An Air Stable Carbene and Mixed Carbene "Dimers"

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Abstract: The air-stable crystalline carbene 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene (2) is produced from the chlorination of 1,3-dimesityimidazol-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 CCl₄ 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.^{4,5} 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.⁶⁻¹⁴ The large singlettriplet gap in imidazol-2-ylidenes (~80 kcal/mol), along with π -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 primilarily with entropy effects that tend to favor the monomeric imidazol-2-ylidene over the corresponding dimer (olefin). A stable saturated imidazolin-2-ylidene carbene¹⁵ and even an acyclic diaminocarbene¹⁶ have been reported which shows that the C4-C5 double bond is not

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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.¹⁷ In this paper we now show that the electronic features of a σ -electronegativity effect and π -interactions can be used in concert to further enhance the stability of the imidazol-2-ylidenes.¹⁸

Results and Discussion

The carbene 1,3-dimesitylimidazol-2-ylidene^{4b} (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 ¹H 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 ¹H NMR spectrum of 2 in benzene-*d*₆ shows resonances at δ 2.09, 2.12, and 6.75 for the *p*- and *o*-methyls and the aromatic ring proton of the mesityl groups, respectively. The ¹³C NMR spectrum in benzene-*d*₆ shows a resonance at δ 219.9 for the carbene center. This carbene resonance is typical of imidazol-2-ylidenes and is very

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similar to the chemical shift of the carbone center of **1** (δ 219.7 in thf- d_8).^{4b}

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 $C^{2/c}$. Molecules of 2 are positioned such that a 2-fold symmetry axis passes through the carbene center and bisects the C4-C5 bond of the imidazole ring. This arrangement is similar to that observed for 1,3,4,5tetramethylimidazol-2-ylidene.4b,8 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 1.¹⁹ 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 2is 101.9° which is characteristic of singlet carbenes.^{4,6} The geometry of the central imidazole ring of 2 is virtually identical to that of carbene 1 from which it is derived.^{4b} 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.^{4,15,17} 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 CCl_4 to produce 2proceeds 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 Cl_3C^- 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 CCl₄ 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 Cl_3C^- as illustrated to produce carbene 2. When this chlorination reaction is followed by ¹H 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 σ -inductive effect of the chlorines and their acidifing effect on the imidazole ring protons.

A different reaction can be observed when 2 equiv of carbene **2** react with CCl₄ (eq 2). This reaction probably initiates along a pathway analogous to that shown in Scheme 1 in which "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 (Cl₃C⁻). Reactions of the trichloroimi-

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property	1	6	2·HCI	$3^{b,c}$	4^d	9	\mathbf{J}^{e}	11/	13^{g}	14^{h}
$r(C_2 - N_{1(3)})$	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)
$r(N_{1(3)}-C_{mes})$	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)
$r(C_{4(5)}-CI_{4(5)})$		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)
^{<i>a</i>} The numbering sct $r(C_3 - CH_3) = 133.0(5)$	teme for all compounds $y = 205.06$	is as indicate $\frac{1}{2} h r(C_{2}-T_{e})$	d for 2. ^b Averages from $= 206.6(3)$	n the three cr	ystallographically uniqu	e cations. c $r(C_{2}-CI) =$	$= 168.8(2).^{d} r$	$(C_2 - CCl_2) =$	135.3(4). ^e n($C_2 - CCl_2) = 133.7(6)$

⁽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.



Figure 1. Space filling KANVAS¹⁹ drawing of the X-ray structure of **2**.

