimidazolium ion by deprotonation at the 4-position to produce chloroform and 2-chloro-1,3-dimesitylimidazolium-4-ate. The imidazolium-4-ate then reacts with additional  $\text{CCl}_4$  to chlorinate the 4-position and produce another trichloromethyl anion. This deprotonation/chlorination process is repeated for the 5-position of the imidazole ring to produce the 1,3-dimesityl-2,4,5-trichloroimidazolium ion. The 2-position of this trichloroimidazolium ion is finally dechlorinated by reaction with **1** or  $\text{Cl}_3\text{C}^-$  as illustrated to produce carbene **2**. When this chlorination reaction is followed by  $^1\text{H}$  NMR, only the initial starting materials and final products are observed (none of the intermediates are detected). The inability to observe intermediates by NMR suggests that each successive step is faster than the preceding step. This accelerated reaction sequence is consistent with the strong  $\sigma$ -inductive effect of the chlorines and their acidifying effect on the imidazole ring protons.

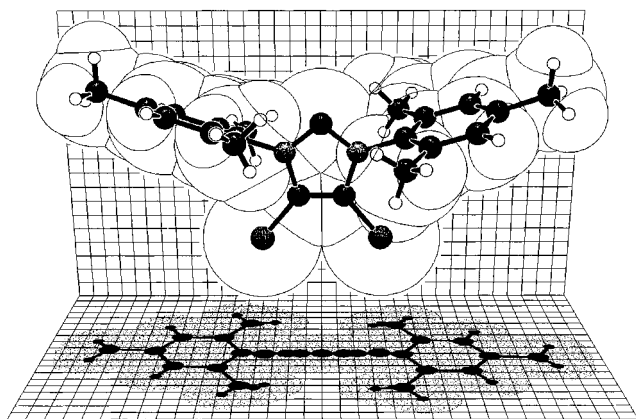
A different reaction can be observed when 2 equiv of carbene **2** react with  $\text{CCl}_4$  (eq 2). This reaction probably initiates along a pathway analogous to that shown in Scheme 1 in which " $\text{Cl}^+$ " is transferred to the 2-position of one molecule of carbene **2** to form a trichloroimidazolium ion with the liberation of the trichloromethyl anion ( $\text{Cl}_3\text{C}^-$ ). Reactions of the trichloroimi-

(19) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universität 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.

Table 1. Selected Bond Lengths (pm) and Angles (deg) in **1**–**14**<sup>a</sup>

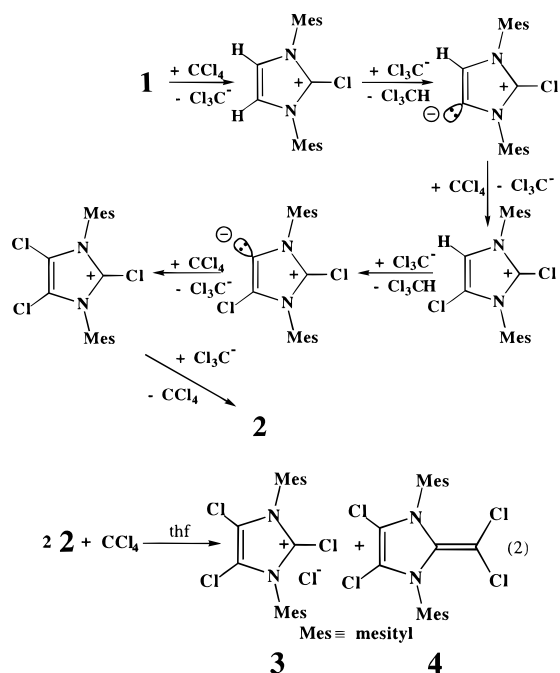
| property                             | <b>1</b>           | <b>2</b> | <b>2·HCl</b>       | <b>3<sup>b,c</sup></b> | <b>4<sup>d</sup></b> | <b>6</b>           | <b>7<sup>e</sup></b> | <b>11<sup>f</sup></b> | <b>13<sup>g</sup></b> | <b>14<sup>h</sup></b> |
|--------------------------------------|--------------------|----------|--------------------|------------------------|----------------------|--------------------|----------------------|-----------------------|-----------------------|-----------------------|
| $r(C_2-N_{1(3)})$                    | 136.5(4), 137.1(4) | 136.4(2) | 133.8(5), 133.6(5) | 133.5(4)               | 140.1(3), 140.8(3)   | 135.2(5), 134.5(5) | 138.7(3)             | 138.7(3)              | 136.7(2)              | 135.9(4), 136.6(4)    |
| $r(C_4-C_5)$                         | 133.1(5)           | 133.0(4) | 132.8(5)           | 133.1(3)               | 130.9(4)             | 150.5(6)           | 148.9(8)             | 149.7(5)              | 135.9(4)              | 133.0(5)              |
| $r(N_{1(3)}-C_{5(4)})$               | 138.1(4), 137.8(4) | 138.0(3) | 138.4(5), 138.8(5) | 139.1(3)               | 140.8(3), 141.6(3)   | 147.5(5), 148.7(5) | 146.8(4)             | 145.8(4)              | 138.5(3)              | 139.0(4), 138.6(4)    |
| $r(N_{1(3)}-C_{5(4)}-C_{4(5)})$      | 144.1(4), 144.2(4) | 144.6(2) | 144.2(5), 145.2(5) | 144.4(4)               | 143.5(4), 144.8(4)   | 142.7(5), 143.7(5) | 143.6(3)             | 142.4(3)              | 143.8(2)              | 144.2(4), 144.1(4)    |
| $r(C_{4(5)}-Cl_{4(5)})$              |                    | 169.8(2) | 169.3(4), 168.5(4) | 168.3(4)               | 169.7(3), 169.3(2)   |                    |                      |                       | 168.3(2)              |                       |
| $\theta(N_1-C_2-N_3)$                | 101.4(2)           | 101.9(2) | 108.4(4)           | 109.9(2)               | 106.5(2)             | 104.7(3)           | 107.8(4)             | 106.4(3)              | 105.3(2)              | 104.7(3)              |
| $\theta(C_{5(4)}-N_{1(3)}-C_2)$      | 112.8(3), 112.8(3) | 112.5(2) | 108.3(3), 108.0(3) | 107.2(3)               | 107.6(2), 106.9(2)   | 115.0(3), 114.6(3) | 110.8(3)             | 110.6(2)              | 110.2(2)              | 110.5(3), 110.2(3)    |
| $\theta(N_{1(3)}-C_{5(4)}-C_{4(5)})$ | 106.5(3), 106.5(3) | 106.6(1) | 107.5(4), 107.8(3) | 107.9(4)               | 109.4(2), 109.5(2)   | 101.6(4), 101.9(4) | 104.5(2)             | 102.3(2)              | 107.1(1)              | 107.2(3), 107.5(3)    |
| $\theta(C_2-N_{1(3)}-C_{mes})$       | 121.8(2), 122.6(2) | 123.3(2) | 126.9(3), 126.6(3) | 125.6(5)               | 127.4(2), 125.3(2)   | 122.9(3), 122.5(3) | 125.1(2)             | 123.0(2)              | 125.3(2)              | 125.3(3), 126.0(3)    |

<sup>a</sup> The numbering scheme for all compounds is as indicated for **2**. <sup>b</sup> Averages from the three crystallographically unique cations. <sup>c</sup>  $r(C_2-Cl) = 168.8(2)$ . <sup>d</sup>  $r(C_2-Cl) = 135.3(4)$ . <sup>e</sup>  $r(C_2-CCl_2) = 133.7(6)$ . <sup>f</sup>  $r(C_2-CH_2) = 133.0(5)$ . <sup>g</sup>  $r(C_2-Te) = 205.0(3)$ . <sup>h</sup>  $r(C_2-Te) = 206.6(3)$ .



