

## New homoleptic carbene transfer ligands and related coinage metal complexes

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### ABSTRACT

The synthesis, spectroscopic and structural characterization of the carbene ligand precursor bis(4-benzyl-1,2,4-triazol-4-ium-1-yl)dihydroborate has been described. Treatment with Ag<sub>2</sub>O leads to the silver(I) complex of the new monoanionic bis(4-benzyl-1,2,4-triazol-5-ylidene-1-yl)dihydroborate dicarbene ligand. The resulting dimetallacycle carbene complex has been used to synthesize the homoleptic gold(I) complex by transmetallation reaction.

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N-Heterocyclic carbenes (NHCs), first proposed by Wanzlick [1] and Öfele [2], and later isolated in the free state by Arduengo et al. [3], are an extremely useful and versatile class of ligands [4]. Their chemical versatility not only implies a wide variety of structural diversity and coordination modes, but also their capability to form stable complexes with a large number of transition metals with different oxidation states. Polydentate NHCs ligands can provide new complexes with enhanced catalytic performances and higher stability [5–8].

Whereas there are many studies describing the coordination of *pincer* N-heterocyclic carbene ligands [8], the use of scorpionate-carbene ligands is still scarce. Recently, Siebert et al. [9,10] described the synthesis and characterization of the first anionic imidazol-2-ylidenes, the 3-borane-1-alkylimidazol-2-ylidenes anions and their metal complexes [11]. The first chelating tricarbene ligand with the topology of Trofimenko's tris(pyrazolyl)borates, tris(3-methylimidazol-2-ylidene-1-yl)borate, has been introduced in 1995 by Fehlhammer and co-workers [12] together with its hexacarbene iron(III) and cobalt(III) complexes [13,14]. The synthesis of monoanionic chelating dicarbene bis(imidazolinyldene)borates and their use as ligands in various homoleptic and heteroleptic palladium(II), platinum(II), gold(I) [15] and nickel(II) [16] complexes has been recently described.

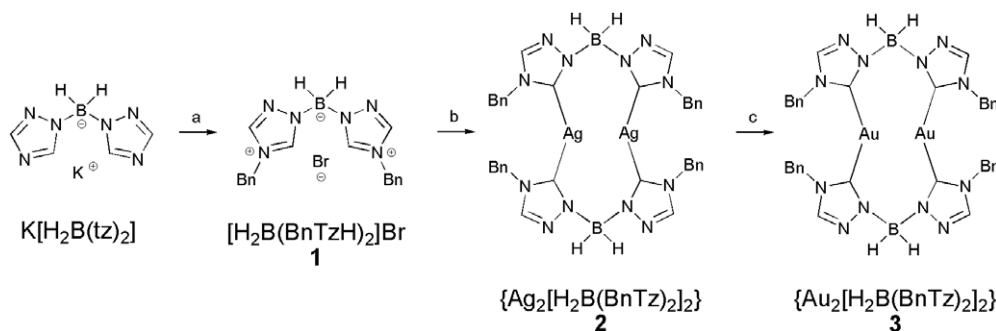
Triazolinyldenes are a class of NHCs that has not been as widely explored as the related imidazole-based carbenes. In 1995

Enders and co-workers [17,18] isolated the first triazol-5-ylidene species. It is interesting to note that 1,2,4-triazolium salts have been used as catalysts for asymmetric benzoin condensations [19,20] and *Stetter* reactions [21] and for the preparation of carbene complexes of different transition metals [22,23]. The application of soluble and immobilized triazolinyldenes transition metal complexes as catalysts in an asymmetric hydrosilylation reaction has also been examined [24]. The possibility of obtaining dicationic triazolium biscarbene precursors to potentially bind two metal centers was suggested early on by Bertrand et al. [25], who described a polymeric silver biscarbene compound [26]. Recently Peris et al. reported the preparation of homo- and hetero-bimetallic complexes of the triazol-3,5-diylidene [27].

