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Imidazol-2-ylidene Reactivity towards Cyanocarbons

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Dedicated to Professor F. Ekkehardt Hahn on the Occasion of His 60th Birthday

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Abstract. The interaction of electron rich imidazol-2-ylidenes with electron poor cyanocarbons is reported. Contrary to previous reports of electron transfer products from imidazol-2-ylidenes and tetracyanoethylene, a number of ring forming cyanocarbon ring structures are isolated and characterized. Cyanation of the imidazole ring was explored by the addition of cyanogen chloride to imidazol-2-ylidenes. Backbone cyanation often occurs when hydrogen atoms are in the C-4/5 positions. When tetrasubstituted imidazol-2-ylidenes are employed, 2-cyanoimidazolium halide salts can be isolated. These salts maintain an electrophilic cyano group and are precursors to thermally stable high nitrogen content imidazolium tetrazolides.

Introduction

The extreme nucleophilic nature of common imidazol-2-ylidenes and the extreme electrophilic character of common cyanocarbons raise interesting questions of how these mutually aggressive reagents might react with one another. Of particular technological and historical interest is tetracyanoethylene (TCNE).[1] Although there is a propensity for TCNE to act as a one or two electron oxidant, previous work highlights that nucleophiles, such as the cyanide anion, cause ring closing reactions rather than oxidation.[2] Hence, cyanogen is not produced from the oxidative dimerization of cyanide anion through one-electron oxidation by TCNE. It was previously reported that electron transfer reactions take place between TCNE and imidazol-2-ylidenes and that these reactions ultimately lead to the formation of bis(imidazolium) ions.[3] In our experience, the reactivity of imidazol-2-ylidenes frequently parallels reactivity observed for the cyanide anion. This simple analogy serves as a useful guide in the exploration of imidazol-2-ylidene chemistry. However, in the instance of imidazol-2-ylidene/TCNE chemistry, the reaction of TCNE with cyanide suggests a very different course of reactivity than that which has been reported with imidazol-2-ylidenes.[2] Given the ionization potentials of 7.68 and 3.86 eV[4a,4b] for imidazol-2-ylidenes, and cyanide (resp.) and an electron affinity for TCNE of 3.16 eV,[4c] electron transfer chemistry would seem unlikely. A lack of clear experimental evidence (^{13}C NMR, structural analysis, and mass spectrometry) combined with the above chemical reasoning led us to re-investigate this area of research.

Furthermore, from the consideration above, initial nucleophilic attack of an imidazol-2-ylidene on a single nitrile group of TCNE is thus expected to initiate reactivity between singlet nucleophilic carbenes and TCNE. This chemistry is reminiscent of halogenations of singlet nucleophilic carbenes by some halocarbons.[5c] The cyano moiety is often regarded as a pseudohalogen because of its effective electronegativity and univalent nature. Hence a general study of "cyanation" of imidazol-2-ylidenes appears warranted.

While some halogenated imidazol-2-ylidenes have been prepared[5a–5e] there has been only a single report of cyano-substituted imidazol-2-ylidenes. Work from *Kuhn* et al. illustrated that cyano groups can be installed onto an *N*,*N*′-disubstituted imidazole ring by treatment of the chloroimidazolium chloride with dicyanoargentate.[6a,6b,6c] This area thus drew our attention and we looked to explore other sources which could be used to install cyano groups on imidazole heterocycles.

With these considerations in mind, reactions of imidazol-2-ylidenes with TCNE and the general reactivity of cyano-substituted imidazoles are promising targets for further investigation.

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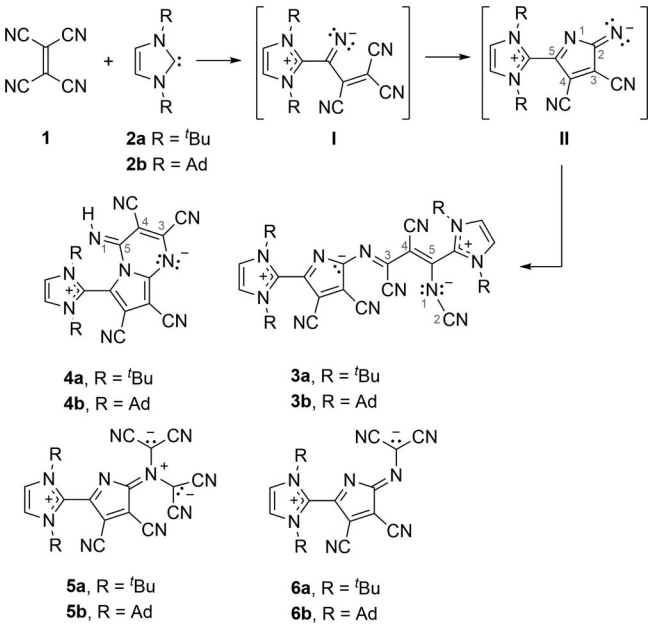
Results and Discussion

Imidazol-2-ylidene Reactivity with TCNE

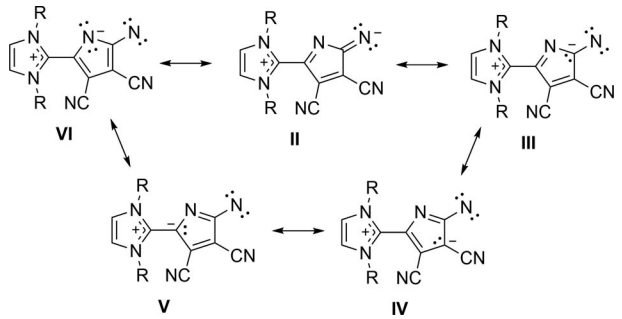
Treating TCNE with carbenes **2a**,**b** at –78 °C typically results in a mixture of red to orange-colored compounds **3**–**6**, all of which may be separated by column chromatography (Scheme 1). The observed products are derived from the TCNE-carbene addition adduct **I** which undergoes an immediate ring-closing reaction with an adjacent cyano group to the zwitterionic imidazolium pyrrolimides **II**. In the presence of large excess of TCNE, the overall product composition does not change compared to the stoichiometric reactions.



Scheme 1. Addition of carbenes **2a,b** to **1** initially forms the zwitterionic heterocycles **II**, which react further to form **3a**,**b** – **6a**,**b**.