**Figure 1.** Space filling KANVAS<sup>19</sup> drawing of the X-ray structure of **2**.

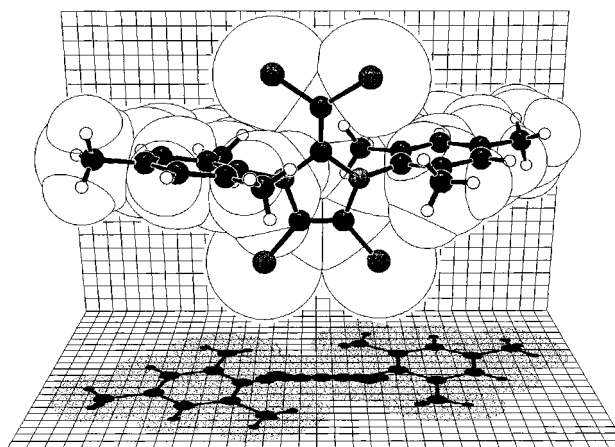
### Scheme 1



dazolium cation of **3** with  $\text{Cl}_3\text{C}^-$  are in essence degenerate and lead directly (or indirectly) to regeneration of **2** and  $\text{CCl}_4$ . However, after sufficient reaction time, another pathway involving the  $\alpha$ -elimination of  $\text{Cl}^-$  from  $\text{Cl}_3\text{C}^-$  to form dichlorocarbene ( $:\text{CCl}_2$ ) becomes important. Under the reaction conditions, dichlorocarbene is captured by a second equivalent of carbene **2** to produce the mixed carbene “dimer” **4**. An analogous process has been reported to couple *in situ* generated dichlorocarbene with triphenylphosphine to produce (dichloromethylene)triphenylphosphorane.<sup>20</sup>

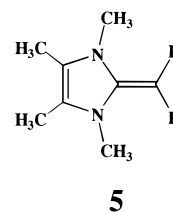
The mixed “dimer” **4** can be easily separated from the byproduct trichloroimidazolium chloride salt (**3**) by extraction into benzene. Solid **4** is a slightly off-white solid that turns pink at 147 °C and melts at 172 °C. The  $^1\text{H}$  NMR spectrum of **4** does not provide much structural information except to indicate that the adduct is different from the carbene (**2**) from which it is derived. The  $^{13}\text{C}$  NMR does indicate the loss of the carbene resonance at  $\delta$  219.9 and the appearance of two new resonances at  $\delta$  70.9 and 140.3 for the new olefinic centers derived, respectively, from  $:\text{CCl}_2$  and **2**. The olefinic resonance at  $\delta$  70.9 is an unusually high field position for the  $\text{CCl}_2$  grouping (*cf.*  $\text{Cl}_2\text{C}=\text{CCl}_2$ ,  $\delta(^{13}\text{C}) = 120.5^{21}$ ) but is actually characteristic

(20) Speziale, A. J.; Ratts, K. W. *J. Am. Chem. Soc.* **1962**, *84*, 854.



**Figure 2.** Space-filling KANVAS<sup>19</sup> drawing of the X-ray structure of **4**.

of these strongly polarized olefins. Kuhn *et al.* have reported a chemical shift of  $\delta$  40.2 for the exocyclic methylene of **5** which correlates well with calculated electron densities in other polarized olefins.<sup>22</sup>

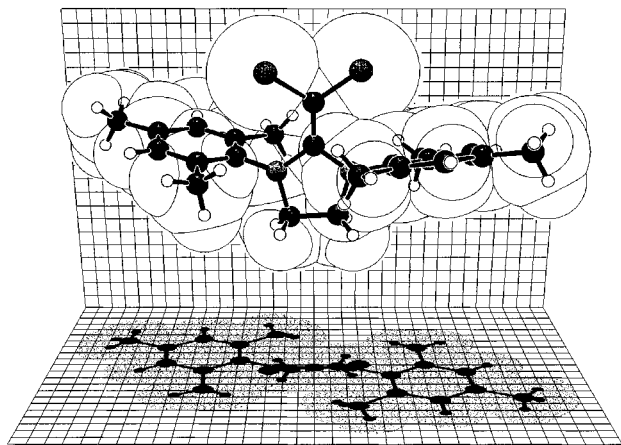


Crystals of **4** were grown by cooling a hexane solution at  $-25$  °C. The X-ray structure of **4** is depicted in Figure 2.<sup>19</sup> The two  $\text{C}=\text{C}$  double bonds in **4** bear the same heteroatoms (two chlorines and two nitrogens with different substitution patterns), and an interesting comparison can be made. The length of the newly formed  $\text{C}=\text{C}$  double bond is 135.3 pm. The  $\text{C}_4=\text{C}_5$  double bond in the imidazole ring is 130.9 pm. The exocyclic double bond is twisted ( $6.9^\circ$ ) slightly more than the endocyclic double bond ( $2.4^\circ$ ). This difference is probably the result of electronic factors that polarize the exocyclic double bond, in addition to any steric factors. The nitrogens in the imidazole ring of **4** are noticeably pyramidal with *anti*-orientations about the imidazole ring. The two nitrogens are 15 pm ( $\text{N}_1$ ) and 23 pm ( $\text{N}_3$ ) out of the plane of their three attached substituents. This *anti*-pyramidalization is evident in the shadow of the drawing in Figure 2. The  $\text{C}_2-\text{N}_{1(3)}$  bond distances in **4** are on average about 4.1 pm longer than in the carbene **2**. The  $\text{C}_{4(5)}-\text{N}_{3(1)}$  distances are about 3.2 pm longer in **4** compared to **2**. These small increases could be expected to arise from a combination of decreased  $\pi$ -interaction in the imidazole ring and increased p-orbital contribution to the  $\sigma$ -bonds arising from the pyramidalization of the nitrogens (more  $\text{sp}^3$ -like in **4**). However, the very small change in the *N*-mesityl bond distances between **4** and **2** (actually 0.4 pm shorter in **4** than **2**) suggests that the contribution from nitrogen rehybridization to the  $\sigma$ -bond length changes is negligible.

The byproduct from the reduction of  $\text{CCl}_4$  by **2** is the trichloroimidazolium chloride **3**. The salt **3** is a high melting solid ( $>250$  °C). It is soluble in polar solvents such as dimethyl sulfoxide and acetonitrile. This trichloroimidazolium ion shows a solid state structure (Table 1) that is typical of imidazolium

(21) Sadtler. *Standard  $^{13}\text{C}$  NMR Spectra*; SADTLER Research Laboratories, Inc.: Philadelphia, 1977; Vol. 10.