Scheme 1



dazolium cation of **3** with Cl_3C^- are in essence degenerate and lead directly (or indirectly) to regeneration of **2** and CCl_4 . However, after sufficient reaction time, another pathway involving the α -elimination of Cl^- from Cl_3C^- to form dichlorocarbene (:CCl₂) 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.²⁰

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 ¹H 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 ¹³C NMR does indicate the loss of the carbene resonance at δ 219.9 and the appearance of two new resonances at δ 70.9 and 140.3 for the new olefinic centers derived, respectively, from :CCl₂ and **2**. The olefinic resonance at δ 70.9 is an unusually high field position for the CCl₂ grouping (*cf.* Cl₂C=CCl₂, δ (¹³C) = 120.5²¹) but is actually characteristic

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Figure 2. Space-filling KANVAS¹⁹ drawing of the X-ray structure of **4**.

of these strongly polarized olefins. Kuhn *et al.* have reported a chemical shift of δ 40.2 for the exocyclic methylene of **5** which correlates well with calculated electron densities in other polarized olefins.²²



Crystals of 4 were grown by cooling a hexane solution at -25 °C. The X-ray structure of **4** is depicted in Figure 2.¹⁹ The two C=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 C=C double bond is 135.3 pm. The $C_4=C_5$ double bond in the imidazole ring is 130.9 pm. The exocyclic double bond is twisted (6.9°) slightly more than the endocyclic double bond (2.4°) . 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 antiorientations about the imidazole ring. The two nitrogens are 15 pm (N_1) and 23 pm (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 $C_2-N_{1(3)}$ bond distances in 4 are on average about 4.1 pm longer than in the carbene 2. The $C_{4(5)}$ - $N_{3(1)}$ 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 π -interaction in the imidazole ring and increased p-orbital contribution to the σ -bonds arising from the pyramidalization of the nitrogens (more sp³-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 σ -bond length changes is negligible.

The byproduct from the reduction of CCl₄ 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 13C NMR Spectra; SADTLER Research Laboratories, Inc.: Philiadelphia, 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 KANVAS¹⁹ drawing of the X-ray structure of **7**.

ions (*e.g.*, **2·HCl**). The imidazolium ring in **3** exhibits the characteristically short $C_2-N_{1(3)}$ bond distances (133.5 pm) and wide $N_1-C_2-N_3$ 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 ($r_{Cl-Cl} \approx 315$ pm, $\theta_{C-Cl-Cl} \approx 175^\circ$). 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 :CCl₂ 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 $C_4=C_5$ 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 ¹H NMR of **7** does not provide any significant structural information except to indicate that **7** is different from the starting material (**6**). The ¹³C NMR of **7** reveals the nature of this product. The original carbene resonance of δ 244.5 in **6** is shifted to 145.8 in **7** for the new olefin carbon, and the CCl₂ olefinic center exhibits a resonance at δ 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 3.¹⁹ 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 C₂-N₁₍₃₎ 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 π -interaction in the imidazoline ring for **7** relative to **6** seems rather small and supports a somewhat limited π -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 :CH₂. 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_2Cl_2 . However, when a mixture of **6** and CH_2Cl_2 in hexane was heated in a sealed tube at 70 °C for 15 h, conversion to the monochloroolefin **9** and the imidazolinium salt **10** was accomplished. The carbene **6** is sufficiently basic that it can deprotonate the intermediate 2-(chloromethyl)imidazolinium chloride to yield the olefin **9**. The byproduct **10** was identified by comparison with an authentic sample.¹⁵

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 ¹H NMR resonance at δ 3.81. This shift is unusually high field for an olefinic center but is



Figure 4. Space-filling KANVAS¹⁹ drawing of the X-ray structure of **11**.

consistent with the results of Kuhn on other highly polarized olefins like 5 (δ CH₂ in 5 is 2.77) and strongly resembles that of olefin **11** (*vide infra*).²² 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 ¹³C NMR of **9** gives a high-field resonance of δ 62.8 for the chloromethylene unit and δ 146.4 for the imidazoline C₂ 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-methylimidazolinium ion (eq 5). This simple 2-methyl residue of this imidazolinium cation that is intermediate in the process of eq 5 is not as acidic as the 2-chloromethyl residue on the intermediate imidazolinium 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 ¹H NMR of **11** shows the terminal methylene resonance at δ 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 ¹³C resonance at δ 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 4.¹⁹ 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 isomorphic. 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 antiorientation about the imidazole ring. As in 9 the $C_2 - N_{1(3)}$ 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 $C_2-N_{1(3)}$ length arising from a decreased π -interaction in the imidazoline ring for 11 relative to 6 is rather small and supports a somewhat limited π -delocalization in 6 and/or a highly polarized olefin structure for 11 (and 9).