The zwitterionic imidazolium pyrrolimides (**II**) are only transiently stable at low temperature and either dimerize to **3a**,**b** through a ring opening reaction, or further react with excess (or unreacted) TCNE yielding a mixture of **5a**,**b** and **6a**,**b** through homolysis of the starting material. It is possible that **6a**,**b** are byproducts of **5a**,**b** as a result of the loss of a dicyanomethide group upon workup. The presence of **5a**,**b** and **6a**,**b** suggests a nitrene-type reactivity of **II**. As illustrated in Scheme 2, four of five valence bond tautomers of **II** can be drawn as nitrenes. Direct observation of **II** by VT-NMR at –80 °C has not been possible as the reaction to form **3a**,**b** – **6a**,**b** appears to be rapid at this temperature. Efforts to trap intermediate **II** with a variety of Lewis acids (MeI, $Me_3O^+BF_4^-$, PPh_3) were not successful and the same distribution of **3a**,**b** – **6a**,**b** were obtained in all cases studied.

Compounds **4a**,**b** are likely rearrangement products of **3a**,**b** in which a pyrrolide nitrogen of one end of the molecule attacks the 5-position (Scheme 1) of the other end of the molecule and subsequent cyclization proceeds. Hydrolysis of any labile N–CN functionalities in air would afford the observed =N–H compounds (**4a**,**b**).



Scheme 2. Resonance structure scheme for **II**–**VI** reveals the potential nitrene-type character.

Generally, the cyanocarbon moieties of adducts exhibit planar or near-planar arrangements suggesting extensive delocalization of the anion charge(s). The imidazolium cations are each planar, but twisted nearly perpendicular to the cyanocarbon heterocycles (Figure 1). There is no clear bond-alternation in the cyanocarbon units which further supports a view of anionic charge delocalization in the adducts. Some disorder in the adamantyl groups of **4b** is observed (Figure 2).

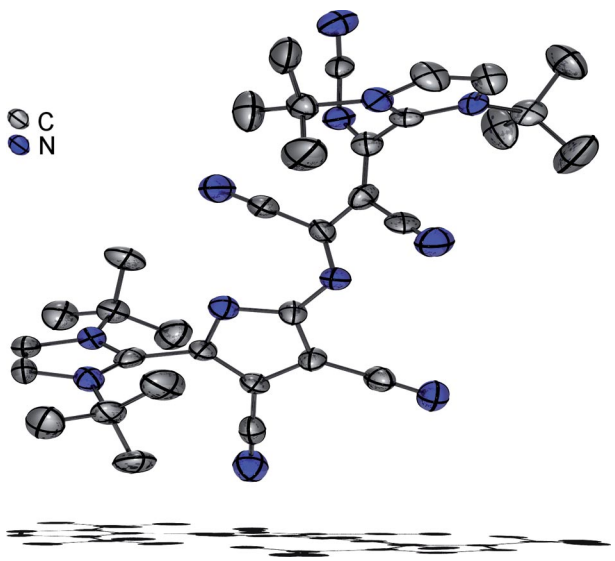


Figure 1. X-ray crystal structures of **3a** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and molecules of solvation are omitted for clarity.

Comparison of the physical characteristics along with the NMR signals of the imidazol-2-ylidene/TCNE addition products here with those results reported by *Clyburne* et al. suggest that identical or similar product mixtures were formed in the two studies.[3] A mistake in product identity is easy to understand given that ^{1}H NMR analysis of the fractions reveal only symmetric imidazolium resonances for the *tert*-butyl or adamantly groups respectively, and imidazole C-4/5 ring protons (there are no hydrogen atoms in the cyanocarbon fragment). The ^{13}C spectra reveal more about the chemical identity of the compounds showing a complex set of signals located in the nitrile region from 105–115 ppm, but long relaxation times make these carbons difficult to observe. IR spectra confirm the

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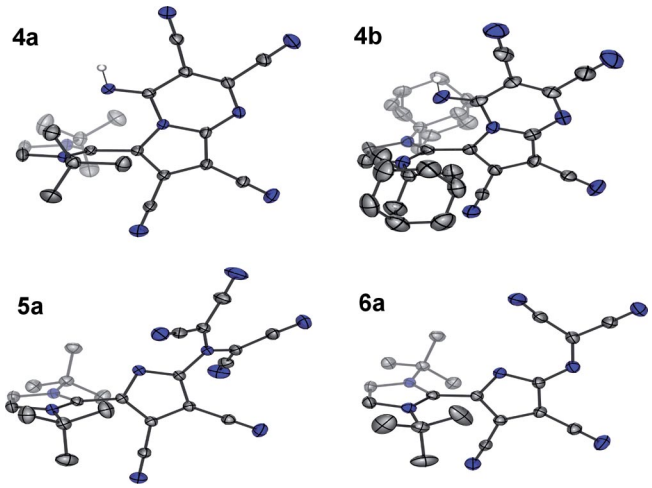


Figure 2. X-ray crystal structures of **4a**, **4b**, **5a**, and **6a** with thermal ellipsoids drawn at the 50 % probability level. C–H hydrogen atoms and molecules of solvation are omitted for clarity.

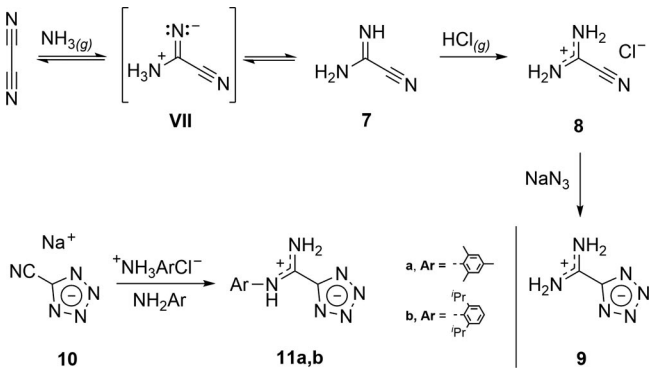
presence of nitrile moieties with C–N stretching frequencies between 2230 cm^{-1} to 2200 cm^{-1}. Elemental analysis also provides a sufficiently sensitive means to correctly determine the product compositions. Adduct **3a** shows 27 % mass composition nitrogen, while the charge transfer complex proposed earlier would have given only a 23 % nitrogen content. Finally, crystal structures of the individual components **3a**–**6a** and **4b** unambiguously confirm the actual product identities.

Preparation and Reactivity of Cyanoiminium Ions

Work to prepare the simplest of 2-cyano substituted carbene systems, the unsubstituted diamino carbene (e.g. cyanoamidinium salts), led to the investigation of the addition of ammonia to cyanogen. This reaction leads to the unsubstituted cyanoamidine **7**. The chemical properties of **7** were unknown as a result of the challenges associated with working with toxic materials and materials with only transient stability. Cyanoformamidine **7** has been reported to be unstable at above –30 °C, and the trapping of this intermediate with acid must be conducted rapidly at low temperature (< –30 °C).[7]

Attempts to synthesize cyanoformamidine **7** as reported in the patent literature[7] were unsuccessful in our hands. Only cyano-containing polymeric byproducts are obtained. Cyanoformamidine **7** and the ammonia adduct of **7** are too thermally sensitive to be isolated. Rapid change in solution color from light yellow to dark brown in liquid ammonia even at –30 °C provides indication of decomposition of the initially formed cyanoamidine.