(22) Kuhn, N.; Bohnen, H.; Kreutzberg, J.; Bläser, D.; Boese, R. *J. Chem. Soc., Chem. Commun.* **1993**, 1993, 1136.

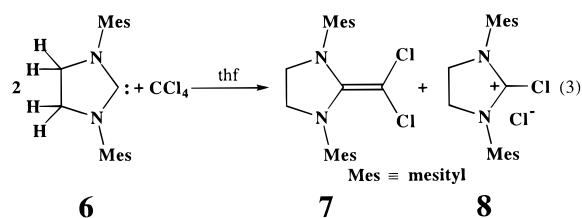


**Figure 3.** Space-filling KANVAS<sup>19</sup> drawing of the X-ray structure of **7**.

ions (e.g., **2**·HCl). The imidazolium ring in **3** exhibits the characteristically short C<sub>2</sub>–N<sub>1(3)</sub> bond distances (133.5 pm) and wide N<sub>1</sub>–C<sub>2</sub>–N<sub>3</sub> angle (109.9°). There is also a close approach of the chloride ion to the chlorine atom in the 2-position of the imidazole ring ( $r_{\text{Cl}-\text{Cl}} \approx 315$  pm,  $\theta_{\text{C}-\text{Cl}-\text{Cl}} \approx 175^\circ$ ). More details of this structure will be discussed in a summary of carbene–halogen adducts to be published elsewhere.

The mixed carbene coupling of **2** and :CCl<sub>2</sub> that leads to the olefin **4** reveals that some of the chemistry expected for a carbene is indeed exhibited by the carbene **2** even though it possesses extraordinary stability. It is useful to compare this type of carbene coupling reaction with those of other nucleophilic carbenes.

The chlorination of the 4- and 5-positions of carbene **1** with carbon tetrachloride is dependent upon the mild acidity of these olefinic centers as suggested by Scheme 1. If the C<sub>4</sub>=C<sub>5</sub> double bond in **1** is removed by saturation, the resulting imidazolin-2-ylidene (**6**) still reduces carbon tetrachloride to form dichlorocarbene which couples with the carbene center of **6** to produce olefin **7** (eq 3).

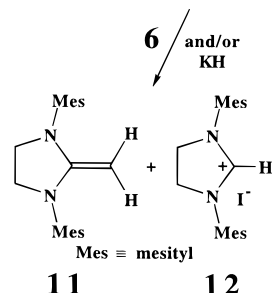
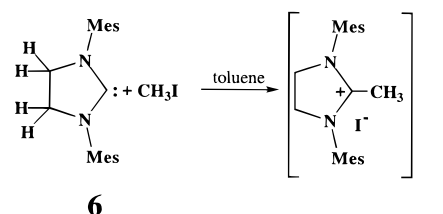
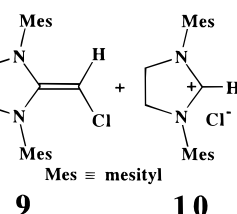
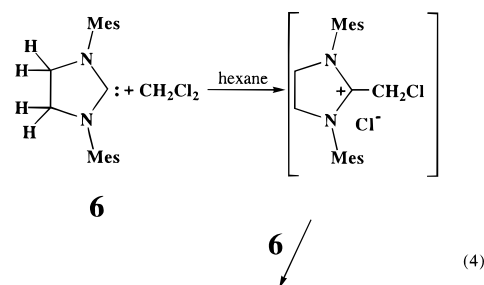


As was the case with **4**, the <sup>1</sup>H NMR of **7** does not provide any significant structural information except to indicate that **7** is different from the starting material (**6**). The <sup>13</sup>C NMR of **7** reveals the nature of this product. The original carbene resonance of  $\delta$  244.5 in **6** is shifted to 145.8 in **7** for the new olefin carbon, and the CCl<sub>2</sub> olefinic center exhibits a resonance at  $\delta$  74.0. This shift pattern is very similar to that observed for **4** (*vide supra*).

The solid state structure of **7** is depicted in Figure 3.<sup>19</sup> The molecule sits along a crystallographically imposed 2-fold rotation axis that runs along the C=C double bond. The C=C double bond in **7** is 133.7 pm long which is slightly shorter than the corresponding bond in **4**. This exocyclic double bond in **7** is twisted 9.5° (slightly greater than the twist in **4**). The nitrogens in the imidazole ring of **7** are distinctly pyramidal. In **7** the two nitrogens are 18.9 pm out of the plane of their three attached substituents with an *anti*-orientation about the imidazole ring. The C<sub>2</sub>–N<sub>1(3)</sub> bond distances in **7** are on average only about 3.9 pm longer than those in the carbene **6**. Thus, the

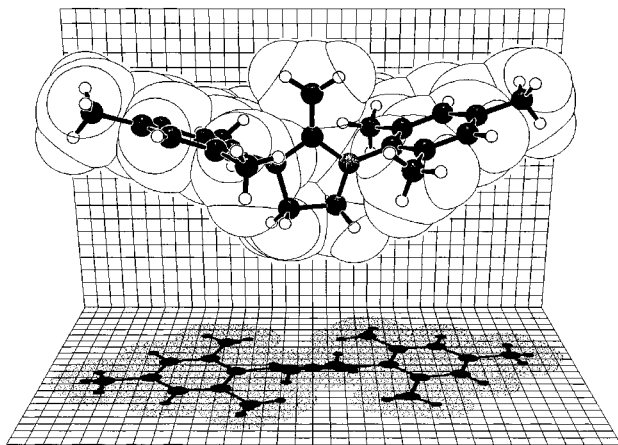
expected increase in length arising from a decreased  $\pi$ -interaction in the imidazole ring for **7** relative to **6** seems rather small and supports a somewhat limited  $\pi$ -delocalization in **6** and/or a highly polarized olefin structure for **7**.

We decided to pursue the syntheses of the monochloro and nonchlorinated analogs of **7** for further comparisons. These compounds would be difficult to prepare by a carbene–carbene coupling route owing to the relatively high and unselective reactivity of :CHCl and :CH<sub>2</sub>. However, alkylation/deprotonation routes as illustrated in eqs 4 and 5 proved to be useful pathways to the same olefins.



