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Nitron: a stable N-heterocyclic carbene that has been commercially available for more than a century \dagger

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The analytical reagent Nitron is a mesoionic compound whose structure consists of a cationic triazolium unit with an anionic PhN substituent. We provide clear evidence for the existence of a singlet diaminocarbene tautomer whose structure is composed of a 1,2,4-triazol-5-ylidene unit bearing an NHPh substituent.

The report of the first N-heterocyclic carbene (NHC) by Arduengo and co-workers in 1991¹ triggered the tremendous development of such singlet carbenes from laboratory curiosities to powerful workhorses in synthesis and catalysis.² They are most commonly generated by deprotonation of the corresponding azolium cations with a strong base.^{2b,3} Conveniently, a limited number of NHCs have become commercially available, with the 1,2,4-triazol-5-ylidene derivative 1 (Fig. 1) introduced by Enders and co-workers⁴ being the earliest such example.^{2f} A major drawback, however, is that prices exceed several hundred US\$ per gram. We found that the low-cost analytical reagent Nitron,⁵ a relative of **1** that has been commercially available for more than a century,^{5c} exhibits a hitherto unrecognised reactivity which is not compatible with its conventional Lewis structure 2, but rather is expected for its NHC-type tautomer 2' (Fig. 1) and closely resembles that of 1 (Scheme 1).

Elemental sulfur reacts smoothly and swiftly with Nitron dissolved in THF, cleanly affording the triazolinethione derivative 2'=S, whose C=S unit gives rise to a diagnostic ¹³C NMR



Fig. 1 The 1,2,4-triazol-5-ylidene 1 (with numbering scheme for the heterocyclic ring), the conventional structure of Nitron (2) and the structure of its NHC-type tautomer 2'.

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Scheme 1 Reactions of Nitron with typical carbene trapping reagents. *Reagents and conditions:* (i) S_8 , THF, room temp.; (ii) CS_2 , THF, reflux; (iii) [{Rh(μ -Cl)(CO)_2]₂], dichloromethane, room temp.; (iv) [{Rh(μ -Cl)(COD)}₂], THF, room temp.

signal at $\delta = 164.5$ ppm, close to the value of 168.5 ppm reported for 1==S.⁶ This reaction is typical of nucleophilic carbenes.⁷ In the same vein, the betainic dithiocarboxylate $2'^{+}$ -CS₂⁻ was obtained from the nucleophilic addition reaction of Nitron with CS₂. The ¹³C NMR signal due to the CS₂⁻ unit is located at $\delta = 219.9$ ppm and the characteristic ν_{as} (CS₂⁻) vibrational band is observed at 1065 cm⁻¹ in the IR spectrum (CH₂Cl₂ solution). Essentially identical values have been reported for 1^{+} -CS₂^{-.6} $2'^{+}$ -CS₂⁻ was structurally characterised by a single-crystal X-ray diffraction study (see ESI‡). Bond parameters are unexceptional and compare well with those of closely related compounds of the type NHC⁺-CS₂^{-.8}

We have synthesised the rhodium carbonyl complex *cis*-[RhCl(**2**')(CO)₂] in order to elucidate the donor properties of **2**'. This compound was obtained in essentially quantitative yield from [{Rh(μ -Cl)(CO)₂}₂] and Nitron in THF. Recrystallisation from a mixture of dichloromethane and diethyl ether afforded single-crystals of the solvate [RhCl(**2**')(CO)₂]-OEt₂ suitable for an X-ray diffraction study (Fig. 2). The exocyclic amino substituent of the carbene ligand **2**' is associated with the solvent molecule through an N–H···O hydrogen bond of

[‡] Electronic supplementary information (ESI) available: Experimental details including analytical and spectroscopic data, crystallographic and computational details, Fig. S1–S7, Tables S1–S3. CCDC 848861–848863. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc16460k



Fig. 2 Molecular structure of *cis*-[RhCl(2')(CO)₂]·OEt₂ in the crystal (ellipsoids drawn at the 30% probability level).

