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## Coinage metal complexes of the carbenic tautomer of Nitron

Charlotte Thie, Sandra Hitzel, Lars Wallbaum, Clemens Bruhn, Ulrich Siemeling\*

Institute of Chemistry, University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

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Dedicated to Prof. Heinrich Lang on the occasion of his 60th birthday.

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## ABSTRACT

The reaction of the inexpensive analytical reagent Nitron (**2**) with coinage metal salts MX in dipolar aprotic solvents cleanly afforded complexes of its carbenic tautomer 1,4-diphenyl-3-phenylamino-1,2,4-triazol-5-ylidene (**2'**) under mild conditions. With a stoichiometric ratio of 1:1, complexes of the type [MX(**2'**)] were obtained (M = Cu, X = Cl, Br, I; M = Ag, X = Cl, Br; M = Au, X = Cl). A stoichiometric ratio of 2:1 furnished complexes of the types [MX(**2'**)<sub>2</sub>] or [M(**2'**)<sub>2</sub>]X (M, X as above and M = Ag, X = [BF<sub>4</sub>], OTf). The structures of the 1:1 complexes [MX(**2'**)] (M = Cu, X = Cl, I; M = Au, X = Cl) and the 2:1 complexes [CuX(**2'**)<sub>2</sub>] (X = Cl, Br, I) and [Ag(**2'**)<sub>2</sub>](OTf) were determined by single-crystal X-ray diffraction. The reaction of Nitron (**2**) with elemental selenium afforded the selenourea derivative **2'**Se, which was also structurally characterized.

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## 1. Introduction

The report of the first N-heterocyclic carbene (NHC) by Arduengo and co-workers in 1991 [1] triggered the development of such singlet carbenes from laboratory curiosities to key compounds for manifold applications in catalysis, materials science and medicinal chemistry [2]. A particularly prominent NHC is the 1,2,4-triazol-5-ylidene derivative **1** (Fig. 1) introduced by Enders and co-workers in 1995 [3], since this compound soon proved to be extremely useful in organocatalysis and therefore was the first NHC to become commercially available [4]. We recently demonstrated that the mesoionic compound Nitron (**2**), which was introduced as an analytical reagent for gravimetric anion analysis in 1905 and has been commercially available since then at a comfortably low price [5], exhibits a reactivity in solution which is typical of an NHC [6]. This can be ascribed to the presence of the carbenic tautomer **2'** (Fig. 1), which is akin to the “Enders carbene” **1** both structurally and electronically, as is reflected by their essentially identical Tolman electronic parameter (TEP) values of ca. 2057 cm<sup>-1</sup> [6].

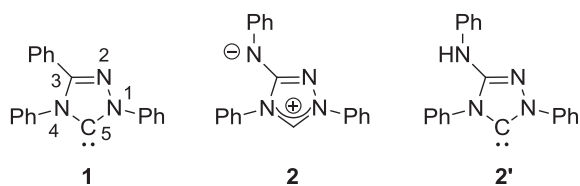
Nitron (**2**) belongs to the class of conjugated mesomeric beta-ines (CMBs) [7]. Related work on other five-membered CMBs in

equilibrium with their tautomeric NHCs was later published by the groups of César and Lavigne [8], Braunstein and Danopoulos [9], and Schmidt [10], who also provided the first review of this burgeoning field [11]. In addition to these experimental studies, theoretical investigations addressing the relative stability of mesoionic and NHC tautomers have been performed by Nyulászai and Streubel [12] and by Ramsden and Oziminski [13].

In our previous work with Nitron (**2**) we have observed the facile formation of Rh<sup>I</sup>, Ru<sup>II</sup> and Ru<sup>III</sup> complexes of its 1,2,4-triazol-5-ylidene tautomer **2'** [6,14]. We have a general interest in pharmaceutically relevant carbene chemistry [15]. Consequently, in view of the current interest in 1,2,4-triazol-5-ylidene coinage metal complexes, which is due to their recently uncovered potential in the field of metallopharmaceuticals [16], we decided to extend our studies in terms of the coordination behavior of Nitron (**2**) towards the monovalent coinage metals. Although the field of coinage metal NHC complexes has been expanding rapidly [17], coinage metal complexes of the iconic “Enders carbene” **1** have not been reported to date. However, we note that Marichev et al. have investigated the copper(I) complexes [CuCl(**2'**)] and [CuX(**2'**)<sub>2</sub>] (X = Cl, I) in terms of their antimicrobial activity [18].

\* Corresponding author.

E-mail address: [siemeling@uni-kassel.de](mailto:siemeling@uni-kassel.de) (U. Siemeling).