Despite the obvious interest in the design of new molecular architectures, discrete molecules with bis(triazolyldene)borate carbene scorpionate-type ligands have not yet been reported. These compounds show potentially facially opposed coordination abilities (Janus-type) thus forming homo-binuclear complexes. In this paper, we have developed a new synthetic pathway to the synthesis of the silver(I) complex {Ag<sub>2</sub>[H<sub>2</sub>B(BnTz)<sub>2</sub>]<sup>−</sup>}, **2**, of the monoanionic bis(4-benzyl-1,2,4-triazol-5-ylidene-1-yl)dihydroborate dicarbene ligand, [H<sub>2</sub>B(BnTz)<sub>2</sub>]<sup>−</sup>. The N-heterocyclic carbene ligand precursor bis(4-benzyl-1,2,4-triazol-4-ium-1-yl)dihydroborate, {[H<sub>2</sub>B(BnTzH)<sub>2</sub>]Br}, **1** (Scheme 1), has been synthesized in chloroform solution via alkylation with benzyl bromide of the starting compound potassium bis(1,2,4-triazol-1-yl)dihydroborate, K[H<sub>2</sub>B(tz)<sub>2</sub>]. It is a consequence of its negative charge that the dicarbene ligand [H<sub>2</sub>B(BnTz)<sub>2</sub>]<sup>−</sup> gives rise to a dimetallacycle by acting

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**Scheme 1.** Preparation of **1**, **2** and **3**. Reaction conditions: (a) room temp., benzylbromide,  $\text{CHCl}_3$ ; (b) room temp.,  $\text{Ag}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$  and (c) room temp.,  $\text{Au}(\text{SMe}_2)\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ .

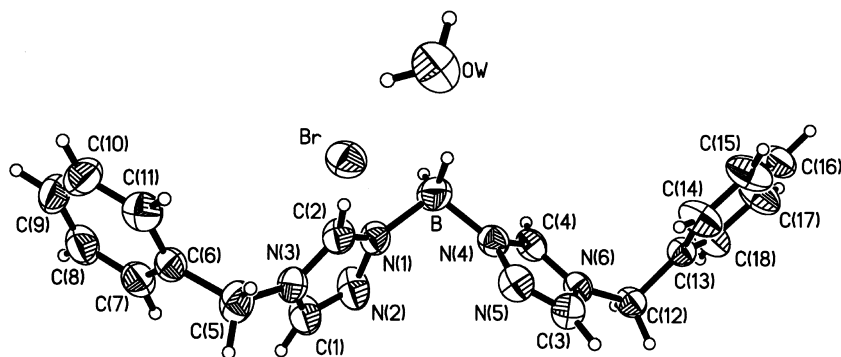
towards silver(I) in a non-chelating  $\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}$ bonding mode [15]; the silver(I) carbene complex  $\{\text{Ag}_2[\text{H}_2\text{B}(\text{BnTz})_2]_2\}$ , **2**, has been obtained from dichloromethane solution via deprotonation of the triazolium salt with  $\text{Ag}_2\text{O}$  (Scheme 1). Owing to the uninegative nature of the bischelate ligand, the resulting complex is neutral, monomeric and organic-soluble.

The transmetalation from a silver(I) NHC complex prepared by treatment of the azolium salt with  $\text{Ag}_2\text{O}$  is an useful coordination method in the preparation of chelating *N*-heterocyclic carbene complexes [28]; in most cases this procedure can be carried out under aerobic conditions, and the process has been successful with a variety of metals such as Au, Cu, Ni, Pd, Pt, Rh, Ir and Ru [29–31].

The silver(I) carbene complex  $\{\text{Ag}_2[\text{H}_2\text{B}(\text{BnTz})_2]_2\}$ , **2**, has been used to synthesize the homoleptic gold(I) complex  $\{\text{Au}_2[\text{H}_2\text{B}(\text{BnTz})_2]_2\}$ , **3**, by a transmetalation reaction with  $\text{Au}(\text{SMe}_2)\text{Cl}$  in dichloromethane solution (Scheme 1). Similar types of complexes have been obtained with bidentate bis(carbene) ligands [32,33]. The ligand **1** and the metal derivatives **2** and **3** have been characterized by analytical and spectral data. The infrared spectra carried out on the solid samples showed all the expected bands for the ligand and the silver or gold moieties: weak absorptions in the range  $3018\text{--}3110\text{ cm}^{-1}$  are due to the azolyl ring C–H stretching modes and medium to strong absorptions in the range  $1521\text{--}1554\text{ cm}^{-1}$  are related to ring “breathing” vibrations. In the infrared spectrum of  $\{[\text{H}_2\text{B}(\text{BnTzH})_2]\text{Br}\}$ , **1**, the B–H stretching vibrations appear as medium broad signals in the range  $2427\text{--}2450\text{ cm}^{-1}$ . Interestingly, on going from the triazolium salt **1** to the carbene complexes **2** and **3**, a red shift of the  $\nu(\text{BH})$  feature is observed. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data reflect significant changes in going from the triazolium salt to the carbene complexes. In particular the  $^1\text{H}$  NMR spectra of **2** and **3** showed the disappearance of the diagnostic 5-*CH* triazolium resonance at 9.66 ppm. The formation of the silver carbene complex **2**