A facile synthesis of **8** is reported herein (Scheme 3). Addition of one equivalent of gaseous ammonia to a diethyl ether solution of cyanogen at –78 °C affords cyanoformamidine **7** as a yellow solution. Treatment of the cold solution of **7** with gaseous hydrogen chloride at –90 °C results in a 3:1 mixture of the desired compound **8** and ammonium chloride, which can be recrystallized from HCl (6 N) at –24 °C to afford **8** as a pure material. The presence of ammonium chloride in the final product suggests that formation of cyanoamidine **7** from cyanogen is reversible and that, depending on the position of the equilibrium, some ammonia can be trapped along with the desired cyanoamidinium choride (hence the need for tight temperature control during the very exothermic protonation reaction). The cyanoformamidinium salt **8** is stable under acidic conditions (up to 60 °C in aqueous solution) but undergoes decomposition in neutral to basic media.



Scheme 3. Preparation of amidinium tetrazolides **9**, **11a**,**b**. Cyanoformamidine (**7**), prepared by ammonia addition to cyanogen, can be isolated as its cyanoamidinium salt (**8**).

The ^{1}H NMR spectrum of **8** is recorded as a broad singlet at δ = 10.7 ppm in [D_6]DMSO, indicating either fast rotation of the amidino (NH_2) groups on the NMR timescale or rapid proton exchange. The cyano and amidinium carbon resonances have the expected downfield shifts at δ = 109.7 and 141.2 ppm in the ^{13}C NMR, illustrating the cationic nature of the organic fragment. Two nitrogen signals at δ = 248.5 and 104.9 ppm are observed in ^{15}N NMR spectrum for the amidinium and cyano nitrogen atoms, respectively. The IR spectrum confirms the presence of the cyano group, which has weak symmetric and asymmetric stretches at 2260, 2236, and 2126 cm^{-1}. The amidino groups exhibit N–H absorptions at 3220 and 2986 cm^{-1} respectively.

Single crystals of cyanoformamidinium chloride **8** were obtained from a saturated solution in HCl (6 N) at –24 °C. X-ray crystallographic analysis reveals that **8** crystallizes as a planar molecule with a C_2 symmetry axis about the cyanocarbon plane (Figure 3A). The chloride anion sits 3.3 Å over the amidinium plane and enjoys an electrostatic interaction with the cation. The chloride anion also builds hydrogen bond bridges with coplanar cyanoamidinium moieties [Cl–N1 (3.541 Å), Cl–N2 (3.716 Å), and Cl–N3 (3.929 Å), Figure 3B]. Intermolecular hydrogen bonding between the amidinium hydrogen atoms and chloride anions dominates the crystal packing interactions.

The cyano group of **8** is sufficiently electrophilic that [3+2] cycloaddition with sodium azide is facile at room temperature, affording a previously reported amidinium tetrazolide **9**.[8] Similar hydrogen bonding networks in the crystal packing are observed for both **8** and **9** where extensive intermolecular hydrogen bonding from the amidinium fragment is observed with the anionic moiety. In the case of **9**, this provides high

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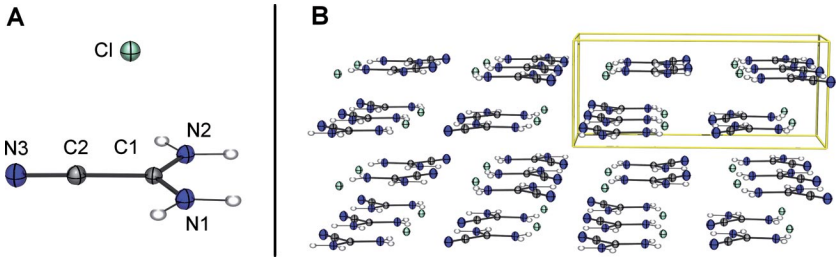

Figure 3. X-ray crystal structure of (A) the asymmetric unit of **8** and (B) the packing diagram. Thermal ellipsoids drawn at the 50 % probability level.

thermal stability with a reported melting point of 254–290 °C, and very low solubility.[8]

N-amidinium substitution with non-hydrogen-bond donors was carried out to perturb the effect of intermolecular hydrogen bonding. *N*-aryl amidinium tetrazolides **11a**,**b** were prepared in moderate yields through the condensation of aryl-substituted ammonium chlorides with sodium cyanotetrazolide **10** in the neat aniline (Scheme 3). Crystal growth of **11a**,**b** from anhydrous solvent systems proved very difficult, presumably because of the disruption of the well-coordinated hydrogen bond donor and hydrogen acceptor centers in the parent amidinium tetrazolide **9**. Single crystals of **11a** grown from moist acetonitrile were, however, easily obtained. It appears that a single water of solvation is required to restore balance to the solid state hydrogen bonding network when a substituent is incorporated onto the amidinium moiety in place of an N–H bond (Figure 4A and B). Two modes of hydrogen bond donation are present: from the amidinium N–H to the water oxygen, and from the water hydrogen atoms to the tetrazolide functionality [NH–O (2.05 Å), OH–N (1.89 Å)]. Some disorder in the methyl groups of the mesityl rings is present. The crystal packing diagram of **11a** indicates some of the same packing interactions as those reported in **9**. Since the number of hydrogen-bond donors is reduced from N-substitution, hydrogen bonding donors from a water of solvation plays a role in the crystal packing.

In an attempt to further explore the chemistry of cyano groups on highly stabilized cationic functionalities, we sought to prepare functionalized cyanoimidazolium cations. As mentioned in the introduction, these compounds have been reported, however their preparation is tedious and isn't applicable to a wide range of imidazole heterocycles.[6] We therefore looked for an alternative approach to cyanoimidazoles.

Cyanogen chloride was previously demonstrated to act as an effective reagent for heterocycle cyanation.[9] Treatment of **2a** with cyanogen chloride results in a mixture of imidazolium chloride **13** and 2,5-dicyanoimidazolium chloride **15**. This product distribution indicates selectivity in nucleophilic attack of the carbene at the nitrile group, rather than the halide. The imidazole ring protons of the initial addition adduct, imidazolium salt **12**, become significantly more acidic upon cyanation, and unreacted carbene **2a** deprotonates the backbone protons of **12** forming imidazolium chloride **13** and a nucleophilic zwitterionic imidazolide **14**. The transient zwitterionic species either directly reacts with cyanogen chloride, or undergoes a rearrangement to a 4-cyanoimidazol-2-ylidene which further reacts with cyanogen chloride to form **15** (Scheme 4).