**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'**.

## 2. Results and discussion

### 2.1. Synthesis and spectroscopic characterization

As a first step we have prepared the selenourea derivative **2'Se** from Nitron (**2**) and elemental selenium, in order to gain additional information beyond the TEP value concerning the electronic similarity of **2'** and the “Enders carbene” **1**. Ganter and co-workers recently established  $^{77}\text{Se}$  NMR spectroscopy of these compounds as a novel and highly convenient method for probing the electronic ligand properties of the corresponding carbenes, with the chemical shift value  $\delta(^{77}\text{Se})$  [19] and the coupling constant  $^1J_{\text{CSe}}$  respectively being related to their  $\pi$ -accepting and  $\sigma$ -donating abilities [20]. This work has been extended by Nolan and co-workers by utilizing a broad range of NHCs, confirming that  $\delta(^{77}\text{Se})$  can be deployed with confidence to quantify their  $\pi$ -accepting capability [21]. Large  $\pi$ -acceptor strengths are indicated by large downfield shifts of the  $^{77}\text{Se}$  NMR signal. In the case of selenourea compounds derived from standard five-membered ring NHCs the chemical shifts lie between ca.  $-20$  and  $200$  ppm [21a]. The selenourea derivative of the “Enders carbene”, **1Se**, although long known [22], has apparently not been investigated by  $^{77}\text{Se}$  NMR spectroscopy so far. We have determined  $^{77}\text{Se}$  chemical shift values of  $110$  and  $106$  ppm for **1Se** and **2'Se**, respectively, in  $\text{CDCl}_3$ . The similarity of these two values indicates almost identical  $\pi$ -accepting abilities of **1** and **2'**. In conjunction with the essentially identical TEP values of **1** and **2'**, this also points to almost identical  $\sigma$ -donating abilities of both carbenes, since the TEP value provides a measure of the net electron donor capacity. This is corroborated by the identical values of the  $^1J_{\text{CH}}$  coupling constant ( $229$  Hz) determined for the triazolium C–H unit of the corresponding protonated carbenes ( $[\mathbf{1H}]\text{ClO}_4$  [23] and  $[\mathbf{2'H}][\text{BF}_4]$  [24] in  $\text{CD}_3\text{CN}$  were used for this purpose). Ganter [20] and Kunz [25] have pointed out that such  $^1J_{\text{CH}}$  coupling constants correlate inversely with the  $\sigma$ -donor strengths of the respective carbenes, since the  $\sigma$ -donor strength decreases with increasing  $s$ -character of the  $\sigma$ -orbital at the divalent carbon atom and large  $^1J_{\text{CH}}$  coupling constants reflect high  $s$ -character of the carbon valence orbital involved in the C–H bond [26]. Not surprisingly, a very good correlation between the  $^1J_{\text{CH}}$  and  $^1J_{\text{CSe}}$  coupling constant values determined for protonated NHCs and the respective NHC-derived selenourea compounds has been observed [20]. We note that the  $^1J_{\text{CH}}$  coupling constant of Nitron (**2**) is significantly smaller than that of **2'H** ( $219$  vs.  $229$  Hz in  $\text{CD}_3\text{CN}$ ), indicating that the corresponding NHC bearing an anionic  $\text{PhN}^-$  substituent in the 3-position is a much better  $\sigma$ -donor than **2'**, which contains an electroneutral  $\text{PhHN}$  substituent.

We now turn our attention to the coinage metal complexes of the carbenic tautomer of Nitron (**2'**) investigated in this study, which are schematically shown in Chart 1. Copper(I) and silver(I) complexes were obtained in good to excellent yields simply by reacting Nitron (**2**) with the corresponding metal halide in a stoichiometric ratio of 1:1 and 2:1, respectively. Dipolar aprotic solvents were used for these reactions. Analytically pure compounds of the compositions  $\text{MX}(\mathbf{2}')$  (named 1:1 complexes in the following) and  $\text{MX}(\mathbf{2}')_2$  (named 2:1 complexes in the following)

were thus obtained with  $\text{CuCl}$ ,  $\text{CuBr}$ ,  $\text{CuI}$ ,  $\text{AgCl}$ , and  $\text{AgBr}$ . The compounds  $\text{CuCl}(\mathbf{2}')_n$  ( $n = 1, 2$ ) and  $\text{CuI}(\mathbf{2}')_2$  had already been briefly described by Marichev et al. [18]. The use of  $\text{AgI}$  gave lower yields and did not afford analytically pure compounds so far. This can be ascribed to the tendency of silver iodide NHC complexes to aggregate to oligomers or polymers containing iodoargentate units of the type  $[\text{Ag}_m\text{I}_n]^{(n-m)-}$  [27,28]. The compounds obtained with  $\text{AgI}$  will not be considered any further here, since more work is needed to identify the species formed. The 1:1 and 2:1 gold(I) complexes of composition  $\text{AuCl}(\mathbf{2}')$  and  $\text{AuCl}(\mathbf{2}')_2$  were obtained from the reaction of Nitron (**2**) with the soluble complex  $[\text{AuCl}(\text{THT})]$  [29] ( $\text{THT}$  = tetrahydrothiophene) in the corresponding stoichiometric ratio.

