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Stable Carbenes

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Crystalline 1*H*-1,2,3-Triazol-5-ylidenes: New Stable Mesoionic Carbenes (MICs)**

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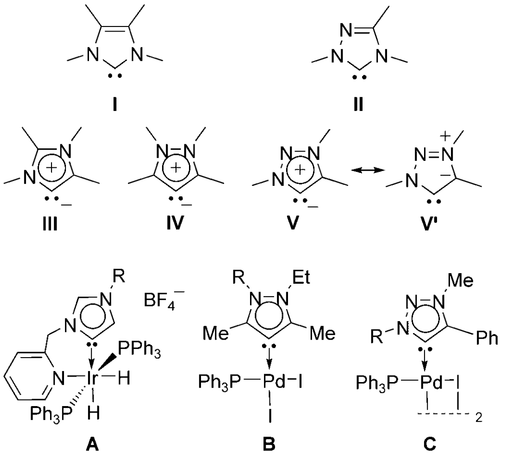
Until recently, the availability of neutral carbon-based κ^1C ligands was limited to carbon monoxide, isocyanides, and carbenes. Compared to phosphorus-based ligands, carbenes tend to bind more strongly to metal centers, avoiding the necessity for the use of excess ligand in catalytic reactions. The corresponding complexes are often less sensitive to air and moisture, and are remarkably resistant to oxidation.[1] As the robustness of carbene complexes is largely due to the presence of strong carbon–metal bonds, other types of carbon-based ligands are highly desirable. It is noteworthy that, although complexes between a carbene and a transition metal have been known for a long time,[2] the recent developments in their application in catalysis[3] have been greatly facilitated by the availability of carbenes that are stable enough to be bottled.[4,5] Moreover, carbenes, especially imidazol-2-ylidenes **I**[4c] and 1,2,4-triazol-5-ylidenes **II**,[4e] are also excellent organocatalysts (Scheme 1).[6]



Scheme 1. Classical NHCs **I** and **II**, their mesoionic carbene isomers **III**–**V**, and the first complexes featuring the latter.

In 2001, Crabtree and co-workers first reported complex **A**, which features an imidazole ring bound at the C5 position (**III**), and not at C2 as commonly observed.[7] More recently, Huynh and co-workers[8] and Albrecht and co-workers[9a] showed that pyrazolium and 1,2,3-triazolium salts can serve as precursors to metal complexes of type **B** and **C**, which feature pyrazolin-4-ylidenes **IV** and 1,2,3-triazol-5-ylidenes **V** as the ligand, respectively. As a consequence of their lineage, these have also been referred to as N-heterocyclic carbenes (NHCs). However, as no reasonable canonical resonance forms containing a carbene can be drawn for free ligands **III**–**V** without additional charges (see **V′**), these ligands have been described as abnormal or remote carbenes (*a*NHCs or *r*NHCs, respectively).[10] As they are, in fact, mesoionic compounds,[11] we suggest naming this family of compounds mesoionic carbenes (MICs). There have been no reported dimerizations of MICs **III** and **IV**, which suggests that the Wanzlick equilibrium pathway for classical carbenes is disfavored;[12] this observation should lead to relaxed steric requirements for their isolation. Moreover, experimental and theoretical data suggest that MICs **III**–**V** are even stronger electron-donating species than NHCs **I** and **II**, which opens up interesting perspectives for their applications.[10]

Our recent success in the isolation of a free imidazol-5-ylidene **III**[13] and pyrazolin-4-ylidenes **IV** (cyclic bent allenes),[14,15] prompted us to investigate the possibility of preparing new types of stable neutral compounds that feature a lone pair of electrons on the carbon atom.[16] Preliminary calculations (B3LYP, 6-311G(d,p); for details, see the Supporting Information) predicted that the parent MIC **V** is located at an energy minimum, about 32 $\text{kcal}\,\text{mol}^{-1}$ above the regioisomeric parent 1,2,4-triazol-5-ylidene **II**. Furthermore, parent **V** is predicted to exhibit an appreciably large singlet–triplet band gap (56 $\text{kcal}\,\text{mol}^{-1}$), which is a good predictor of carbene stability and thus of possible isolation. Herein, we report the preparation, isolation, and characterization of two free 1,2,3-triazol-5-ylidenes of type **V**.