HMBC correlation spectroscopy shows symmetric and asymmetric imidazolium resonances and confirms a mixture of **13** and **15**. The C4–H resonance of **15** (Figure 5, green) at δ = 8.26 ppm shows ^{3}J correlations to the C-2 imidazolium carbon at δ = 114.79 ppm and one of the *t*Bu resonances at δ = 65.65 ppm. Additionally, a weak ^{3}J coupling to the backbone cyano group at δ = 107.74 ppm can be observed along with the direct ^{1}J coupling at δ = 124.55 ppm. The ^{1}H, ^{13}C, and HMBC spectra of **15** indicate "abnormal" imidazolium ion character where the C-5 carbon resonance is observed in a region where the C-2 carbon of imidazolium ions typically resonate while the resonance for the C-2 carbon of **15** appears significantly upfield of typical C-2 chemical shifts. The symmetric imidazolium resonances of **13** match the reported values (Figure 5, red).

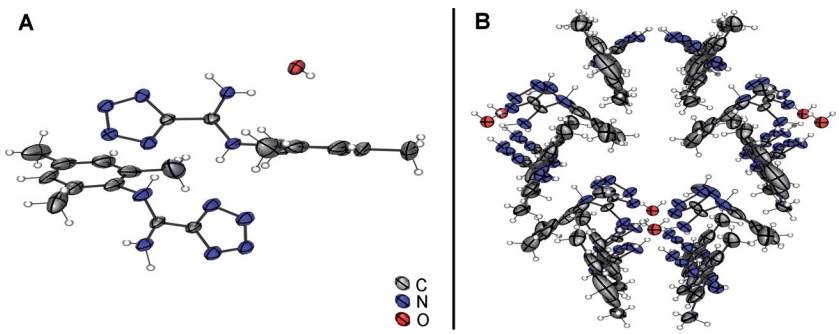

Figure 4. X-ray crystal structure of the (A) asymmetric unit and (B) packing diagram of **11a**. Thermal ellipsoids drawn at the 50 % probability level.

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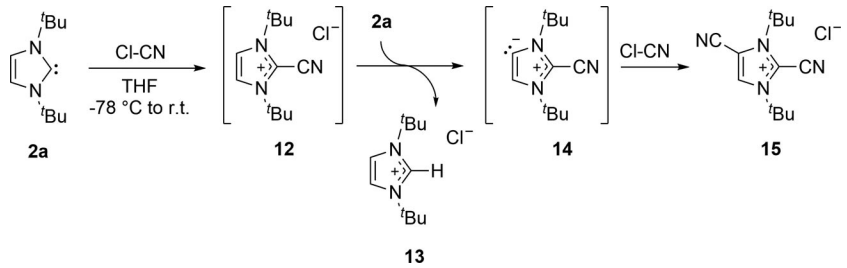


Scheme 4. Addition of excess cyanogen chloride to **2a** results in a mixture of **13** and **15**.

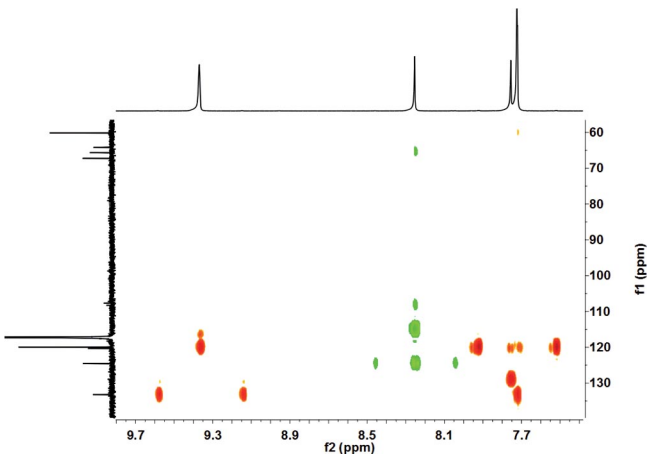
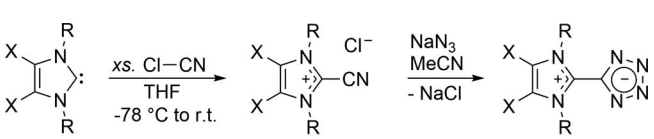


Figure 5. HMBC correlation spectroscopy of a mixture of **13** (red) and **15** (green) in CD_3CN at 25 °C. The backbone C4–H signal of **15** at δ = 8.26 ppm shows ^3J coupling to the asymmetric ^{13}C imidazolium resonances.

Tetra-substituted imidazol-2-ylidenes were employed to preclude imidazole-backbone deprotonation. Addition of excess cyanogen chloride to 4,5-disubstituted imidazol-2-ylidenes (**16** and **17**) suppresses backbone reactivity and results in the clean formation of 2-cyanoimidazolium chlorides **18** and **19** (Scheme 5). These compounds can be isolated from the crude mixture as moisture sensitive solids. The yield and ease of isolation is dependent on limiting the addition of large excesses of cyanogen chloride. If the exact quantity of ClCN is not employed, there is variability in the yield and degree of cyanocarbon containing by-products. The ^{13}C NMR shifts of the cyano (CN, $\delta \approx 107$ ppm) and imidazolium carbon (C-2, $\delta \approx$ 130 ppm) resonances are slightly upfield of those in **8** as a result of the electron releasing nature of the imidazolium ring.



16 R = X = Me
17 R = Mes, X = Cl
18 R = X = Me
19 R = Mes, X = Cl
20 R = X = Me
21 R = Mes, X = Cl

Scheme 5. Addition of excess ClCN gas to backbone functionalized carbenes **16**, **17** results in 2-cyanoimidazolium salts **18**, **19**. The C2 cyano groups rapidly undergo cyclization with azide to form the tetrazolides **20**, **21**.

The crystal structure of **19** reveals that there is a significant Cl···CN interaction with Cl–C distances of 3.14 Å, much shorter than that found in **8**. Furthermore, the cyano group deviates from linearity with a C3–C4–N3 bond angle of 169.3° (Figure 6).

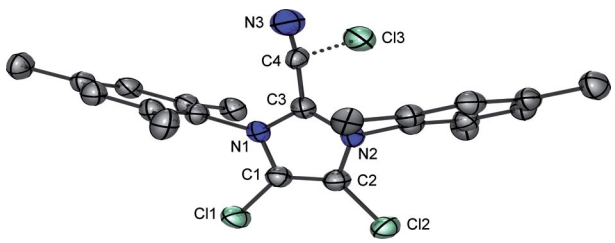


Figure 6. X-ray crystal structure of **19** with thermal ellipsoids drawn to the 50% probability level. Hydrogen atoms and THF of solvation are omitted for clarity.

