# **ORGANOMETALLICS**

# Synthesis and Structure of Silver and Rhodium 1,2,3-Triazol-5-ylidene Mesoionic Carbene Complexes

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**Supporting Information** 



**ABSTRACT:** New mono- and bidentate 1,2,3-triazol-5-ylidene mesoionic carbene (MIC) ligands have been synthesized and reacted with silver oxide, forming cationic 1:2 and 2:2 Ag:MIC ( $[AgL_2]Br$  and  $[Ag_2L_2][Ag_2Br_4]$ ) complexes, respectively. These complexes have been isolated and characterized. They were further found to be potent transmetalation agents toward rhodium, resulting in the preparation of mono- and bimetallic rhodium complexes. The reaction of the 2:2 Ag:L complex with  $[Rh(COD)_2]BF_4$  results in the first reported example of a cationic bimetallic rhodium MIC complex. This complex was fully characterized, and its X-ray structure is reported. Interestingly, this complex exhibits various secondary noncovalent interactions in the solid state of the general type C–H…X, where X = F, Cl.

# INTRODUCTION

N-heterocyclic carbenes (NHCs) have been shown to be powerful ligands in catalytic transformations<sup>1</sup> and to provide stabilization of reactive metal centers.<sup>2</sup> As a result, the development of novel NHC ligands that vary in either their electronic or their steric properties and the synthesis of late transitionmetal complexes of these ligands has been a highly active field of chemistry.<sup>3</sup> In comparison, heterocyclic carbenes that are stabilized by only one heteroatom have received significantly less attention.<sup>4</sup> Because no neutral canonical representation of these species is possible, these ligands are often termed abnormal N-heterocyclic carbenes (aNHCs), or mesoionic carbenes (MICs). In general, the decreased heteroatom stabilization of these ligands results in stronger donation toward a metal center than even the very basic imidazole-derived NHCs. As a result, the properties of the carbenes themselves and their complexes are being extensively studied by the groups of Bertrand, <sup>5,6</sup> Albrecht, <sup>7,8</sup> and others.<sup>9</sup> Yet still, MICs represent a class of largely unexploited ligands in homogeneous catalysis.<sup>6b,c,7c,8b,d,e,10,11</sup>

Albrecht and co-workers have recently described a facile synthesis of MICs based on 1,2,3-triazolium salts and investigated their coordination properties with several transition metals.<sup>8a</sup> Since this report, several examples have appeared of transitionmetal complexes utilizing these ligands.<sup>11,12</sup> However, the free 1,2,3-triazol-5-ylidene carbenes tend to be unstable in comparison with traditional NHCs, which has limited the study of their coordination chemistry. Because of this, the coordination of these ligands to a metal is generally achieved through transmetalation from a Ag-MIC complex.<sup>13</sup> Although a wide variety of silver NHC complexes with remarkable structural diversity have been reported,<sup>13b,c</sup> until very recently, there were no reports of structurally characterized Ag triazole-MIC complexes.<sup>11a</sup>

During the preparation of this paper, Bielawski and Sessler reported the structure of the first 1,2,3-triazolylidene silver complex in a 1:2 ([L<sub>2</sub>Ag<sub>4</sub>]) ligand-to-metal ratio.<sup>11a</sup> The ligand in question was functionalized with a pyrrole wingtip group that was also coordinated to silver. This complex underwent transmetalation to ruthenium to form a bimetallic complex that was found to be active in ring-opening metathesis polymerization (ROMP) reactions. Similarly, Schubert and co-workers have reported the synthesis of a mixture of 1,2,3-triazolylidene silver complexes that were transmetalated to ruthenium to give a remarkable CNC pincer framework.<sup>12c</sup> Interestingly, this complex displayed vibrant photophysical properties, further illustrating the potential of triazole MIC complexes outside of catalysis. These encouraging results, along with the remarkable strides being made in the synthesis of these ligands and their complexes by the Bertrand group,<sup>6</sup> suggest that triazole MIC complexes have significant value in a variety of applications.