Figure 5. Space-filling KANVAS¹⁹ 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.²³ Polarized chalcones (O, S, Se, Te) have been more recently reported from reactions of isolated stable nucleophilic carbenes with chalcogens.^{24–26} 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 ¹H NMR spectrum of 13 provides only sparse information and indicates that a symmetric adduct, different from the initial carbene 2, is formed. The ¹³C NMR spectrum of 13 shows a resonance for the carbon bound to tellurium of δ 134.26 (86 ppm upfield of the carbene resonance in 2). The ¹²⁵Te resonance for tellurone 13 is δ –4. This shift is substantially downfield of the resonance reported by Kuhn *et al.* for 1,3-diisopropyl-4,5-dimethylimidazole-2-tellurone (δ –167.82) and may signal the strong electron-withdrawing σ -influence of the chlorines.²⁶

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 C2/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 that 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*-

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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.²⁷⁻³⁴

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 ¹H 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 ¹³C NMR spectrum of **14** shows a resonance for the carbon bound to tellurium of δ 133.05 similar to the corresponding shift that was recorded for **13** (134.26). The ¹²⁵Te resonance for tellurone **14** is δ –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 (δ –167.82).²⁶ Thus, it appears that the anomalously low field ¹²⁵Te 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 that 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 N1 and N3, 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 CCl₄ 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 KANVAS¹⁹ 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-1,3dimesitylimidazol-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 ¹H or ¹³C NMR spectra that reflect the substantial difference in stabilities. Indeed the ¹³C 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,^{4b} a carbene of such exceptional stability does not result. In our hands 1,3-bis(4chlorophenyl)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 (δ -4) for the tellurium center compared to **14** (δ -150) and 1,3-diisopropyl-4,5-dimethylimidazole-2-tellurone (δ -168).²⁶ The low-field shift of the tellurium center in **13** could be the result of a strong σ -electron-withdrawing effect of the chlorines. Consistent with this intrepretation, 1,3-diisopropyl-4,5-dimethylimidazole-2-tellurone galkyl substituents on the imidazole has the highest ¹²⁵Te shift observed among these three tellurones.

The influence of the chlorine substituents on carbenes like 2 can include both a π -electron-releasing component by virtue of the chlorine lone pair electrons and a σ -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 σ -electronegativity effect has not previously been a great aid to enhancing the stability (lowering the reactivity) of nucleophilic carbenes. The σ -electron withdrawal by the chlorines substantially reduces the basicity of the σ -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 been 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_4 with imidazol-2-ylidenes that produces chlorinated carbenes such as **2**, we have found that CCl_4 will further react with carbenes like **2** and **6** to reduce

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the CCl₄ to a :CCl₂ fragment. Under appropriate reaction conditions the *in situ* generated :CCl₂ 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 CCl₄ with triphenylphosphine that leads to the in situ generation of (dichloromethylene)triphenylphosphorane.²⁰ 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 ¹³C chemical shifts for the terminal CCl_2 groups (δ 70.86 for **4** and δ 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.²² Interestingly, this reduction of CCl₄ by a carboncentered reagent to produce :CCl₂ is reminiscent of the report by Schmeisser and Schröter of the conproportionation of charcoal and CCl₄.³⁵ 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 CCl₄ is reduced to dichlorocarbene.