Surprisingly the reaction of imidazolin-2-ylidene **6** with methylene chloride was very sluggish at room temperature, and after seven days no conversion was evident. This is in contrast to carbene **1** which reacts rapidly with CH<sub>2</sub>Cl<sub>2</sub>. However, when a mixture of **6** and CH<sub>2</sub>Cl<sub>2</sub> in hexane was heated in a sealed tube at 70 °C for 15 h, conversion to the monochloroolefin **9** and the imidazolium salt **10** was accomplished. The carbene **6** is sufficiently basic that it can deprotonate the intermediate 2-(chloromethyl)imidazolium chloride to yield the olefin **9**. The byproduct **10** was identified by comparison with an authentic sample.<sup>15</sup>

The olefin **9** proved to be rather unstable and difficult to handle such that we have not grown satisfactory crystals for X-ray structure determination. However, NMR studies reveal the character and structure of the compound. The unique olefinic proton in **9** shows a <sup>1</sup>H NMR resonance at  $\delta$  3.81. This shift is unusually high field for an olefinic center but is



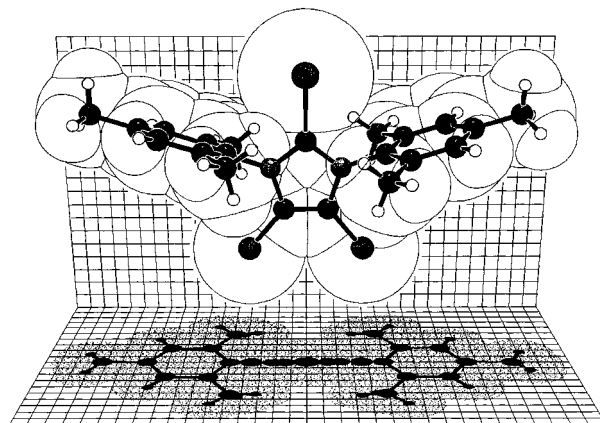
**Figure 4.** Space-filling KANVAS<sup>19</sup> drawing of the X-ray structure of **11**.

consistent with the results of Kuhn on other highly polarized olefins like **5** ( $\delta$   $CH_2$  in **5** is 2.77) and strongly resembles that of olefin **11** (*vide infra*).<sup>22</sup> Both the two mesityl groups and the two imidazoline 4- and 5-centers in **9** show slightly different sets of shifts due to the asymmetry introduced by the chloromethylene moiety at position 2. These separated resonances indicate that the olefin is conformationally locked at room temperature and does not freely rotate as might have been expected from a strongly polarized "olefinic" bond. The <sup>13</sup>C NMR of **9** gives a high-field resonance of  $\delta$  62.8 for the chloromethylene unit and  $\delta$  146.4 for the imidazoline C<sub>2</sub> carbon. These shifts are similar to those observed for **7** and **4**.

The reaction of imidazolin-2-ylidene **6** with methyl iodide proceeds rapidly to alkylate the carbene center and produce a 2-methylimidazolium ion (eq 5). This simple 2-methyl residue of this imidazolium cation that is intermediate in the process of eq 5 is not as acidic as the 2-chloromethyl residue on the intermediate imidazolium cation that is an intermediate in the process of eq 4. As a result of this reduced acidity, deprotonation by carbene **6** is not satisfactory for the production of the olefin **11** in good yield. To facilitate the deprotonation that is required to produce **11**, potassium hydride is added to the reaction mixture as described in the Experimental Section.

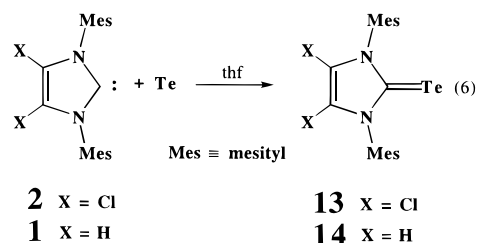
The olefin **11** is a colorless solid with a melting range of 135–8 °C. The <sup>1</sup>H NMR of **11** shows the terminal methylene resonance at  $\delta$  3.31 which is somewhat higher field than that observed in **9**. This slightly lower field shift in **9** is probably due to the deshielding effect of the chlorine atom. The terminal carbon atom in **11** exhibits a <sup>13</sup>C resonance at  $\delta$  48.7, again suggesting a polarized olefin structure as found for **9**, **7**, and **4**.

Unlike **9**, the olefin **11** was sufficiently stable to allow the growth of quality crystals for X-ray structure determination. The solid state structure of **11** is shown in Figure 4.<sup>19</sup> The molecule sits along a crystallographically imposed 2-fold rotation axis that runs along the C=C double bond as found with **7** although the two structures are not isomorphous. The C=C double bond in **11** is 133.0 pm long which is slightly shorter than the corresponding bond in **7**. The nitrogens in the imidazole ring of **11** are distinctly pyramidal as in the analogs **9**, **7**, and **4** and reside 17.6 pm out of the plane of their three attached substituents. The mesityl groups again adopt the usual *anti*-orientation about the imidazole ring. As in **9** the C<sub>2</sub>–N<sub>1(3)</sub> bond distances in **11** are only about 3.9 pm longer than in the carbene **6**. As with the previous adducts, the expected increase in the C<sub>2</sub>–N<sub>1(3)</sub> length arising from a decreased  $\pi$ -interaction in the imidazoline ring for **11** relative to **6** is rather small and supports a somewhat limited  $\pi$ -delocalization in **6** and/or a highly polarized olefin structure for **11** (and **9**).



**Figure 5.** Space-filling KANVAS<sup>19</sup> drawing of the X-ray structure of **13**.

We first reported the reaction of an *in situ* generated nucleophilic carbene with sulfur, selenium, or tellurium to produce the corresponding ketone analogs.<sup>23</sup> Polarized chalcones (O, S, Se, Te) have been more recently reported from reactions of isolated stable nucleophilic carbenes with chalcogens.<sup>24–26</sup> We decided to use the reactions of carbenes **1** and **2** with tellurium (eq 6) as another preliminary probe of the reactivity of the exceptionally stable carbene **2** versus its less stable parent **1**.



Carbene **2** reacts smoothly with tellurium in thf at room temperature to produce the tellurone **13**. The tellurone **13** is a yellow crystalline solid that melts at 189 °C with decomposition. The <sup>1</sup>H NMR spectrum of **13** provides only sparse information and indicates that a symmetric adduct, different from the initial carbene **2**, is formed. The <sup>13</sup>C NMR spectrum of **13** shows a resonance for the carbon bound to tellurium of  $\delta$  134.26 (86 ppm upfield of the carbene resonance in **2**). The <sup>125</sup>Te resonance for tellurone **13** is  $\delta$  –4. This shift is substantially downfield of the resonance reported by Kuhn *et al.* for 1,3-diisopropyl-4,5-dimethylimidazole-2-tellurone ( $\delta$  –167.82) and may signal the strong electron-withdrawing  $\sigma$ -influence of the chlorines.<sup>26</sup>

Crystals of **13** suitable for X-ray diffraction studies were grown from a toluene/thf solution on cooling to –25 °C. The molecule crystallizes in a C<sub>2</sub>/c space group with the crystallographic 2-fold axis running along the C–Te bond. The solid state structure of **13** is illustrated in Figure 5, and selected bond lengths and angles are included in Table 1. The imidazole ring in **13** is planar with no atom deviating more than 0.1 pm from the average plane. As required by symmetry, the tellurium atom lies in the average plane of the imidazole ring. The nitrogen centers are essentially planar, with the nitrogen rising only 1.5 pm above the plane of its three attached atoms. The *ipso*-

(23) Benac, B. L.; Burgess, E. M.; Arduengo, A. J., III. *Org. Synth.* **1986**, 64, 92.

