

Persistent carbenes containing acetylenes: 4,5-dialkynylimidazol-2-ylidene

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A nucleophilic imidazole carbene featuring acetylene substituents in the 4- and 5-positions is prepared in three steps from dialkynyl diimines and is characterised by low temperature NMR spectroscopy and trapping reactions with MeI, CS₂ and HgCl₂.

The remarkable renaissance of nucleophilic carbenes, triggered by the isolation of the first crystalline imidazol-2-ylidene by Arduengo *et al.*,¹ is witnessed by recent syntheses of a variety of derivatives of this class of compounds² and has culminated in the development of imidazol-2-ylidenes as versatile ligands in transition metal complexes for use in catalysis applications.³ In the course of these investigations it emerged that the variation of the 4,5-imidazole substituents can have striking effects on the stability of the corresponding carbenes. For example, the notion that a CC double bond between these positions is a crucial prerequisite for the generation of isolable carbenes could not be maintained after the preparation of a stable imidazolidine carbene.⁴ Furthermore, a 4,5-dichloroimidazol-2-ylidene proved to be the first heterocyclic carbene stable to the air,⁵ and an analogous 4,5-bistrifluoromethyl derivative could even be subjected to bulb-to-bulb distillations.⁶

We were intrigued by the challenge to introduce seemingly carbene-incompatible alkynyl groups into the 4,5-positions of imidazol-2-ylidenes as in **1** (Fig. 1), and are driven by the prospect to use the acetylene substituents as delocalising linkages able to connect several carbene sites within one molecular framework (**2**). Monomolecular multi-carbene arrays like **2** are deemed to be of particular interest with respect to metal coordination and to the exploitation of synergistic metal cooperativity. We report here the synthesis of a 4,5-dialkynyl imidazol-2-ylidene as the first representative of this class of compounds.

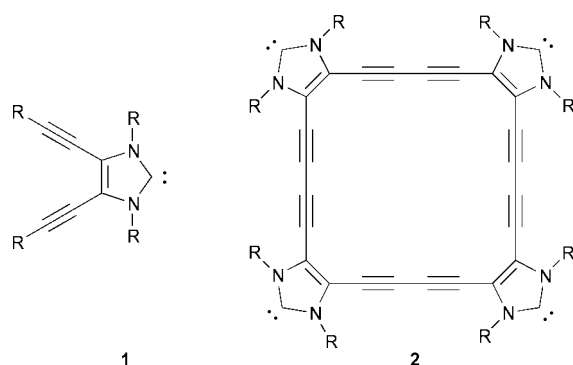
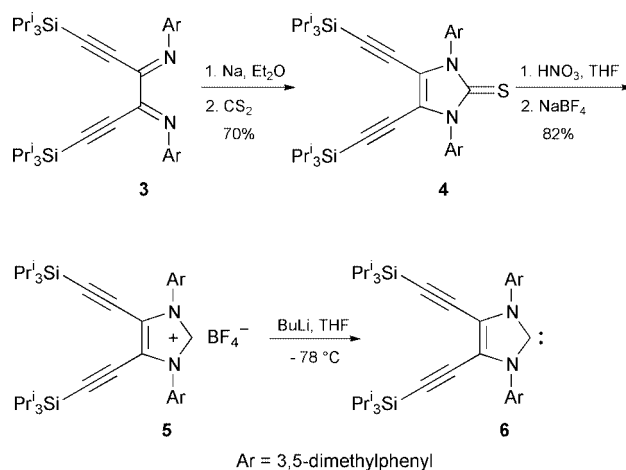


Fig. 1

We have recently reported two complementary pathways to dialkynyldiimines such as **3** (Scheme 1) from oxalyl chloride and bisimidoyl chlorides, respectively.^{7,8} These building blocks were deemed to be convenient starting materials for the rapid assembly of the 4,5-diacetylenyl imidazole core, since ring closure to the corresponding imidazole-2-thiones can be