The reaction of nucleophilic carbenes with 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),³⁶ 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. ¹³C spectra were recorded on a GE Omega 300WB spectrometer. NMR references are (CH₃)₄Si (¹H, ¹³C) and (CH₃)₂Te and 1 M TeCl₄ in THF d_8 (¹²⁵Te). 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 CCl₄ 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 4,5dichloro-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%). ¹H NMR (C₆D₆): δ 2.09 (s, 6 H, p-CH₃), 2.12 (s, 12 H, o-CH₃), 6.75 (s, 4 H, Ar-H). ¹H NMR (thf- d_8): δ 2.07 (s, 12 H, o-CH₃) , 2.33 (s, 6 H, p-CH₃), 7.01 (s, 4 H, Ar-H). ¹³C NMR (C₆D₆): δ 17.86 (s, o-CH₃), 20.99 (s, p-CH₃), 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 C21H22N2Cl2: 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 CCl₄ (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 CH₃CN.

The benzenze extract containing **4** was concentrated to 5 mL, and 3 mL of hexane was added. The solution was cooled to ~0 °C. Light yellow crystals of **4** were collected by filtration (115 mg, 93% yield). Mp: 172 °C. ¹H NMR (C₆D₆, ppm): δ 2.06 (s, 6 H, *p*-CH₃), 2.25 (s, 12 H, *o*-CH₃), 6.69 (s, 4 H, Ar-H). ¹³C NMR (C₆D₆): δ 18.14 (s, *o*-CH₃), 21.01 (s, *p*-CH₃), 70.86 (s, *C*Cl₂), 112.06 (s, *NC*CN), 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 C₂₂H₂₂N₂Cl₄: 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). ¹H NMR (CD₃CN): δ 2.14 (s, 12 H, *o*-CH₃), 2.40 (s, 6 H, *p*-CH₃), 7.27 (s, 4 H, Ar-H). ¹³C NMR (CD₃CN): δ 17.59 (s, *o*-CH₃), 21.32 (s, *p*-CH₃), 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 C₂₁H₂₂N₂Cl₄ (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-chloroimidazolinium Chloride (8) and 1,3-Dimesityl-2-(dichloromethyleneimidazoline (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. ¹H NMR (dmso-*d*₆): δ 2.31 (s, 6 H, *p*-CH₃), 2.33 (s, 12 H, *o*-CH₃), 4.67 (s, 4 H, NCH₂), 7.16 (s, 4 H, Ar-H). ¹³C NMR (DMSO-*d*₆): δ 16.83 (s, *o*-CH₃), 20.53 (s, *p*-CH₃), 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, 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%). ¹H NMR (C₆D₆): δ 2.12 (s, 6 H, *p*-CH₃), 2.29 (s, 12 H, *o*-CH₃), 3.12 (s, 4 H, NCH₂), 6.79 (s, 4 H, Ar-H). ¹³C NMR (C₆D₆): δ 18.49 (s, *o*-CH₃], 20.94 (s, *p*-CH₃), 50.96 (s, NCCN) 73.97 (s, CCl₂), 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) [M⁺, calcd for C₂₂H₂₆Cl₂N₂ 388.1473], 373.1242 (15) [M⁺ - CH₃, 373.1238], 353.1762 (25) [M⁺ - Cl, 353.1785], 338.1514 (40) [M⁺ - CH₃Cl, 338.1560], 305.2147 (100) [M⁺ - CHCl₂, 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 ¹H 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 imidazolinium salt 10 by ¹H NMR), and the filtrate was evaporated to give 9 as a light yellow solid. The olefin 9 decomposed upon attempted crystallization from hexane. ¹H NMR (C₆D₆): δ 2.11, 2.14 (s, 6 H, p-CH₃), 2.22, 2.41 (s, 12 H, o-CH₃), 3.1-3.3 (m, 4 H, 4,5-H), 3.81 (s, 1 H, CHCl), 6.74, 6.82 (s, 4 H, m-CH). ¹³C NMR (C₆D₆): δ 17.95, 18.35 (s, *o*-CH₃), 20.96, 21.04 (s, *p*-CH₃), 47.83, 50.17 (s, NCCN), 62.84 (s, 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-methylimidazolinium Iodide (10) and 1,3-Dimesityl-2-methyleneimidazolidine (11). To a solution of 0.150 g (0.49 mmol) of 1,3-dimesitylylimidazolin-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. ¹H and ¹³C NMR revealed it to be 1,3-dimesityl-2-methylimidazolinium iodide containing a small amount