(24) Williams, D. J.; Fawcett-Brown, M. R.; Raye, R. R.; VanDerveer, D.; Jones, R. L. *Heteroatom Chem.* **1993**, 4, 409.

(25) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J.-P.; Ebel, K.; Brode, S. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1021.

(26) Kuhn, N.; Henkel, G.; Kratz, T. *Chem. Ber.* **1993**, 126, 2047.

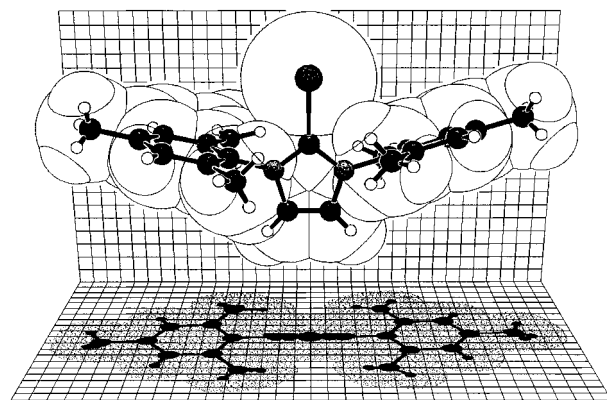
carbons of the mesityl substituents are displaced only 4.5 pm from the plane of the imidazole ring. The chlorine atoms are also very nearly planar with the imidazole ring and deviate by only 3 pm. The N–C–N at the former carbene center of **13** is 105.3° which is intermediate between that found for the carbene (**2**) and its corresponding carbenium ion (**2·HCl**). The remaining metric parameters (Table 1) in the imidazole ring are also intermediate between those of the imidazol-2-ylidene and imidazolium structures. This partial retention of carbene-like structural characteristics has been noted for other dative bonded adducts of imidazol-2-ylidenes with some main group elements and transition metal coordination complexes.<sup>27–34</sup>

As expected the more reactive carbene, **1**, also reacts with tellurium in thf at room temperature to produce the tellurone **14**. Like the tellurone **13**, **14** is a yellow crystalline solid. The <sup>1</sup>H NMR spectrum of **14** reveals that the imidazole ring protons in **14** have shifted 0.1 ppm downfield of their positions in the parent carbene **1**. The <sup>13</sup>C NMR spectrum of **14** shows a resonance for the carbon bound to tellurium of  $\delta$  133.05 similar to the corresponding shift that was recorded for **13** (134.26). The <sup>125</sup>Te resonance for tellurone **14** is  $\delta$  –149.8. This shift is substantially upfield of the resonance observed for **13** but is much closer to that reported by Kuhn *et al.* for 1,3-diisopropyl-4,5-dimethylimidazole-2-tellurone ( $\delta$  –167.82).<sup>26</sup> Thus, it appears that the anomalously low field <sup>125</sup>Te shift observed in **13** does signal the unique influence of the chlorine substituents.

Crystals of **14** suitable for X-ray diffraction studies were grown from a hexane/thf solution on cooling to –25 °C. The solid state structure of **14** is illustrated in Figure 5, and selected bond lengths and angles are included in Table 1. The imidazole ring in **14** is essentially planar with no atom deviating more than 0.2 pm from the average plane. The tellurium atom lies 3.4 pm out of the average plane of the imidazole ring. The nitrogen centers are essentially planar with the N<sub>1</sub> and N<sub>3</sub>, respectively, lying 2.9 and 3.4 pm out of the plane of their three attached substituents. The slight pyramidalization of the nitrogens results in a small *anti*-displacement of the mesityl substituents above and below the plane of the imidazole ring. The *ipso*-carbons of the mesityl substituents deviate 7.3 and 10.4 pm from the plane of the imidazole ring. The gross structural features (Table 1) of tellurone **14** are quite similar to those observed for **13**. Thus, it is apparent that **14** also retains some carbene-like structural characteristics as had **13**.

## Conclusions

The reactions of imidazol-2-ylidenes that bear hydrogens at the 4- and 5-positions of the imidazole ring with CCl<sub>4</sub> provide a surprising and convenient way to halogenate the imidazole ring. The 4,5-dichloroimidazol-2-ylidenes produced by these reactions show extraordinary stability compared to their unhalogenated analogs. These dichloroimidazol-2-ylidenes exhibit enhanced stability toward air, moisture, and acidic halogenated



**Figure 6.** Space-filling KANVAS<sup>19</sup> drawing of the X-ray structure of **14**.

solvents like chloroform and methylene chloride. The structures of 1,3-dimesitylimidazol-2-ylidene (**1**) and 4,5-dichloro-1,3-dimesitylimidazol-2-ylidene (**2**) are very similar and provide no suggestion of the dramatically enhanced stability of the latter carbene. There are also no changes in the <sup>1</sup>H or <sup>13</sup>C NMR spectra that reflect the substantial difference in stabilities. Indeed the <sup>13</sup>C resonances for the two carbene centers are less than 0.2 ppm apart. The introduction of halogen (chlorine) in the 4- and 5-positions of the imidazole ring appears to have a special stabilizing effect on the carbene that is not seen from other positions. For example, when the halogen is introduced into the *para*-position of a phenyl substituent on nitrogen as in 1,3-bis(4-chlorophenyl)imidazol-2-ylidene,<sup>4b</sup> a carbene of such exceptional stability does not result. In our hands 1,3-bis(4-chlorophenyl)imidazol-2-ylidene actually appears somewhat more reactive than 1,3-dimesitylimidazol-2-ylidene.

The first spectral indication of the special influence of the chlorines is observed in the dative bonded tellurium adducts, or tellurones, **13** and **14**. The tellurone **13** has an unusually low field shift ( $\delta$  –4) for the tellurium center compared to **14** ( $\delta$  –150) and 1,3-diisopropyl-4,5-dimethylimidazole-2-tellurone ( $\delta$  –168).<sup>26</sup> The low-field shift of the tellurium center in **13** could be the result of a strong  $\sigma$ -electron-withdrawing effect of the chlorines. Consistent with this interpretation, 1,3-diisopropyl-4,5-dimethylimidazole-2-tellurone with four electron-releasing alkyl substituents on the imidazole has the highest <sup>125</sup>Te shift observed among these three tellurones.

The influence of the chlorine substituents on carbenes like **2** can include both a  $\pi$ -electron-releasing component by virtue of the chlorine lone pair electrons and a  $\sigma$ -electron withdrawal by virtue of chlorine's high electronegativity. Both of these effects can act in concert to enhance the stability of a carbene center at C2 of the imidazole ring. Other than the electronegativity inherent in the nitrogen centers on most stable nucleophilic carbenes, a  $\sigma$ -electronegativity effect has not previously been a great aid to enhancing the stability (lowering the reactivity) of nucleophilic carbenes. The  $\sigma$ -electron withdrawal by the chlorines substantially reduces the basicity of the  $\sigma$ -lone pair of electrons at the carbene center. This reduced basicity is immediately apparent in the tolerance of the halogenated imidazol-2-ylidenes for acidic solvents like chloroform which react rapidly with carbenes like **1** and **6**. As can be seen for compound **2**, this stabilizing effect can be quite dramatic and brings the "handability" of such stable carbenes to a new level. Further studies to understand the enhanced stability and range of reactivity for carbenes like **2** are currently underway.

