Published in final edited form as:

Organometallics. 2011 September 26; 30(18): 5033–5037. doi:10.1021/om200670f.

Structurally Characterized Cationic Silver(I) and Ruthenium(II)carbene complexes of 1,2,3-Triazol-5-ylidenes

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Abstract

A novel 1,3,4-substituted 1,2,3-triazolium salt was found to function as an effective precursor for the synthesis of the first structurally characterized cationic silver(I) and ruthenium(II)carbene complexes of overall 1:2 ligand-to-metal stoichiometry. The Ag(I) complex crystallized in the form of an eight silver atom-containing cluster, whereas the Ru(II) complex proved to be a discrete species and was found to be capable of initiating the ring-opening metathesis polymerization of norbornene upon activation with (trimethylsilyl)diazomethane.

N-Heterocyclic carbenes (NHCs) have attracted considerable attention recently as ligands for use in transition metal-based catalysis,¹ as promoters of organocatalysis,² and many other applications, as detailed by our group^{3a-f} and others.^{1b,3g-i} In general, NHC complexes exhibit higher thermal stabilities than their phosphine analogues, an effect ascribed in part to the fact that NHC ligands are strong donors.⁴ To date, the majority of work with NHCs has focused the 1,3-disubstituted imidazolylidenes **A** and 1,4-disubstituted 1,2,4-triazolylidenes **B** (Chart 1).⁵ Both of these species display remarkable stability, in addition to utility in catalytically active complexes. This enhancement has prompted efforts to explore and to develop NHCs with other structural features. An early example was reported by Crabtree and co-workers in 2001, who described an abnormal NHC complex that featured an imidazole ring bound at the C5 position rather than at the C2 position (**C**, Chart 1).⁶ Since that time, several other abnormal NHC complexes derived from other non-classic NHC ligands have been reported; these include the pyrazolin-4-ylidene **D**⁷ and the cyclic (alkyl)-(amino)carbene **E**.⁸ It has also been shown recently that mesoionic carbenes (MICs) **C**, **D** and **F** can be isolated in their free states.⁹ Compared to more classical NHC complexes, these abnormal NHCs are relatively strong σ -donors,¹⁰ a feature that has made them of interest in terms of exploring their utility in catalysis.¹¹

To date, relatively few reports have described the synthesis of 1,2,3-triazolylidene supported transition metal complexes and their application to catalyst studies.^{12,20,21} In 2008, Albrecht and co-workers first reported the synthesis of 1,2,3-triazolylidenes (structure **F**; Chart 1) as highly modular precursors for a new class of carbenes and their metalation with a variety of

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Supporting Information Available: Synthetic summary and characterization data for compounds **2**, **3** and **4**, details of ring opening metathesis polymerization, and crystallographic data for compounds **2**, **3** and **4** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

transition metals (Pd, Ru, Rh and Ir).^{12(a)} Since then, silver complexes of these carbenes have been extensively studied. While we are aware of at least eleven reports of 1,2,3-triazolylidene silver complexes,^{12a-j,20} to the best of our knowledge none of the complexes in question have been structurally characterized via single crystal X-ray diffraction analysis. We thought that this deficiency could be overcome through the use of modified 1,2,3-triazolylidene ligands containing ancillary coordinating groups. With this consideration in mind, we have prepared and report here the first structurally characterized 1,2,3-triazolylidene silver complex **3**, a species synthesized from the pyrrole-containing triazole and triazolium precursors, **1** and **2**. We also report the first structurally characterized bis-ruthenium complex supported by a 1,2,3-triazolylidene-containing framework. Both complexes are identified by an overall 1:2 ligand-to-metal stoichiometry. The Ag(I) complex was found to exist as eight-silver atom cluster, whereas its Ru congener proved to be a discrete bimetallic complex. The Ru(II) complex was explored as a ring opening metathesis polymerization (ROMP) catalyst and, as detailed below, proved active for the polymerization of norbornene when activated with (trimethylsilyl)diazomethane (TMSD).

The design of complex **4** was predicated on the combined use of 1,2,3-triazolylidene donor subunits and pyrrole chelating groups. Pyrrole is known to be a useful ligand in catalytic systems when chelated to various transition metals.¹³ Its use in the present instance was expected to allow for the ditopic coordination of a ruthenium(II) center. Likewise, the incorporation of two pyrrole subunits, along with two 1,2,3-triazole moieties, into a single molecular framework was expected to allow for the complexation of two Ru(II) cations, while simplifying the synthesis of the starting metal-free form, **1**.