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of 1,3-dimesitylimidazolinium iodide (**12**). The spectral data for 1,3dimesityl-2-methylimidazolinium iodide were as follows. ¹H NMR (dmso-*d*₆): δ 1.81 (s, 3 H, NCCH₃), 2.31 (s, 6 H, *p*-CH₃), 2.34 (s, 12 H, *o*-CH₃), 4.38 (s, 4 H, CH₂), 7.12 (s, 4 H, Ar-H). ¹³C NMR (DMSO*d*₆): δ 10.84 (s, (NCCH₃), 16.91 (s, *o*-CH₃), 20.60 (s, *p*-CH₃), 49.56 (s, NCCN), 129.80 (s, *m*-C), 130.16 (s, *ipso*-C), 135.50 (s, *o*-C), 139.97 (s, *p*-C), 167.11 (s, NCN). The evaporated mother liquor yielded a small quantity of the olefin **11**. The crude 1,3-dimesityl-2-methylimidazolinium iodide was used without further purification in the deprotonation step.

Crude 1,3-dimesityl-2-methylimidazolinium 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. ¹H NMR (C₆D₆): δ 2.14 (s, 6 H, *p*-CH₃), 2.34 (s, 12 H, *o*-CH₃), 2.59 (s, 2 H, C=CH₂), 3.31 (s, 4 H, CH₂), 6.82 (s, 4 H, Ar-H). ¹³C NMR (C₆D₆) δ 17.20 (s, *o*-CH₃), 20.30 (s, *p*-CH₃), 47.57 (s, NCCN), 48.70 (s, C=CH₂), 129.72 (s, *m*-C), 136.87 (s, *p*-C), 137.28 (s, *ipso*-C), 138.22 (s, *o*-C), 151.78 (s, NCN). MS (70 eV): *m/z* (rel intens) 320.2230 (65) [M⁺, calcd for C₂₂H₂₈N₂ 320.2252], 305.2052 (100) [M⁺ – CH₃, 305.2018], 148.1123 (25) [C₁₀H₁₄N⁺, 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. ¹H NMR (thf-*d*₈): δ 2.10 (s, 12 H, *o*-CH₃), 2.35 (s, 6 H, *p*-CH₃), 7.05 (s, 4 H,

m-CH). ¹³C NMR (thf-*d*₈): δ 18.42 (s, *o*-CH₃), 21.26 (s, *p*-CH₃), 116.59 (s, NCCN), 130.08 (s, *m*-C), 133.86 (s, *ipso*-C), 134.26 (s, *C*=Te), 136.78 (s, *o*-C), 140.92 (s, *p*-C). ¹²⁵Te (94.763 MHz) NMR (thf-*d*₈): δ -4.08 (ref neat Me₂Te); +1730.45 (ref 1 M TeCl₄ in thf-*d*₈). Anal. Calcd for C₂₁H₂₂N₂Cl₂Te: 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 vellow 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. ¹H NMR (thf-d₈): δ 2.06 (s, 12 H, o-CH₃), 2.36 (s, 6 H, p-CH₃), 7.03 (s, 4 H, m-CH), 7.15 (s, 2 H, NCH). ¹³C NMR (thf-d₈): δ 18.72 (s, o-CH₃), 21.20 (s, p-CH₃), 123.48 (s, NCCN), 129.66 (s, m-C), 133.05 (s, C=Te), 136.25 (s, o-C), 136.98 (s, *ipso-C*), 139.53 (s, *p-C*). ¹²⁵Te NMR (thf- d_8 , ref neat Me₂Te): δ -149.8. Anal. Calcd for C₂₁H₂₄N₂Te: C, 58.38; H, 5.60; N, 6.48. Found: C, 58.65; H, 5.62; N, 6.33.

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Supporting Information Available: A complete description of the X-ray crystallographic determinations on 2, 2·HCl, 3·CH₃CN, 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.

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