was confirmed by the appearance of the 5-C resonance of the 1,2,4-triazol-5-ylidene as a broad doublet at 189.30 ppm, due to coupling of 5-C with the two spin 1/2 isotopes of silver. The individual coupling to the two isotopes of silver was not resolved in this spectrum ( $^1J(\text{C-Ag}) = 189\text{ Hz}$ ), although the observed coupling constant is in the range of the average values for the resolved  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  coupling constants found in similar silver(I) *N*-heterocyclic carbenes [30,34,35]. In the  $^{13}\text{C}$  NMR spectrum of the gold(I) complex **3** the 5-C resonance of the 1,2,4-triazol-5-ylidene appeared as a singlet at 188.75 ppm; the chemical shift value for the carbene carbon is in good agreement with the carbene carbon chemical shifts of similar dinuclear bis(carbene)gold species [15,32,33]. Mass spectra (ESIMS) of all the new compounds have been recorded (See Supplementary Data). The general appearance of the molecular ions followed by characteristic fragmentations supports the structural assignments. The structure of the triazolium salt **1** was confirmed by the presence of a peak at  $m/z$  331 ( $[\text{H}_2\text{B}(\text{BnTzH})_2]^+$ ) in the positive-ion mode electrospray ionization mass spectrum. The structures of complexes **2** and **3** were confirmed by the presence in their positive-ion mass spectra of peaks due to dinuclear species at  $m/z$  933 and 1053, due to the species  $[\text{Ag}_2\{\text{H}_2\text{B}(\text{BnTz})_2\}_2 + \text{NaCl} + \text{H}]^+$  and  $[\text{Au}_2\{\text{H}_2\text{B}(\text{BnTz})_2\}_2 + \text{H}]^+$ , respectively. No fragment ions were observed, showing that the silver and gold complexes were stable under the conditions of the electrospray ionization and detection.

Well-formed single crystals of  $\{[\text{H}_2\text{B}(\text{BnTzH})_2]\text{Br}\} \cdot \text{H}_2\text{O}$ , **1**  $\cdot$   $\text{H}_2\text{O}$ , were obtained from a  $\text{CH}_2\text{Cl}_2/\text{THF}$  (1:2) solution and the related molecular structure was established by X-ray diffraction analysis. The ORTEP [36] representation and the numbering scheme of compound **1**  $\cdot$   $\text{H}_2\text{O}$  is illustrated in Fig. 1, where it appears that the environment surrounding the boron center is tetrahedral. To compare the main metrical parameters in **1**  $\cdot$   $\text{H}_2\text{O}$  with existing data, we



**Fig. 1.** Perspective view of the molecular structure of  $\{[\text{H}_2\text{B}(\text{BnTzH})_2]\text{Br}\} \cdot \text{H}_2\text{O}$ , **1**  $\cdot$   $\text{H}_2\text{O}$ . Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and bond angles (°): B–N(1) 1.558(9); B–N(4) 1.549(9); N(1)–N(2) 1.361(7); N(4)–N(5) 1.368(6); N(1)–C(2) 1.309(7); N(4)–C(4) 1.317(7); N(2)–C(1) 1.286(8); N(5)–C(3) 1.299(7); N(3)–C(1) 1.347(7); N(6)–C(3) 1.353(7); N(3)–C(2) 1.322(7); N(6)–C(4) 1.323(7); N(3)–C(5) 1.477(7); N(6)–C(12) 1.470(6). C(2)–N(1)–N(2) 108.9(5); C(4)–N(4)–N(5) 109.0(5); N(1)–N(2)–C(1) 104.8(5); N(4)–N(5)–C(3) 105.1(4); N(2)–C(1)–N(3) 112.3(6); N(5)–C(3)–N(6) 111.3(5); C(1)–N(3)–C(2) 104.7(5); C(3)–N(6)–C(4) 105.8(5); N(3)–C(2)–N(1) 109.3(5); N(6)–C(4)–N(4) 108.8(5); N(3)–C(5)–C(6) 111.3(5); N(6)–C(12)–C(13) 111.9(4) and N(1)–B–N(4) 106.6(5).

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