Cyanoimidazolium salts **18** and **19** exhibit a similar reactivity as **8** for [3+2] cyclization with azide, providing a convenient route to functionalized imidazolium tetrazolides (**20**, **21**). As with **11**, crystal growth of **20** and **21** from anhydrous solvents proved to be problematic. However, large crystals of **20** are easily obtained from water. Molecules of **20** crystallize as head-to-tail pairs, suggesting that electrostatics and dipole pairing play a dominant role in crystal packing. The N–C–C–N dihedral angle between the two ring systems varies between 9.4–10.9° such that some degree of conjugation may exist between the tetrazolide and imidazolium moieties. The geometric parameters for the imidazolium[5c,10a–10f] and tetrazolide[8,11a–11e] groups are in good agreement to other examples reported herein (and elsewhere). Interestingly, the structure of **20** contains five water molecules of solvation that encase the tetrazolide group in a ring of "ice". This solvation further demonstrates the affinity of the tetrazolide group (an isoster for carboxylate) to participate in hydrogen bonding networks.

Comparison of the water of solvation in the crystal structures of a previously reported amidinium tetrazolide **9**, *N*-mesitylamidinium tetrazolide **11a**, and an imidazolium tetrazolide **20** illustrates that as the degree of *N*-amidinium substitution increases, hydrogen bonding from aqueous solvent becomes more prevalent. Tetrazolide **9** has no water of solvation in the crystal structure despite being grown from acidic aqueous medium. The crystal structure of *N*-substituted tetrazolide **11a**, contains one half of a water of solvation, which acts as both a

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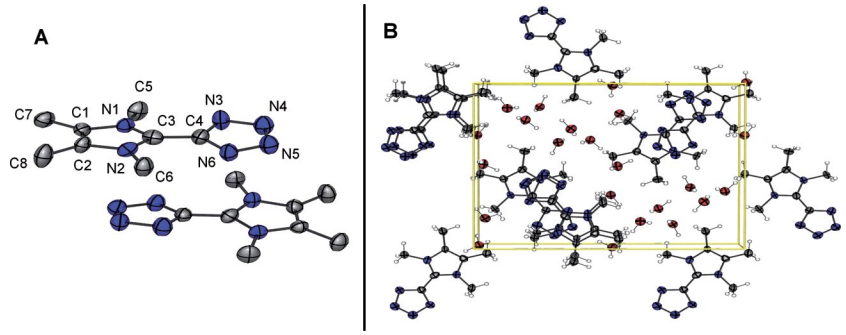

Figure 7. X-ray crystal structure of the (A) asymmetric unit with head-to-tail stacking (hydrogen atoms are omitted for clarity) and (B) packing diagram of **20** (including water of solvation). Thermal ellipsoids drawn to the 50% probability level.

hydrogen-bond acceptor and donor. Ultimately, when the amidinium group is completely substituted and there are no N–H donors present as in **9**, intermolecular hydrogen bonding from waters of solvation plays a critical role in the solid-state structure. In the crystal structure of **20**, the five water molecules of solvation act exclusively as hydrogen bond donors to the tetrazolide group and acceptors and donors to one another. This interaction is sufficiently well-organized that the crystal does not show signs of crystallographic disorder until one approaches temperatures near 60 °C. In this respect, the water is "frozen" through hydrogen bonding even above the melting point for ice (Figure 7).

Conclusions

The addition of nucleophilic imidazol-2-ylidenes to cyano groups was explored. In contrast to earlier reports where electron transfer was claimed to dominate, it was found that the interactions of imidazol-2-ylidenes with TCNE invoke a ring-closing reaction exposing a wealth of chemistry associated with cyclization and condensation reactions. Current methods to trap the first reactive intermediate from cyclization have been unsuccessful due to the rapid subsequent reactions with unreacted TCNE. A number of highly unsaturated zwitterionic cyanocarbons are formed, which were all characterized spectroscopically and structurally, and their reactivity and applications are currently being investigated. Reactions of singlet nucleophilic carbenes with electron deficient fluoroolefins will be reported in a subsequent publication.[12]

Treatment of carbenes with cyanogen chloride results in nucleophilic attack at the cyano group, where cyano-substituted imidazolium salts are formed. Backbone cyanation occurs with imidazol-2-ylidenes which are unsubstituted in the C-4/5 positions. Treatment of tetra-substituted imidazol-2-ylidenes with cyanogen chloride forms 2-cyanoimidazolium chlorides. These species maintain an electrophilic cyanocarbon center and undergo cyclization reactions with sodium azide. Thermally stable imidazolium tetrazolides (m.p. ≈ 240 °C) were isolated and characterized, which show analogies to imidazolium carboxylates.

Experimental Section

General Considerations: All moisture and air sensitive reactions and manipulations were carried out in oven-dried glassware in a dry nitrogen atmosphere, either in a Vacuum Atmosphere® dry-box or by using standard Schlenk techniques. Unless otherwise noted, reagents were used as obtained from commercial sources. Tetrahydrofuran was dried with calcium hydride then distilled from sodium/benzophenone and stored in the drybox. Hexane, toluene, and Et_2O were distilled from calcium hydride and stored in the drybox. Solvents removed in vacuo were done so using a mechanical vacuum pump. Melting points were obtained using a Laboratory Device MEL-TEMP® II apparatus and are uncorrected. ^{1}H NMR spectra were obtained with a Bruker® AM-500 MHz spectrometer. ^{1}H NMR chemical shifts are reported in parts per million (ppm) using residual solvent protons as the internal standard are reported as referenced to tetramethylsilane (δ scale) with positive shifts downfield using an internal standard from the solvent, [D_3]acetonitrile (δ =1.94 ppm), [D_6]DMSO (δ =2.50 ppm), [D_2]dichloromethane (δ =5.32 ppm), and [D_3]nitromethane (δ =4.30 ppm). ^{13}C NMR spectra were recorded at 125.8 MHz and chemical shifts are reported in ppm relative to tetramethylsilane (δ scale) using an internal standard from the solvent, [D_3]acetonitrile (118.7 and 1.4 ppm), [D_6]DMSO (δ =39.5 ppm), [D_2]dichloromethane (δ =54.0 ppm), and [D_3]nitromethane (δ =57.3 ppm). ^{15}N NMR spectra were recorded at 50.7 MHz and chemical shifts are reported in ppm relative to ammonium sulfate (δ scale). Spectral data are listed as follows: chemical shift (multiplicity, relative number of hydrogen atoms, coupling constant). Multiplicities are denoted as follows: s (singlet), d (doublet), dd (doublet of doublets), dq (doublet of quartets), t (triplet), q (quartet), m (multiplet), br (broad), quin (quintet), hpt (heptet). Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, Georgia, and are reported as relative percent of each element analyzed. FT-IR measurements were recorded with a JASCO FT-IR 4100 using a KBr pellet. Signals are reported in reciprocal wavelength (cm^{-1}) as strong (s), weak (w), or broad (br.).