The synthesis of **1** has been reported earlier.¹⁴ It relies on the “click”-type copper-catalyzed [3+2] cycloaddition of an aryl diazide and with an alkyne-functionalized pyrrole to create the key triazole functionality.¹⁵ A variety of 1,2,3-triazoles bearing a wide range of functional groups at the 1- and 4-positions can be synthesized *via* the click reaction.¹⁶ In the present instance, dimethylsulfate was used to alkylate the 3-position of the simple triazole **1** to afford the triazolium salt **2** in 20% yield (Scheme 1).

The triazolium salt **2** was tested as a possible carbene precursor by subjecting to metalation with silver oxide in the presence of tetrabutylammonium chloride. This afforded the bis(triazolylidene) silver complex **3** in 84% yield,¹⁷ wherein the silver center is attached to carbon C(5) (Scheme 1). Complex **3**, in turn, was tested as a carbene transfer agent. For example, the new bis ruthenium(II) complex **4**, containing two triazolylidene donor groups, was prepared in 95% yield *via* a transmetalation procedure that consisted of adding [Ru(*p*-cymene)Cl₂]₂ to the silver complex **3** in CH₂Cl₂.

The structures of **2-4** were elucidated by X-ray diffraction analysis (Table S1). In salt **2**, the bis-1,2,3-triazolium ligand displayed a twisted conformation with the two triazolium rings rotated in opposite directions relative to the central benzene ring (Figure 1). The dihedral angle between the two triazolium rings was measured to be 53.4°. In each arm of the ligand, the triazolium and pyrrole rings were found to be nearly planar, with dihedral angles between the pair of triazolium and pyrrole rings being 9.1° and 5.4°, respectively. In complex **3**, eight Ag⁺ ions are surrounded by four abnormal bis-1,2,3-triazolylidene ligands to form a twisted macrocycle (Figure 2). All eight Ag⁺ ions have similar coordination environments and each is coordinated to one abnormal NHC carbon atom and one pyrrole nitrogen atom. The C-Ag-N bond angles were nearly linear and range from 170.2(2)° to 176.2(3)°. The average Ag-C and Ag-N distances were measured to be 2.074 Å and 2.088 Å, respectively, which are close to literature values.¹⁸ The average Ag-Ag distance between two adjacent Ag⁺ ions was measured to be 2.843 Å, which is shorter than the sum of the Van der Waals radii for silver(0), 3.440 Å, a finding consistent with a strong metal-metal

interaction.¹⁹ It is also noteworthy that the triazolylidene and pyrrole rings appear to rotate in different directions relative to one another, with the dihedral angles between these two subunits varying from 26.9° to 44.4°. These variations are much larger than those present in the metal-free triazolium precursor **2**. Intramolecular π - π and C-H $\cdots\pi$ interactions are also inferred from the X-ray structure of **3** (Figure 2). For instance, the distances between the adjacent aryl units range from 3.387 to 3.576 Å. These values are consistent with inter-aryl interactions, which may add to the overall stability of the twisted macrocyclic structure. Based on the results of a microanalytic study (cf. ESI), it is believed that the key tetrameric structure of **3** is also present in the bulk material.

In complex **4**, two Ru²⁺ ions are present on either face of what is formally a ditopic ligand; they are separated from one another by 8.149 Å (Figure 3). Both Ru²⁺ ions have three-legged piano-stool geometries and each is coordinated to one carbene nucleus, one pyrrole nitrogen atom, one Cl⁻ anion and one cymene group. The average Ru-C distance is 2.035 Å, a value that is similar to that reported for other complexes in the literature.²⁰ Interestingly, the bis-1,2,3-triazolylidene ligand present in complex **4** shows the same twisted conformation as that found in precursor **2**.

Proton nuclear magnetic resonance spectroscopic studies show that both complex **3** and **4** are stable in DMSO-*d*₆ solutions at 300 K. As can be seen from an inspection of Figure 4, the ¹H NMR spectrum contains 14 signals corresponding to the ruthenium ditopic complex, which is in good agreement with the solid-state structure described above. A 2D-COSY NMR analysis allowed for assignment of the signals (see Figure S10). Complex **4** displays three signals corresponding to the pyrrole ligand. These resonances appear at δ 7.31, 6.45 and 6.09 ppm, respectively, and are shifted to higher field than those of the free ligand, **2**. The silver complex **3** was also analyzed by ¹H NMR spectroscopy in DMSO-*d*₆; this revealed a spectrum consistent with the structure deduced from the solid state structural analysis (see Figure S8).