In addition to the reaction of CCl<sub>4</sub> with imidazol-2-ylidenes that produces chlorinated carbenes such as **2**, we have found that CCl<sub>4</sub> will further react with carbenes like **2** and **6** to reduce

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

(28) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1992**, *114*, 9724.

(29) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Inorg. Chem.* **1993**, *32*, 1541.

(30) Arduengo, A. J., III; Dias, H. V. R.; Davidson, F.; Harlow, R. L. *J. Organomet. Chem.* **1993**, *462*, 13.

(31) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405.

(32) Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391.

(33) Arduengo, A. J., III; Tamm, M.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 3625.

(34) Arduengo, A. J., III; Tamm, M.; McLain, S. J.; Calabrese, J. C.; Davidson, F.; Marshall, W. J. *J. Am. Chem. Soc.* **1994**, *116*, 7927.

the  $\text{CCl}_4$  to a  $:\text{CCl}_2$  fragment. Under appropriate reaction conditions the *in situ* generated  $:\text{CCl}_2$  can be trapped by the initial imidazol-2-ylidene or imidazolin-2-ylidene to form mixed carbene "dimers". Other trapping reagents are being explored to further support the postulate that dichlorocarbene is actually intermediate in this process. This reaction is somewhat analogous to the reaction of  $\text{CCl}_4$  with triphenylphosphine that leads to the *in situ* generation of (dichloromethylene)triphenylphosphorane.<sup>20</sup> Unlike their phosphorus analogs the olefins **4** and **7** are stable enough to be easily isolated and fully characterized. The olefins appear to be highly polarized as indicated by the high-field  $^{13}\text{C}$  chemical shifts for the terminal  $\text{CCl}_2$  groups ( $\delta$  70.86 for **4** and  $\delta$  73.97 for **7**). A related nonhalogenated polarized olefin (formally the coupling product of methylene and 1,3,4,5-tetramethylimidazol-2-ylidene) has been previously reported by Kuhn *et al.* and is consistent with our result.<sup>22</sup> Interestingly, this reduction of  $\text{CCl}_4$  by a carbon-centered reagent to produce  $:\text{CCl}_2$  is reminiscent of the report by Schmeisser and Schröter of the conproportionation of charcoal and  $\text{CCl}_4$ .<sup>35</sup> In our case the reaction proceeds under much milder conditions. The reducing agent is the imidazol(in)-2-ylidene (**2** or **6**), and the reaction can also be thought of as a sort of carbene exchange in which the carbene center of an imidazol(in)-2-ylidene is oxidized to a carbon(IV) center while the carbon(IV) center in  $\text{CCl}_4$  is reduced to dichlorocarbene.

The reaction of nucleophilic carbenes with  $\text{CCl}_4$  has proved to be a surprisingly rich area for investigation. It has led to a new class of exceptionally stable carbenes and provided a route to the synthesis of mixed carbene dimers.

## Experimental Section

Reactions and manipulations were carried out under an atmosphere of dry nitrogen, either in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Solvents were dried (using standard procedures),<sup>36</sup> distilled, and deoxygenated prior to use, unless otherwise indicated. Glassware was oven-dried at 160 °C overnight.  $^1\text{H}$  NMR spectra were recorded on a General Electric QE-300 spectrometer.  $^{13}\text{C}$  spectra were recorded on a GE Omega 300WB spectrometer. NMR references are  $(\text{CH}_3)_4\text{Si}$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and  $(\text{CH}_3)_2\text{Te}$  and 1 M  $\text{TeCl}_4$  in  $\text{THF}-d_8$  ( $^{125}\text{Te}$ ). Mass spectra were obtained using a VG-ZAB-E mass spectrometer. Melting points were obtained on a Thomas-Hoover capillary apparatus and were not corrected. Elemental analyses were performed by Micro-Analyses Inc., Wilmington, DE, or Oneida Research Services, Whitesboro, NY.

**Preparation of 4,5-Dichloro-1,3-dimesitylimidazol-2-ylidene (2).** In a drybox, a 200 mL round bottom flask was charged with 4.00 g (13.2 mmol) of 1,3-dimesitylimidazol-2-ylidene (**1**) and 80 mL of thf. To this solution was added 4.05 g (2.50 mL, 26.3 mmol) of  $\text{CCl}_4$  in 20 mL of thf, and the solution was stirred at 23 °C for 20 min. Subsequent removal of the volatiles under reduced pressure gave 4.16 g of 4,5-dichloro-1,3-dimesitylimidazol-2-ylidene (**2**) as a yellow solid. Further purification was accomplished by recrystallization from thf to give light yellow crystals. Mp 180–2°. Yield: 4.16 g (85%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  2.09 (s, 6 H, *p*- $\text{CH}_3$ ), 2.12 (s, 12 H, *o*- $\text{CH}_3$ ), 6.75 (s, 4 H, Ar-H).  $^1\text{H}$  NMR (thf- $d_8$ ):  $\delta$  2.07 (s, 12 H, *o*- $\text{CH}_3$ ), 2.33 (s, 6 H, *p*- $\text{CH}_3$ ), 7.01 (s, 4 H, Ar-H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  17.86 (s, *o*- $\text{CH}_3$ ), 20.99 (s, *p*- $\text{CH}_3$ ), 116.16 (s, NCCN), 129.3 (s, *m*-C), 135.67 (s, *ipso*-C), 136.05 (s, *o*-C), 138.53 (s, *p*-C), 219.89 (s, NCN). Anal. Calcd for  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{Cl}_2$ : C, 67.56; H, 5.94; N, 7.50. Found: C, 66.94; H, 5.74; N, 7.32.

**Preparation of 2-(Dichloromethylene)-4,5-dichloro-1,3-dimesitylimidazole (4) and 1,3-Dimesityl-2,4,5-trichloroimidazolium Chloride (3).** In a drybox, a 25 mL round bottom flask was charged with 0.20 g (0.54 mmol) of 4,5-dichloro-1,3-dimesitylimidazol-2-ylidene (**2**) and 1.50 mL of  $\text{CCl}_4$  (2.39 g, 15.5 mmol). The flask was closed with

a septum, and the mixture was stirred for two days. The volatiles were removed under reduced pressure to give a brown residue (240 mg). This residue was extracted with 20 mL of warm benzene to dissolve the olefin **4**. The benzene insoluble imidazolium salt **3** was dissolved in 20 mL of  $\text{CH}_3\text{CN}$ .