CAUTION! Cyanogen chloride is a toxic volatile gas and all manipulations were carried in a well ventilated fume hood.

Isolation of 3a: In an inert nitrogen atmosphere, carbene **2a** (0.500 g, 2.78 mmol) in THF (30 mL) was slowly added to a solution of TCNE (0.355 g, 2.78 mmol) in THF (25 mL) at –78 °C. The reaction was allowed to warm to room temperature yielding a deep red solution. The reaction was transferred to a drybox where THF was removed in vacuo to afford a red solid, which was further suspended in CH_2Cl_2 and filtered to remove any imidazolium salts. **3a** (0.390 g, mmol, 46%

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yield) was isolated from the crude reaction mixture by crystallization from MeCN at –26 °C, producing red X-ray quality crystals. M.p. 200 °C (dec, black). **^{1}H NMR** (500 MHz, [D_3]acetonitrile): δ = 7.79 (s, 2 H), 7.68 (s, 2 H), 1.80 (s, 18 H), 1.52 (s, 18 H). **^{1}H NMR** (500 MHz, [D_2]dichloromethane): δ = 7.52 (s, 2 H), 7.46 (s, 2 H), 1.86 (s, 18 H), 1.57 (s, 18 H). **^{13}C NMR** (125.8 MHz, [D_3]acetonitrile): δ = 30.00, 30.10, 65.70, 66.28, 101.03, 114.25, 115.53, 116.72, 119.17, 120.53, 121.06, 122.48, 131.07, 140.19, 141.33, 152.40, 159.11. $C_{17}H_6N_{20}$: calcd. C 66.21; H 6.54; N 27.28 %; found: C 65.79; H 6.90; N 27.46 %.

General Procedure for the Addition of 2a,b to 1: Within the drybox, a solution of carbene (0.1–0.2 M) in THF was prepared in a Schlenk flask equipped with a rubber septum. A second Schlenk flask of TCNE in THF (0.1–0.2 M) equipped with a rubber septum and stir bar was prepared within the drybox. The flasks were transferred outside of the drybox, placed in an inert nitrogen atmosphere, and cooled to –70 °C in a dry ice/acetone bath. The carbene solution was added dropwise to the TCNE solution by syringe. After complete addition, the reaction flask was slowly left to warm to room temperature. The solvent was evaporated in vacuo and the solids that remained were further separated by column chromotography on silica gel.

Isolation of 4a: The reaction of carbene **2a** (0.250 g, 1.37 mmol) and TCNE (0.176 g, 1.38 mmol) yields **4a** (0.100 g, 0.243 mmol, 18 % yield) as a gold-yellow solid. **4a** can be isolated from the crude reaction mixture by chromatography on neutral silica gel in air using a 5 % MeCN/CH_2Cl_2 eluent. X-ray quality gold irregular-block crystals of **4a** can be grown by heating and cooling a saturated DMSO solution. **^{1}H NMR** (500 MHz, [D_6]DMSO): δ = 8.38 (s, 2 H), 7.67 (s, 0.3 H), 1.40 (s, 18 H). **^{13}C NMR** (125.8 MHz, [D_3]acetonitrile): δ = 149.97, 147.44, 136.58, 131.47, 122.93, 116.12, 115.67, 112.87, 112.13, 111.55, 105.88, 85.03, 83.68, 64.39, 29.87.

Isolation of 4b: The reaction of carbene **2b** (0.336 g, 1.00 mmol) and TCNE (0.128 g, 1.0 mmol) yields **4b** (0.085 g, 0.15 mmol, 15 % yield) as a yellow solid. **4b** can be isolated from the crude reaction mixture by chromatography on neutral silica gel in air using a 10 % MeCN/CH_2Cl_2 eluent. X-ray quality crystals of **4b** can be grown by cooling a saturated EtOAc solution from room temperature to –20 °C to afford colorless crystals. M.p. > 250 °C. **^{1}H NMR** (500 MHz, [D_6]DMSO): δ = 8.47 (s, 2 H), 7.56 (s, 1 H), 2.08 (br., 6 H), 1.90 (m, 12 H), 1.60 (m, 12 H). **^{13}C NMR** (125.8 MHz, [D_6]DMSO): δ = 149.85, 147.30, 136.57, 131.08, 116.32, 115.77, 113.08, 112.09, 111.93, 106.16, 84.66, 83.81, 65.69, 41.84, 34.99, 29.71.

Isolation of 5a: The reaction of carbene **2a** (0.245 g, 1.36 mmol) and TCNE (0.972 g, 6.81 mmol) yields **5a** as a red solid. **5a** can be isolated from the crude reaction mixture by chromatography on neutral silica gel in air using a 7.5 % MeCN/CH_2Cl_2 eluent. X-ray quality red crystals of **5a** can be grown by heating and cooling a saturated DMSO solution. M.p. 211–214 °C (dec). **^{1}H NMR** (500 MHz, [D_3]acetonitrile): δ = 7.77 (s, 2 H), 1.52 (s, 18 H). **^{13}C NMR** (125.8 MHz, [D_3]acetonitrile): δ = 136.57, 135.95, 132.28, 120.97, 112.67, 112.35, 111.36, 110.95, 107.73, 105.86, 96.52, 64.26, 29.74. **FT-IR** (KBr): $\tilde{\nu}$ = 3190.65 (w, CH_3), 3163.65 (w, CH_3), 3007.44 (w, CH_3), 2938.98 (w, CH_3), 2228.34 (s, CN), 2210.49 (w, CN) 2209.06 (s, CN), 2204.24 (w, CN), 1582.31 (w), 1441.53 (s) cm^{-1}.

Isolation of 6a: The reaction of carbene **2a** (0.500 g, 2.78 mmol) and TCNE (0.434 g, 3.39 mmol, 1.22 equiv.) yields **6a** (0.172 g, 0.46 mmol, 17 % yield) as an orange solid. **6a** can be isolated from the crude reaction mixture by chromatography on neutral silica gel in air using a 7.5 % MeCN/CH_2Cl_2 eluent. X-ray quality crystals of **6a** can be grown by cooling a saturated 1:1 MeCN/toluene solution from room temperature to –20 °C. M.p. 205–209 °C (dec). **^{1}H NMR** (500 MHz, [D_3]acetonitrile): δ = 7.76 (s, 2 H), 1.55 (s, 18 H). **^{13}C NMR** (125.8 MHz, [D_3]acetonitrile): δ = 148.45, 137.91, 133.72, 120.69, 114.92, 113.80, 122.88, 111.92, 104.86, 103.64, 99.96, 64.01, 29.89. **MS-FAB** ($M+H_2+H^+$) = 375.21. **FT-IR** (KBr): $\tilde{\nu}$ = 3186.79 (w, CH_3), 3152.08 (w, CH_3), 3007.44 (w, CH_3), 2989.12 (w, CH_3), 2223.52 (s, CN), 2206.17 (w, CN), 1574.59 (w), 1433.82 (s) cm^{-1}.