moderate strength according to commonly accepted criteria $[N \cdots O 2.886(6) \text{ Å}, H \cdots O 1.921(6) \text{ Å}, N-H-O 156(4)^{\circ}]^{.9}$ The Rh-C_{carbene} bond length is 2.077(5) Å. The significantly different Rh-CO distances of 1.844(7) and 1.909(6) Å for the carbonyl ligand *cis* and *trans* to 2', respectively, reflect the strong *trans*influence of NHC ligands.¹⁰ These values agree well with those reported for closely related compounds.11 The 13C NMR spectrum of cis-[RhCl(2')(CO)₂] reveals three low-field doublets, which can be assigned to the carbonyl ($\delta = 184.9$ and 181.7 ppm, ${}^{1}J_{CRh} =$ 55.8 and 73.8 Hz, respectively) and carbene C atom (δ = 175.9 ppm, ${}^{1}J_{CRh} = 43.8$ Hz) resonances. The Tolman electronic parameter (TEP) was calculated to be 2057.4 cm⁻¹ from the two ν (CO) bands at 2086 and 2007 cm⁻¹ observed in the IR spectrum (CH₂Cl₂ solution), using a well-established linear regression.^{2b} This TEP value is essentially identical to that reported for 1 $(2057.3 \text{ cm}^{-1})^{12}$ and indicates an NHC of moderate donor strength.

In an analogous reaction, [RhCl(2')(COD)] (COD = cycloocta-1,5-diene) was obtained from $[\{Rh(\mu-Cl)(COD)\}_2]$ and Nitron in THF. The complex was structurally characterised by a singlecrystal X-ray diffraction study (Fig. 3). The Rh–C_{carbene} distance is 2.030(4) Å. Owing to the strong *trans*-influence of 2' (*vide supra*), the Rh–C_{COD} bond lengths are significantly longer for the carbon atoms *trans* to the NHC ligand than for those *trans* to the chlorido ligand (average value *ca.* 2.23 *vs.* 2.12 Å). These structural features compare well with those reported for other complexes of the type [RhCl(NHC)(COD)].¹³

The reactions summarised in Scheme 1 clearly indicate that the NHC-type tautomer 2', although present at concentrations below the detection limit of NMR spectroscopy (see ESI[‡]), plays an important role for the reactivity of Nitron in solution. This is supported by results of DFT calculations (BP86/def2-SVP) which reveal that in the gas phase 2' is only slightly less stable than 2 ($\Delta G^0 = 5.7$ kcal mol⁻¹ for the process $2 \rightarrow 2'$).

The reactivity of singlet carbenes is governed by the presence of a vacant p-type orbital and an occupied orbital



Fig. 3 Molecular structure of [RhCl(2')(COD)] in the crystal (ellipsoids drawn at the 30% probability level).

perpendicular to this empty orbital which contains the lone pair of electrons at the divalent carbon atom.⁷ Since the chemical behaviour of 2' is very similar to that of the 1,2,4-triazol-5-ylidene 1 (including the essentially identical TEP values), the energies of their corresponding relevant molecular orbitals are expected to be very similar. This is indeed the case according to the results of our DFT calculations (BP86/def2-SVP). The energy of the molecular orbital which corresponds to the vacant p-type orbital is -1.73 eV for 1 and -1.93 eV for 2', while that of the molecular orbital which corresponds to the C_{carbene} lone pair is -5.15 eV for 1 and -5.18 eV for 2' (see ESI‡).

In summary, the hitherto unrecognised reactivity of the well known analytical reagent Nitron towards carbene trapping reagents reflects the presence of the NHC-type tautomer 2' in solution. This tautomer, which is closely related to Enders' 1,2,4-triazol-5-ylidene 1, has never been considered before.¹⁴ This instant carbene has been commercially available for more than a century, and is by far the cheapest NHC, available at a fraction of the price of 1.

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