The benzene extract containing **4** was concentrated to 5 mL, and 3 mL of hexane was added. The solution was cooled to  $\sim 0$  °C. Light yellow crystals of **4** were collected by filtration (115 mg, 93% yield). Mp: 172 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm):  $\delta$  2.06 (s, 6 H, *p*- $\text{CH}_3$ ), 2.25 (s, 12 H, *o*- $\text{CH}_3$ ), 6.69 (s, 4 H, Ar-H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  18.14 (s, *o*- $\text{CH}_3$ ), 21.01 (s, *p*- $\text{CH}_3$ ), 70.86 (s,  $\text{CCl}_2$ ), 112.06 (s, NCCN), 129.19 (s, *m*-C), 132.61 (s, *ipso*-C), 138.35 (s, *o*-C), 138.98 (s, *p*-C), 140.25 (s, NCN). Anal. Calcd for  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{Cl}_4$ : C, 57.92; H, 4.86; N, 6.14. Found: C, 57.54; H, 4.67; N, 5.98.

The original acetonitrile extract containing **3** was concentrated to 4 mL *in vacuo*, and 4 mL of hexane was added. Colorless crystals of the imidazolium salt **3** monoacetonitrile solvate were obtained when the solution was cooled to  $-20$  °C (105 mg, 81% yield).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  2.14 (s, 12 H, *o*- $\text{CH}_3$ ), 2.40 (s, 6 H, *p*- $\text{CH}_3$ ), 7.27 (s, 4 H, Ar-H).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  17.59 (s, *o*- $\text{CH}_3$ ), 21.32 (s, *p*- $\text{CH}_3$ ), 123.60 (s, NCCN), 124.55 (s, NCN), 127.38 (s, *ipso*-C), 131.37 (s, *m*-C), 136.53 (s, *o*-C), 144.93 (s, *p*-C). Anal. Calcd for  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{Cl}_4$  (vacuum dried): C, 56.78; H, 4.99; N, 6.31. Found: C, 56.51; H, 4.77; N, 6.25.

**Preparation of 1,3-Dimesityl-2-chloroimidazolium Chloride (8) and 1,3-Dimesityl-2-(dichloromethylene)imidazoline (7).** To a solution of 0.276 g (0.90 mmol) of 1,3-dimesitylimidazolin-2-ylidene **6** in 30 mL of hexane was added at room temperature 0.14 g (0.9 mmol) of carbon tetrachloride whereupon **8** precipitated immediately as a colorless solid which was filtered off after 15 min of stirring at 23 °C. The salt **8** was rinsed with 10 mL of toluene, dried *in vacuo*, and recrystallized from acetonitrile to yield 0.15 g (88%). Mp:  $>250$  °C.  $^1\text{H}$  NMR ( $\text{dmsol}-d_6$ ):  $\delta$  2.31 (s, 6 H, *p*- $\text{CH}_3$ ), 2.33 (s, 12 H, *o*- $\text{CH}_3$ ), 4.67 (s, 4 H,  $\text{NCH}_2$ ), 7.16 (s, 4 H, Ar-H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  16.83 (s, *o*- $\text{CH}_3$ ), 20.53 (s, *p*- $\text{CH}_3$ ), 50.52 (s, NCCN), 129.34 (s, *ipso*-C), 129.75 (s, *m*-C), 135.33 (s, *o*-C), 140.65 (s, *p*-C), 158.51 (s,  $\text{CCl}$ ).

The original mother liquor and toluene washes were combined and evaporated to dryness. The solid residue was recrystallized from hexane/toluene by cooling a saturated 23 °C solution to  $-25$  °C. The olefin **7** was isolated by filtration and dried to yield a light yellow solid with mp 220–4 °C dec (0.13 g, 67%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  2.12 (s, 6 H, *p*- $\text{CH}_3$ ), 2.29 (s, 12 H, *o*- $\text{CH}_3$ ), 3.12 (s, 4 H,  $\text{NCH}_2$ ), 6.79 (s, 4 H, Ar-H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  18.49 (s, *o*- $\text{CH}_3$ ), 20.94 (s, *p*- $\text{CH}_3$ ), 50.96 (s, NCCN) 73.97 (s,  $\text{CCl}_2$ ), 129.61 (s, *m*-C), 136.21 (s, *p*-C), 136.30 (s, *o*-C), 139.48 (s, *ipso*-C), 145.76 (s, NCN). MS (EI, 70 eV): *m/z* (rel intens) 388.1454 (50) [ $\text{M}^+$ , calcd for  $\text{C}_{22}\text{H}_{26}\text{Cl}_2\text{N}_2$  388.1473], 373.1242 (15) [ $\text{M}^+ - \text{CH}_3$ , 373.1238], 353.1762 (25) [ $\text{M}^+ - \text{Cl}$ , 353.1785], 338.1514 (40) [ $\text{M}^+ - \text{CH}_2\text{Cl}$ , 338.1560], 305.2147 (100) [ $\text{M}^+ - \text{CHCl}_2$ , 305.2018].

**Preparation of 1,3-Dimesityl-2-(chloromethylene)imidazolidine (9).** A solution of 0.153 g (0.5 mmol) of the 1,3-dimesitylimidazolin-2-ylidene (**1**) in 20 mL of hexane was treated at 23 °C with 1.8 g (21.2 mmol) of dichloromethane. Samples investigated by  $^1\text{H}$  NMR indicated that also after seven days no reaction had taken place. The mixture was transferred to a thick-walled glass tube and heated to 70 °C for 15 h. The formation of a colorless solid was observed. This was filtered off (0.052 g, identified as imidazolium salt **10** by  $^1\text{H}$  NMR), and the filtrate was evaporated to give **9** as a light yellow solid. The olefin **9** decomposed upon attempted crystallization from hexane.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  2.11, 2.14 (s, 6 H, *p*- $\text{CH}_3$ ), 2.22, 2.41 (s, 12 H, *o*- $\text{CH}_3$ ), 3.1–3.3 (m, 4 H, 4,5-H), 3.81 (s, 1 H,  $\text{CHCl}$ ), 6.74, 6.82 (s, 4 H, *m*-CH).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  17.95, 18.35 (s, *o*- $\text{CH}_3$ ), 20.96, 21.04 (s, *p*- $\text{CH}_3$ ), 47.83, 50.17 (s, NCCN), 62.84 (s,  $\text{CHCl}$ ), 129.25 (s, *m*-C), 129.95 (s, *m*-C), 136.06 (s, *ipso*-C), 136.72 (s, *ipso*-C), 136.49 (s, *p*-C), 137.04 (s, *p*-C), 137.25 (s, *o*-C), 137.87 (s, *o*-C), 146.39 (s, NCN).

**Preparation of 1,3-Dimesityl-2-methylimidazolium Iodide (10) and 1,3-Dimesityl-2-methyleneimidazolidine (11).** To a solution of 0.150 g (0.49 mmol) of 1,3-dimesitylimidazolin-2-ylidene (**1**) in 30 mL of toluene was added at 23 °C 0.92 g (6.5 mmol) of methyl iodide. Immediately a colorless solid precipitated which was filtered off after 3 h of stirring at 23 °C.  $^1\text{H}$  and  $^{13}\text{C}$  NMR revealed it to be 1,3-dimesityl-2-methylimidazolium iodide containing a small amount

(35) Schmeisser, M.; Schröter, H. *Angew. Chem.* **1960**, *72*, 349.