Upon the completing the synthesis and characterization of the ruthenium complex **4**, it was tested as a ROMP catalyst.²¹ When (trimethylsilyl)diazomethane (TMSD) was added as an initiator,²² the complex initiated the ROMP of norbornene. The norbornene polymerization reaction was carried out in chlorobenzene under an atmosphere of nitrogen at 60 °C for 15 hrs with 0.5 mol % **4** and 3.0 mol % TMSD. Under these conditions, in 95% yield of polynorbornene was obtained (Scheme 2). The polymer was determined by gel permeation chromatography (GPC) to exhibit a number average molecular weight (*M*_n) of 46.3 kDa and a polydispersity index (PDI) of 1.52 relative to polystyrene standards. The importance of the TMSD can be seen in the polymerization kinetics profiles shown in Figure 5. Although effective for norbornene, it is to be noted that the combination of **4** and TMSD did not prove active for the ring opening metathesis polymerization (ROMP) of low-strain cyclic olefins, such as cyclooctene, *cis*, *cis*-1,5-cyclooctadiene and cyclopentene.

In summary, we have successfully synthesized a novel 1,3,4-substituted 1,2,3-triazolium salt that functioned as an effective precursor for the synthesis of new carbene complexes with silver(I) and ruthenium(II) cations. The presence of pyrrole subunits within the ligand framework contributes to the complexation of the Ru(II) centers in a ditopic fashion and gave rise to a novel bis-ruthenium complex that is capable of polymerizing norbornene when activated with (trimethylsilyl)diazomethane (TMSD). Based on these results, triazolylidene ligands such as those described here are expected to find utility both in the stabilization of new transition metal complexes and the development of new catalytic systems. Efforts to explore these possibilities are currently under way.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by the National Institutes of Health (Grant No. GM58907 to J.L.S.), the National Science Foundation (Grants Nos. CHE-1057904 to J.L.S., CHE-0645563 to C. W. B., and 0741973 for the X-ray diffractometer), and the Robert A. Welch Foundation (Grants F-1621 and F-1018 to C.W.B. and J.L.S., respectively).

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Figure 1.

Single crystal X-ray structure of **2**. All solvent molecules have been omitted for clarity. The dihedral angle between the two triazolium rings is 53.4° . The dihedral angles between the triazolium and pyrrole rings are 9.1° (Plane N_5 / Plane N_8) and 5.4° (Plane N_2 / Plane N_1).

Figure 2.

Single crystal X-ray structure of **3**. All solvent molecules have been omitted for clarity. Short intermolecular π - π distances (X1A...X1B: 3.543 Å, X1C...X1D: 3.387 Å and X1E...X1F: 3.576 Å) and C-H... π interactions (C(68)-H... π : 2.484 Å, C-H- π : 164.6° and C(44)-H... π : 2.894 Å, C-H- π : 111.2°) are seen in this octa-Ag(I) complex.

Figure 3.

Single crystal X-ray structure of **4**. All solvent molecules have been omitted for clarity. The dihedral angle between two triazolyldiene rings is 50.9°. The dihedral angles between the triazolyldiene and pyrrole rings are 3.0° (Plane N₅ / Plane N₈) and 4.1° (Plane N₂ / Plane N₁). Selected bond lengths (Å) and angles (deg): Ru(1)-C(6)=2.025(6) Å, Ru(1)-N(1)=2.096(6) Å, Ru(1)-Cl(1)=2.432(2) Å, Ru(1)-C(centroid)=1.708 Å; C(6)-Ru(1)-N(1)=76.3(2)°, C(6)-Ru(1)-Cl(1)=85.21(18)°, N(1)-Ru(1)-Cl(1)=87.74(16)°.

Figure 4.
¹H NMR spectrum of **4** in DMSO-*d*₆ at 300 K

Figure 5. Norbornene Conversion as a function of time with two different catalyst systems.

Scheme 1.
Synthesis of Compounds **1** – **4**.

Scheme 2. Polymerization of Norbornene by the bis-Ruthenium Complex **4**

Chart 1.

N-Heterocyclic carbenes, including “classical” NHC systems (**A-B**) as well as representatives of various subclasses (**C-F**).