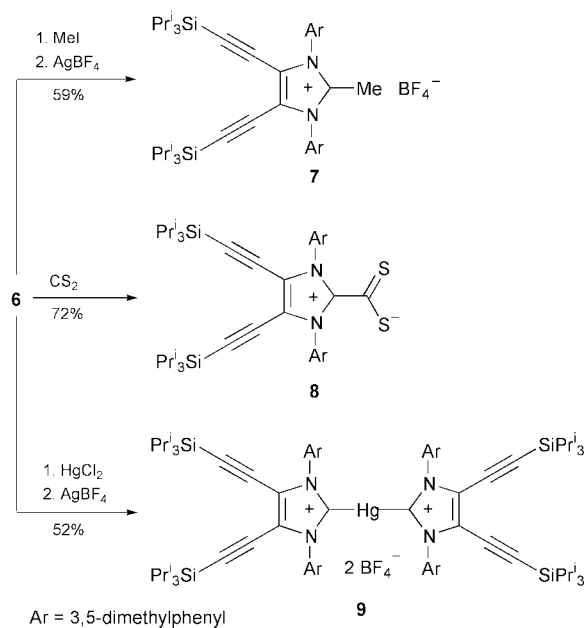


Ar = 3,5-dimethylphenyl

Scheme 1

effected by quenching diimine dianions with CS₂.⁹ Imidazole-2-thiones in turn are precursors to Arduengo-type carbenes which can be obtained either directly by alkali metal reduction of the thiones¹⁰ or *via* deprotonation of an intermediate imidazolium salt derived from them.¹ Hence, stirring **3** together with sodium in dry diethyl ether at room temperature furnished an initially deep blue solution which slowly turned orange-red to indicate the formation of the dianion of **3**. Treatment of this solution with CS₂ led to the imidazole-2-thione **4** in 70% yield. Attempts to isolate an acetylenic carbene directly from **4** by a potassium-mediated reductive desulfurisation were unsuccessful and led only to the decomposition of the starting material. We therefore prepared the dialkynyl imidazolium salt **5** by oxidative desulfurisation of **4** with dilute nitric acid in THF followed by anion exchange with sodium tetrafluoroborate. Gratifyingly, deprotonation of **5** could be effected with BuLi in THF at $-78\text{ }^{\circ}\text{C}$ and resulted in a yellow-coloured solution of 4,5-dialkynyl imidazol-2-ylidene **6**. Interestingly, carbene **6** could only be generated from **5** using BuLi or LDA in THF. With potassium *tert*-butanolate, sodium or potassium hydride in either THF or DMSO on the other hand, only decomposition products were observed even at temperatures as low as $-100\text{ }^{\circ}\text{C}$.

The acetylenic carbene **6** was clearly identified in the low temperature ¹³C NMR spectrum (90.56 MHz, THF with external D₂O-lock, $-78\text{ }^{\circ}\text{C}$) featuring a diagnostic signal for the ylidene carbon at 214.3 ppm.¹¹ However, and in contrast to many non-acetylenic imidazol-2-ylidenes, we were unable to isolate **6** in neat or in crystalline form. THF solutions of **6** could be kept at $-78\text{ }^{\circ}\text{C}$ for several hours without change, but allowing the solutions to gradually warm to $-40\text{ }^{\circ}\text{C}$ led to brown, unidentified decomposition products. Apparently, a 4,5-diacetylene substitution appears to have a detrimental effect on the thermal stability of the imidazol-2-ylidene. While this finding is somewhat unexpected in light of the remarkable persistence of 4,5-dichloroimidazol-2-ylidene⁵ and the elec-



Scheme 2

tron-withdrawing properties of alkynyl substituents, it should be noted that nucleophilic carbenes are known to react with activated acetylenes¹² and that **6** therefore may be susceptible to intermolecular cycloaddition reactions.

The reactivity of **6** even at low temperature prompted us to further establish its identity by trapping reactions with various electrophiles (Scheme 2). Hence, treatment of a solution of **6** in THF with methyl iodide furnished, after anion exchange, the corresponding 2-methylimidazolium ion **7** in 58% yield. Similarly, the zwitterionic imidazolium dithiocarboxylate **8** could be obtained from the reaction of **6** with CS₂. Lastly, a further indirect proof of the intermediacy of carbene **6** was assembled by performing one of Wanzlick's original experiments,^{13,14} namely the reaction of **6** with mercury dichloride. The reaction furnished, after anion exchange, the diimidazol-2-yl-mercurium salt **9** as a colourless solid. All adducts of **6** are fully characterised by spectroscopic data and elemental analyses. In addition, a qualitative X-ray diffraction study performed

on crystals of **9** confirmed the presence of a bridging mercury atom between two imidazole ring structures. Unfortunately, severe disorder in the crystals caused by the anions and the floppy triisopropylsilyl groups prevented a refinement of the observed data below an *R*-value of 15%.

This work has demonstrated the feasibility of introducing alkynyl groups into the structural framework of nucleophilic carbenes and has therefore opened the way for the exploration of the metal coordination behaviour of these species and for the assembly of acetylene-linked, multinuclear metal-carbene complexes. Developments along those lines are currently underway.

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