Synthesis of Amidinium Salt 8: An oven-dried 300 mL triple-neck round-bottomed flask equipped with a dry-ice condensor, stir bar, inlet gas bubbler, and thermometer was setup. The dry-ice condensor outlet was fitted to one end of an in-line oil bubbler with "T" and negative pressure catch, and the other end was fitted to a nitrogen line with a slow stream of nitrogen. The inlet gas bubbler was connected to a cylinder of cyanogen via a 1/16″ coiled flexible polypropylene tubing (40 cm in linear length). This coiled connection tubing allowed for tensionless weighing of the attached gas cylinders. The amount of cyanogen condensed in the reaction vessel was determined by mass loss from the cylinder. Dry diethyl ether (100 mL) was placed in the 300 mL reaction flask and cooled to –78 °C by a dry ice/2-propanol bath. Cyanogen (11.1 g, 214 mmol) was slowly condensed into the cold diethyl ether. After the condensation of the cyanogen was complete, the cyanogen cylinder was detached from the tubing, and the tubing back-purged with dry nitrogen to remove any residual cyanogen from the transfer system. Next, a cylinder of ammonia was connected to the system and, as with the cyanogen, was NH_3 (4.80 g, 282.3 mmol) condensed into the cyanogen/ether solution at –78 °C. After the addition of the ammonia was complete the ammonia cylinder was disconnected from the setup and the connecting tubing was again back-purged with dry nitrogen to remove residual ammonia from the delivery lines. The ether solution of cyanoamidine and ammonia was stirred for an additional 10 min at –78 °C and then cooled to –90 °C by means of a liq. N_2/EtOH bath. A cylinder of dry HCl was connected to the system and at –90 °C HCl (10.3 g, 282.2 mmol) was slowly condensed into the reaction vessel to avoid temperature excursions and shifting the ammonia/cyanoamidine equilibrium. Protonations at higher temperatures lead to formation of more ammonium chloride. As the HCl was added the solution becomes light brown and copious solids precipitate from the ether. The HCl cylinder was disconnected from the system and the connecting tubing is back-purged with dry nitrogen to remove residual HCl. The reaction suspension was allowed to warm to room temperature and the solids collected by filtration under nitrogen as a light brown solid and washed with 20 mL dry ether. The crude product (25.3 g) is a 3:1 mixture of cyanoamidium chloride, **8**, and ammonium chloride. Recrystallization of crude solid from 6*N* aq. HCl (ca. 40 mL) gave cyanoformamidinum chloride **8** (16.2 g, mmol, 72 %) as a beige solid. The freshly filtered product was washed with 10 mL 8N aq. HCl and dried under a stream of dry nitrogen overnight. The isolated cyanoamidinium chloride was 99 % pure as indicated by ^{1}H NMR spectroscopy. Brown solid (from 6N HCl), mp. 154–190 °C (in a nitrogen atmosphere, dec, black) [mp. 150–170 °C[7] (dec)], **^{1}H NMR** (500 MHz, [D_6]DMSO): δ = 10.71 (br. s, NH_2). **^{13}C NMR** (125.8 MHz, [D_6]DMSO): δ = 141.2 (q, $C(NH_2)_2$), 109.7 (q, CN). **^{15}N NMR** (50.7 MHz, [D_6]DMSO): δ = 104.9 (NH_2), 248.5 (CN). **FT-IR** (KBr): $\tilde{\nu}$ = 3221 (m), 2986 (s), 2778 (w), 2728 (w), 2678 (w), 2260 (vw), 2236 (vw), 2126 (vw), 1698 (vs), 1684 (vs), 1599 (vw), 1579 (vw), 1473 (m), 1397 (m), 1145 (w), 902 (w), 702 (m), 664 (w), 594 (w), 485 (m), 475 (m) cm^{-1}.

Synthesis of 11a: In a 20 mL round flask with a T-shaped glass tube, a solution of sodium cyanotetrazolide (100 mg, 0.840 mmol), 1,3,5-trimethylaniline hydrochloric acid salt (146 mg, 0.840 mmol) in 1,3,5-trimethylaniline (1 mL) was stirred at 80 °C for 7 d in a nitrogen flow.

Filtration of the reaction mixture gave the white solid containing 1,3,5-trimethylaniline after washing with $CHCl_3$ (0.5 mL). The white solid was washed with a hexane:$CHCl_3$ mixture (20:1) at ca. 60 °C. The white solid (141 mg, 0.613 mmol, 73 % yield) was obtained after drying in air. M.p. 260–264 °C (dec). **^{1}H NMR** (500 MHz, [D_6]DMSO): δ = 11.25 (s, 1 H), 9.53 (s, 1 H), 8.49 (s, 1 H), 7.04 (s, 2 H), 2.30 (s, 3 H), 2.15 (s, 6 H). **^{13}C NMR** (125.8 MHz, [D_6]DMSO): δ = 154.3, 153.3, 138.5, 135.6, 129.8, 129.5, 21.1, 17.8. **IR** (KBr): $\tilde{\nu}$ = 3431 (w), 3068 (m), 2983 (s), 2365, 2345, 1685, 1625, 1389 cm^{-1}. **EI-MS** (70 eV, Int) *m/z* 230 (M).

Synthesis of 11b: In a 20 mL round flask with a T-shaped glass tube, a solution of sodium cyanotetrazolide (50 mg, 0.43 mmol), 2,6-diisopropylaniline hydrochloric acid salt (91 mg, 0.43 mmol) in 2,6-diisopropylaniline (2 mL) was stirred at 100 °C for 5 d in a nitrogen flow. Filtration of the reaction mixture gave the white solid contained 2,6-diisopropylaniline after washing with $CHCl_3$ (0.5 mL). The white solid was washed with a hexane:$CHCl_3$ mixture (20:1) at ca. 60 °C. The white solid (75 mg, 0.28 mmol, 65 % yield) was obtained after drying in air. M.p. 272–273 °C (dec). **^{1}H NMR** (500 MHz, [D_6]DMSO): δ = 11.43 (s, 1 H, NH), 9.55 (s, 1 H, NH), 8.50 (s, 1 H, NH), 7.45 (t, 1 H, *J* = 8.0 Hz), 7.32 (d, 2 H, *J* = 8.0 Hz), 2.91 (2 H, hpt, *J* = 7.0 Hz), 1.20 (d, 6 H, *J* = 7.0 Hz), 1.17 (d, 6 H, *J* = 6.5 Hz). **^{13}C NMR** (125.8 MHz, [D_6]DMSO): δ = 155.7 (q), 153.3 (q), 146.1 (q, C2,6), 130.1 (t, C4), 129.3 (q, C1), 124.7 (t, C3,5), 28.76 (t, CH), 24.35 (t, CH_3), 23.40 (t, CH_3). **IR** (KBr): $\tilde{\nu}$ = 3423 (w), 3082 (m), 2966 (s), 2871 (m), 1686 (m), 1670 (m), 1625 (s), 1459 (m), 1389 (m), 1365 (w), 1329 (w), 1291 (w), 1183 (w), 1143 (w), 1108 (w), 1058 (w), 1034 (w), 937 (w), 849 (w), 807 (w), 734 (w), 677 (w), 532 (w), 488 (w) cm^{-1}. **EI-MS** (70 eV, Int) *m/z* 272 [M$^+$, 85], 244 (M–N2, 10), 229 (M–*i*Pr, 82), 201 (M–71, 100), 186 (DiipNC, 51), 174 (DiipNH, 32).