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

of 1,3-dimesitylimidazolium iodide (**12**). The spectral data for 1,3-dimesityl-2-methylimidazolium iodide were as follows.  $^1\text{H}$  NMR (dms- $d_6$ ):  $\delta$  1.81 (s, 3 H,  $\text{NCCH}_3$ ), 2.31 (s, 6 H,  $p\text{-CH}_3$ ), 2.34 (s, 12 H,  $o\text{-CH}_3$ ), 4.38 (s, 4 H,  $\text{CH}_2$ ), 7.12 (s, 4 H, Ar-H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  10.84 (s, ( $\text{NCCH}_3$ ), 16.91 (s,  $o\text{-CH}_3$ ), 20.60 (s,  $p\text{-CH}_3$ ), 49.56 (s, NCCN), 129.80 (s,  $m\text{-C}$ ), 130.16 (s,  $ipso\text{-C}$ ), 135.50 (s,  $o\text{-C}$ ), 139.97 (s,  $p\text{-C}$ ), 167.11 (s, NCN). The evaporated mother liquor yielded a small quantity of the olefin **11**. The crude 1,3-dimesityl-2-methylimidazolium iodide was used without further purification in the deprotonation step.

Crude 1,3-dimesityl-2-methylimidazolium iodide was suspended in 10 mL of thf, and 0.22 g of a 35% suspension of potassium hydride in mineral oil (corresponding to 1.9 mmol of potassium hydride) was added at 23 °C. After the evolution of gas had ceased (*ca.* 3 h), the mixture was filtered, and the filtrate was evaporated to give a yellow oil. Recrystallization from hexane at -25 °C gave colorless crystals of the olefin **11**. Yield: 44 mg (28%). Mp: 135–138 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  2.14 (s, 6 H,  $p\text{-CH}_3$ ), 2.34 (s, 12 H,  $o\text{-CH}_3$ ), 2.59 (s, 2 H,  $\text{C}=\text{CH}_2$ ), 3.31 (s, 4 H,  $\text{CH}_2$ ), 6.82 (s, 4 H, Ar-H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  17.20 (s,  $o\text{-CH}_3$ ), 20.30 (s,  $p\text{-CH}_3$ ), 47.57 (s, NCCN), 48.70 (s,  $\text{C}=\text{CH}_2$ ), 129.72 (s,  $m\text{-C}$ ), 136.87 (s,  $p\text{-C}$ ), 137.28 (s,  $ipso\text{-C}$ ), 138.22 (s,  $o\text{-C}$ ), 151.78 (s, NCN). MS (70 eV):  $m/z$  (rel intens) 320.2230 (65) [ $\text{M}^+$ , calcd for  $\text{C}_{22}\text{H}_{28}\text{N}_2$  320.2252], 305.2052 (100) [ $\text{M}^+ - \text{CH}_3$ , 305.2018], 148.1123 (25) [ $\text{C}_{10}\text{H}_{14}\text{N}^+$ , 148.1126].

**Preparation of 1,3-Dimesityl-4,5-dichloroimidazole-2-tellurone (13).** In a drybox, a 100 mL round bottom flask was charged with 0.20 g (0.66 mmol) of carbene **2** and 20 mL of thf. The solution was stirred for a few minutes, and then 0.084 g (0.66 mmol) of tellurium powder was added. The solution slowly turned yellow as the reaction progressed. After the reaction mixture was stirred for 16 h, an additional 20 mL of thf was added and the solution filtered over Celite to obtain a clear yellow solution. After concentration of the filtrate to 5 mL, and addition of 4 mL of hexane, the flask was cooled in the refrigerator to -20 °C. Yellow crystals (280 mg, 100%) were collected from the cooled solution by filtration. Mp: 189 °C dec.  $^1\text{H}$  NMR (thf- $d_8$ ):  $\delta$  2.10 (s, 12 H,  $o\text{-CH}_3$ ), 2.35 (s, 6 H,  $p\text{-CH}_3$ ), 7.05 (s, 4 H,

$m\text{-CH}$ ).  $^{13}\text{C}$  NMR (thf- $d_8$ ):  $\delta$  18.42 (s,  $o\text{-CH}_3$ ), 21.26 (s,  $p\text{-CH}_3$ ), 116.59 (s, NCCN), 130.08 (s,  $m\text{-C}$ ), 133.86 (s,  $ipso\text{-C}$ ), 134.26 (s,  $\text{C}=\text{Te}$ ), 136.78 (s,  $o\text{-C}$ ), 140.92 (s,  $p\text{-C}$ ).  $^{125}\text{Te}$  (94.763 MHz) NMR (thf- $d_8$ ):  $\delta$  -4.08 (ref neat  $\text{Me}_2\text{Te}$ ); +1730.45 (ref 1 M  $\text{TeCl}_4$  in thf- $d_8$ ). Anal. Calcd for  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{Cl}_2\text{Te}$ : C, 50.33; H, 4.40; N, 5.59. Found: C, 49.86; H, 4.77; N, 5.43.

**Preparation of 1,3-Dimesitylimidazole-2-tellurone (14).** In a drybox a 200 mL round bottom flask was charged with carbene **1** (1.00 g, 3.28 mmol), tellurium (0.418 g, 3.29 mmol), and thf (100 mL). The mixture was stirred for 12 h, after which time the solution was slightly cloudy. This solution was warmed to obtain a clear yellow solution, filtered over Celite, and concentrated until crystallization began. Hexane was added, and the crystallization was allowed to continue at -20 °C. The tellurone **14** was isolated by filtration as yellow crystals (1.4 g, 100%). A sample that was recrystallized from THF gave the following data: Mp: 317–318 °C.  $^1\text{H}$  NMR (thf- $d_8$ ):  $\delta$  2.06 (s, 12 H,  $o\text{-CH}_3$ ), 2.36 (s, 6 H,  $p\text{-CH}_3$ ), 7.03 (s, 4 H,  $m\text{-CH}$ ), 7.15 (s, 2 H, NCH).  $^{13}\text{C}$  NMR (thf- $d_8$ ):  $\delta$  18.72 (s,  $o\text{-CH}_3$ ), 21.20 (s,  $p\text{-CH}_3$ ), 123.48 (s, NCCN), 129.66 (s,  $m\text{-C}$ ), 133.05 (s,  $\text{C}=\text{Te}$ ), 136.25 (s,  $o\text{-C}$ ), 136.98 (s,  $ipso\text{-C}$ ), 139.53 (s,  $p\text{-C}$ ).  $^{125}\text{Te}$  NMR (thf- $d_8$ , ref neat  $\text{Me}_2\text{Te}$ ):  $\delta$  -149.8. Anal. Calcd for  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{Te}$ : C, 58.38; H, 5.60; N, 6.48. Found: C, 58.65; H, 5.62; N, 6.33.

**Acknowledgment.** A.J.A. is indebted to the Alexander von Humboldt Stiftung for a senior research prize that made the completion of this work possible.

**Supporting Information Available:** A complete description of the X-ray crystallographic determinations on **2**, **2·HCl**, **3·CH<sub>3</sub>CN**, **4**, **7**, **9**, **11**, **13**, and **14**, including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles and ORTEP drawings (60 pages). See any current masthead page for ordering and Internet access instructions.

JA973241O