By analogy with the synthetic route used for preparing NHCs and the related species **III** and **IV**, 1,2,3-triazolium salts (**2a**,**b**) were targeted as precursors for the desired 1,2,3-triazol-5-ylidenes (**Va**,**b**). A sterically hindered flanking aryl substituent (2,6-diisopropylphenyl, Dipp) was selected to provide kinetic stabilization to the ensuing free ligand. 1,2,3-Triazole **1** was obtained in 83% yield from the copper-catalyzed azide–alkyne cycloaddition (CuAAC, click chemistry) of 2,6-diisopropylphenyl azide and phenylacetylene.[17] The one-pot conversion of aniline into the desired aryl azide, followed in situ by CuAAC as reported by Moses and co-workers[18] was found to be especially convenient for the synthesis of **1**. Alkylation of **1** with methyl or isopropyl

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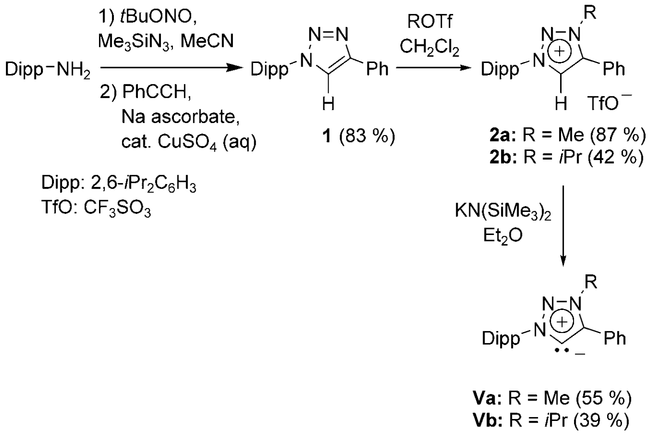
trifluoromethanesulfonate afforded the corresponding triazolium salts in moderate to excellent yields (**2a** and **2b**, respectively; Scheme 2).



Scheme 2. Synthesis of the free 1,2,3-triazol-5-ylidenes **Va**,**b**.

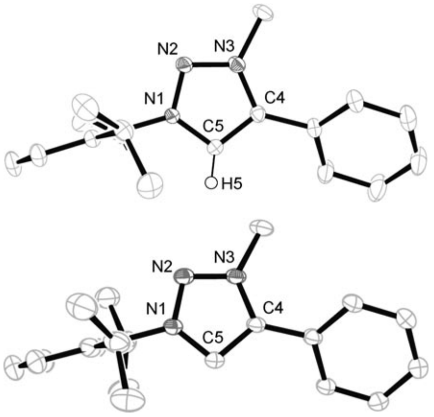
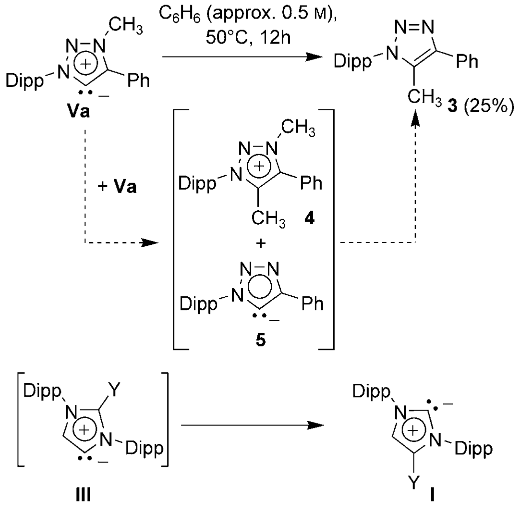


Figure 1. Molecular views (thermal ellipsoids set at 50% probability) of **2a** (top) and **Va** (bottom) in the solid state. For clarity, counter ions, solvent molecules, and H atoms are omitted, except for the ring hydrogen of **2a**. Selected bond lengths [Å] and angles [°] for **2a**: N1–N2 1.3208(16), N2–N3 1.3183(16), N3–C4 1.3559(17), C4–C5 1.3647(19), C5–N1 1.3446(17); N1-C5-C4 105.85(12). **Va**: N1–N2 1.3439(12), N2–N3 1.3216(13), N3–C4 1.3682(13), C4–C5 1.4053(14), C5–N1 1.3662(13); N1-C5-C4 99.70(8).

Potassium bases have been identified as the reagents of choice for the depronation of carbene precursors, as they avoid the formation of stable carbene–alkali-metal adducts that are commonly encountered when lithium bases are used.[12,13,14a,19] Gratifyingly, triazolium salts **2a**,**b** were cleanly deprotonated with either potassium bis(trimethylsilyl)amide or potassium *tert*-butoxide in ethereal solvents to afford the corresponding MICs **Va** and **Vb** in 55 and 39% yield, respectively. Deprotonation was evidenced by the disappearance of the triazolium C*H* signal in their ^{1}H NMR spectra (**2a**: $\delta = 8.62$ ppm; **2b**: $\delta = 8.85$ ppm) and the appearance of a signal at low field in the ^{13}C NMR spectrum (**Va**: $\delta = 202.1$ ppm; **Vb**: $\delta = 198.3$ ppm). The structure of **Va** was unambiguously confirmed by X-ray crystallography (Figure 1).[20] In the solid state, **Va** contains a planar heterocycle, characterized by bond lengths that are intermediate between those of single and double bonds; both of these features are indicative of electronic delocalization. Upon deprotonation, the C5 carbon bond angle becomes more acute (**2a**: 106°; **Va**: 100°), which is consistent with an increased s character in the σ lone pair orbital of **Va** compared to the C–H bonding orbital of the precursor **2a**. This is in agreement with the generally observed trend for carbenes and their conjugate acids.[5]