General Procedure for the Addition of Cyanogen Chloride to Carbenes: Within the drybox, carbenes **6a**, **16**, or **17** dissolved in 5 mL of THF was added to a 100 mL Schlenk tube equipped with a stir bar and gas bubbler (with stopcock fitting). The bubbler was positioned so that the bottom of the gas outlet tube was just above the surface of the THF solution. With both stopcocks closed, the flask was transferred outside of the drybox where it was connected to both a Schlenk line, and a cylinder of cyanogen chloride through a three-way connector via the gas bubbler side stopcock adaptor. The Schlenk tube stopcock was equipped with an oil immersion bubbler (with negative pressure catch) which had exhuast gas pass through a concentrated solution of potassium hydroxide. After purging the headspace of the three-way adaptor with a vacuum-N_2 cycle, the Schlenk tube was cooled to –30 °C using a liq. N_2/EtOH bath, while ensuring a moderate stirring velocity. Both stopcocks on the reaction flask were opened and a slight vacuum was applied to the whole system. The Schlenk line and three-way adaptor were adjusted so that only the gas cylinder and reaction flask were connected. The gas cylinder was opened just enough to transfer a visible amount of cyanogen chloride (m.p. –6.6 °C) to the carbene solution. After this point, the cooling flask was removed and the reaction was allowed to slowly warm to room temperature. A deep brown color developed upon warming. After stirring at room temperature for 10 min., a positive nitrogen pressure from the Schlenk line was applied to the entire system to push any cyanogen chloride remaining the in the headspace of the three-way connector through the reaction flask and into the caustic solution. Both stopcocks on the Schlenk flask were closed, the gas transfer setup careful disassembled, and the Schlenk flask transferred back into the drybox. Within the drybox, THF was removed in vacuo and the light brown solids that remained were collected as crude product. Evacuated volatiles from the reaction were carefully disposed of as residual cyanogen chloride could be present.

Identification of 15: Yields cream solids. **^{1}H NMR** (500 MHz, [D_6]DMSO): δ = 8.26 (s, 1 H), 1.85 (s, 9 H), 1.76 (s, 9 H). **^{13}C NMR** (125.8 MHz, [D_6]DMSO): δ = 124.55, 120.36, 114.52, 107.74, 107.72, 65.65, 64.23, 28.73, 27.95.

Isolation of 18: Yields brown colored crude material. Light yellow product of satisfactory purity can be obtained by precipitation of the crude material from a saturated 1:2 anhydrous THF/Et_2O solution from room temperature to –20 °C. M.p. 94–97 °C (in a nitrogen atmosphere, dec.). **^{1}H NMR** (500 MHz, [D_6]DMSO): δ = 3.91 (s, 6 H), 2.38 (s, 6 H). **^{13}C NMR** (125.8 MHz, [D_6]DMSO): δ = 132.63, 118.17, 106.22, 35.09, 9.14. $C_8H_{12}ClN_3$: Calcd. C 51.76; H 6.52; N 22.63 %; found: C 53.95; H 5.32; N 24.12 %.

Isolation of 19: Yields a brown solid. Colorless X-ray quality crystals can be obtained by cooling a saturated 1:2 anhydrous THF/Et_2O solution from room temperature to –20 °C (0.774 g, 1.78 mmol, 43 %). M.p. 200–201 °C (in a nitrogen atmosphere). **^{1}H NMR** (500 MHz, [D_3]nitromethane): δ = 7.05 (s, 4 H), 2.31 (s, 6 H), 2.17 (s,12 H). **^{13}C NMR** (125.8 MHz, [D_3]nitromethane): δ = 144.10, 136.24, 133.63, 124.96, 124.85, 103.44, 15.76, 12.53. **^{13}C NMR** (125.8 MHz, [D_6]DMSO): δ = 144.06, 135.83, 130.92, 12757, 126.67, 117.60, 104.34, 21.25, 17.45. $C_{22}H_{22}Cl_3N_3$: calcd. C 60.77; H 5.10; N 9.66 %; found: C 64.78; H 5.96; N 7.25 %.

Synthesis of Imidazolium Tetrazolide (20): Within a Schlenk flask in the drybox, **11** (0.155 g, 0.619 mmol) was dissolved in acetonitrile (2 mL). The flask was equipped with a stir bar and stopper and taken outside the drybox where NaN_3 (0.040 g, 0.619 mmol) was added in a nitrogen flow. The mixture was left to stir for 16 h upon which time a microcrystalline solid formed. The solids were filtered off and acetonitrile removed in vacuo to yield a cream solid (0.110 g, 0.572 mmol, 92.4 %). From the crude material, X-ray quality crystals can be obtained by letting a hot saturated water solution cool to room temperature. M.p. 242–244 °C (dec, sealed in nitrogen, crystalline sublimate). **^{1}H NMR** (500 MHz, [D_6]DMSO): δ = 3.98 (s, 6 H), 2.32 (s, 6 H). **^{13}C NMR** (125.8 MHz, [D_6]DMSO): δ = 149.13, 137.00, 127.39, 33.92, 8.78. $C_8H_{12}N_6$: calcd. C 49.99; H 6.29; N 43.72 %; found: C 49.45; H 6.29; N 41.99 %.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1418845 (**3a**), CCDC-1418846 (**4a**), CCDC-1418847 (**4b**), CCDC-1418848 (**5a**), CCDC-1418849 (**6a**), CCDC-1418850 (**8**), CCDC-1418851 (**11a**), CCDC-1418852 (**19**), and CCDC-1418853 (**20**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): ORTEP diagrams and atomic parameters for structures **3a**–**6a**, **4b**, **8**, **11a**, **19**, and **20**.

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