Some general trends concerning the solubilities of these coinage metal complexes can be made out. The solubility of 2:1 complexes is generally lower than that of 1:1 complexes. The solubilities are highest for  $\text{M} = \text{Cu}$  and lowest for  $\text{M} = \text{Ag}$ . At ambient temperature, dichloromethane–acetonitrile mixtures turned out to work particularly well as solvent. The solubility in dimethyl sulfoxide, although significantly lower, was still sufficient in each case for obtaining satisfactory  $^{13}\text{C}$  NMR spectra in  $\text{DMSO}-d_6$ . The complexes are hardly soluble in tetrahydrofuran and acetone, which were therefore not suitable for NMR purposes. In view of the rather poor solubilities of the complexes obtained with the silver halides,  $[\text{Ag}(\mathbf{2}')_2][\text{BF}_4]$  and  $[\text{Ag}(\mathbf{2}')_2](\text{OTf})$  were synthesized by reacting Nitron (**2**) with silver(I) tetrafluoroborate and silver(I) triflate, respectively. Indeed, these products containing non-nucleophilic anions exhibit comparatively high solubilities, particularly in dichloromethane.

The metal-coordinated  $\text{C}_{\text{carbene}}$  atom gives rise to a diagnostic low-field signal located at ca.  $180$  ppm in the  $^{13}\text{C}$  NMR spectrum of each complex in  $\text{DMSO}-d_6$ . The exception is the 1:1 gold(I) complex  $[\text{AuCl}(\mathbf{2}')$ , whose carbenic  $^{13}\text{C}$  NMR signal is observed at  $170.3$  ppm. In the case of the silver complexes  $[\text{Ag}(\mathbf{2}')_2]\text{X}$  ( $\text{X} = [\text{BF}_4]$ ,  $\text{OTf}$ ), this signal is observed as a pair of doublets with nicely resolved couplings between carbon and silver of  $^1J(^{13}\text{C},^{109}\text{Ag}) \approx 220$  Hz and  $^1J(^{13}\text{C},^{107}\text{Ag}) \approx 190$  Hz, indicating that the silver–carbon bond is not labile [30,31]. No such coupling was observed for the complexes obtained with  $\text{AgCl}$  and  $\text{AgBr}$ , pointing to a rapid exchange of the carbene ligands on the NMR time scale in these cases, as is frequently described for silver(I) complexes of five-membered ring NHCs [30,32]. In the case of complexes obtained from  $\text{AgX}$  and an NHC in a stoichiometric ratio of 1:1 such fluxional behavior is known to give rise to mixtures of  $[\text{AgX}(\text{NHC})]$  and  $[\text{Ag}(\text{NHC})_2][\text{AgX}_2]$  in solution [33]. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the 2:1 complexes obtained with  $\text{AgCl}$  and  $\text{AgBr}$  clearly show signals due to uncoordinated Nitron (**2**) (see Figs. S25–S28 of the Supplementary Information), indicating partial dissociation in dimethyl sulfoxide solution. In the case of the 2:1 complexes obtained with the copper halides  $\text{CuX}$ , two  $^{13}\text{C}$  NMR signals are observed at ca.  $180$  and  $183$  ppm in  $\text{DMSO}-d_6$  (see Figs. S16, S20 and S24 of the Supplementary Information), which are both distinct from the  $\text{C}_{\text{carbene}}$  signal of the corresponding 1:1 complex  $[\text{CuX}(\mathbf{2}')$  located at ca.  $177$  ppm. However, with  $\text{CDCl}_3$  as solvent, only a single signal due to the  $\text{C}_{\text{carbene}}$  atom is observed for the 2:1 complexes of  $\text{CuBr}$  and  $\text{CuI}$  (the solubility of the  $\text{CuCl}$  complex in  $\text{CDCl}_3$  was not sufficient for  $^{13}\text{C}$  NMR spectroscopy). Likewise, the  $^1\text{H}$  NMR spectra of the 2:1 complexes recorded in  $\text{DMSO}-d_6$  exhibit two signals due to the  $\text{NH}$  unit of **2'**, whereas in  $\text{CDCl}_3$  only a single  $\text{NH}$  signal is observed. Signals due to uncoordinated Nitron (**2**) are essentially absent in each case. This behavior is compatible with a partial dissociation in the very polar solvent dimethyl sulfoxide (dielectric constant  $\epsilon = 47$ ) [34] which concerns predominantly the halide ligand of  $[\text{CuX}(\mathbf{2}')_2]$  and does not occur to a noticeable extent in the much less polar solvent chloroform ( $\epsilon = 5$ ) [34].

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