In the solid state, with the exclusion of oxygen and moisture, free 1,2,3-triazol-5-ylidene **Va** (m.p. 50–52 °C decomp.) remained stable for several days at −30 °C and for a few hours at room temperature. By contrast, **Vb** (m.p. 110–112 °C) was significantly more stable, showing no sign of decomposition after three days at room temperature in the solid state. Upon heating in a benzene solution for 12 hours at 50 °C, **Va** decomposed to give, among other products, triazole **3** (Scheme 3; for details, see the Supporting Information). We surmise that the latter product results from a nucleophilic attack of the carbon lone pair of **Va** on the methyl group of a second molecule of **Va**, giving rise to heterocycles **4** and **5**, which react together to afford the observed product **3**. This apparent rearrangement is reminiscent of that recently observed in the formation of imidazol-2-ylidenes of type **I** from imidazol-5-ylidenes of type **III** that contain an electrophilic Y group.[21] In agreement with this hypothesis, MIC **Vb**, which contains the less-electrophilic isopropyl group at the N3 position, appears much more robust with respect to this decomposition pathway.



Scheme 3. Degradation of free 1,2,3-triazol-5-ylidene **Va**, and analogy with the rearrangement of **III** into **I**.

To evaluate the donor properties of 1,2,3-triazol-5-ylidenes, the [(**Va**)Ir(CO)$_2$Cl] complex was prepared by addition of **Va** to [{Ir(cod)Cl}$_2$] (cod = 1,5-cyclooctadiene), followed by treatment with an excess of carbon monoxide. The CO vibration frequencies ($\nu = 2061$ and $1977\ \mathrm{cm}^{-1}$; $\nu_{avg} = 2019\ \mathrm{cm}^{-1}$) are in line with those of the analogous iridium complex, previously reported by Albrecht and co-workers ($\nu_{avg} = 2021\ \mathrm{cm}^{-1}$),[9a] and are indicative of donor properties that are superior to those of NHCs **I** and **II** ($\nu_{avg} = 2022$-$2031\ \mathrm{cm^{-1}}$),[22] but inferior to those of MICs **III** ($\nu_{avg} = 2003$-$2006\ \mathrm{cm^{-1}}$)[23] and **IV** ($\nu_{avg} = 2002\ \mathrm{cm^{-1}}$).[14b]

Free 1*H*-1,2,3-triazol-5-ylidenes, as exemplified by compounds **Va**,**b**, possess an ensemble of properties that portend to their utility. The synthesis of their precursors is short and efficient, from readily available starting materials, yet is modular and thus amenable to a wide variety of potential analogues. As with other mesoionic carbenes **III** and **IV**, the dimerization of MICs of type **V** has not been observed; therefore, the preparation of comparatively unhindered MICs is predicted to be viable. Their donor properties are greater than those of NHCs of type **I** and **II**, but they are nonetheless available by deprotonation using mild bases (e.g. alkoxides), thus signaling their potential for applications, such as nucleophilic organocatalysis. Free triazolylidenes **V** complement the rapidly growing numbers of neutral carbon-based κ^1C ligands that are now available. We predict that many other classes of MICs, that are derived from a variety of heteroaromatic scaffolds, can be isolated. This endeavor is currently the object of ongoing efforts in our laboratory.

Experimental Section

1*H*-1,2,3-triazol-5-ylidenes (**Va**,**b**): Anhydrous Et_2O (7 mL) was added to a Schlenk flask containing triazolium salt **2a** (0.40 g, 0.85 mmol) and $KN(SiMe_3)_2$ (0.18 g, 0.9 mmol) that had been cooled to −78 °C. The reaction mixture was stirred at −78°C for 10 min, and allowed to warm to room temperature for 50 min before the solvent was evaporated under reduced pressure. The residue was extracted twice by trituration in anhydrous hexanes (2 × 5 mL). After filtration and transfer into a second Schlenk flask using a filter cannula, the solvent was evaporated to give **Va** as a pale purplish-white solid (0.149 g, 55 %). Using a similar procedure, **Vb** was obtained as pinkish-white solid (0.053 g, 39 %).

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