We have been actively studying the preparation of rhodium N-heterocyclic carbene complexes,<sup>14</sup> including their catalytic activity,<sup>15</sup> their ability to activate small molecules,<sup>16,17</sup> and their

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crystal-to-crystal transformations.<sup>17</sup> Although monomeric Rh NHC complexes have shown significant promise as catalysts for organic transformations,<sup>14a,18</sup> homobimetallic NHC complexes of rhodium are also interesting, as they have been demonstrated to be active and potentially important species in both the hydrosilylation of alkynes<sup>19</sup> and the hydroformylation of alkenes.<sup>20</sup> Furthermore, they have been utilized in the fabrication of perforated organometallic nanotubes.<sup>21</sup> Interestingly, all examples that we are aware of involve coordination through traditional imidazole-based NHCs, and no work has appeared utilizing more strongly donating triazole MIC ligands.<sup>19-22</sup> To address this deficiency, we have prepared bimetallic rhodium carbene complexes coordinated to triazole MICs in the hopes that their stronger electronic donation, and facile steric tuning, may lead to rhodium complexes that are highly active in a variety of organic transformations. Herein, we report the synthesis and structural characterization of cationic 1:2 and 2:2 Ag:L silver triazole MIC complexes and their transmetalation to form monometallic ([Rh(L)(COD)Br]) and cationic homobimetallic  $([L_1Rh_2][BF_4]_2)$  rhodium triazole MIC complexes, which have been fully characterized.

#### RESULTS AND DISCUSSION

Our studies began with monodentate triazole MIC precursor 2 reported previously by Bertrand and co-workers.<sup>6a</sup> Methylation of triazole 1 was performed with  $Me_3OBF_4$  in  $CF_3Ph$  at room temperature, resulting in the formation of 2 in 88% isolated yield (eq 1). The bidentate version of this species, MIC ligand



**6**, was synthesized as shown in Scheme 1. Its structure was modeled on the 1,3-bis(alkyl-imidazole) benzene framework initially reported by Hollis.<sup>23</sup> This framework has been reported to be flexibile with regard to its coordination to metals, giving both bridging and pincer-type complexes of rhodium<sup>19,24</sup> and iridium,<sup>21,24b,25</sup> and similar MIC frameworks have been reported for both bimetallic and pincer complexes of ruthenium,<sup>111,12c</sup> gold,<sup>11b</sup> and palladium.

A significant benefit of the 1,2,3-triazol-5-ylidene MIC ligand framework is that these species can be constructed using coppercatalyzed [2 + 3] Huigsen or "*click*" cycloaddition chemistry,<sup>26</sup> which provides significantly greater flexibility for the introduction of carbene wingtip groups compared to typical synthetic strategies for the preparation of imidazole NHCs. For our first-generation ligand, 2,6-diisopropylphenyl (Dipp) wingtip groups were selected for the triazole in order to provide significant steric bulk around the metal center. The synthesis of bistriazole **5** was easily achieved by the cycloaddition of 2,6-diisopropylphenyl (Dipp) azide **3** with a protected version of 1,3-diethynyl benzene.<sup>26b</sup> In a procedure similar to that described by Moses,<sup>27</sup> azide **3** could be prepared *in situ* and reacted directly with TMS-protected acetylene **4** in the presence of TBAF under standard conditions (CuSO<sub>4</sub> and sodium ascorbate) (Scheme 1).

The optimized procedure involves *three reactions performed in one pot* in good overall yield (63%) and avoids the isolation of the potentially sensitive azide. The methylation of **5** was easily performed with Me<sub>3</sub>OBF<sub>4</sub> in dichloromethane, resulting in triazolium salt **6** in 82% yield (Scheme 1). Clean bismethylation was confirmed by the presence of a sharp singlet at 4.55 ppm, integrating for 6Hs in the highly symmetrical <sup>1</sup>H NMR spectrum, in accordance with previous reports.<sup>28</sup>

Rather than employing the deprotonation strategy described by Bertrand<sup>6a</sup> that requires isolation of the resulting free carbenes, we opted for the preparation of silver complexes of both 2 and 6 for eventual transmetalation to rhodium. The conditions we employed were similar to those described by Cavell,<sup>29</sup> in which the triazolium salts were treated with excess Ag<sub>2</sub>O and KBr in MeCN at room temperature. Thus exposure of 2 and 6 to these conditions resulted in the formation of air stable complexes 7 and 8, respectively, in which each silver atom is bound to two MICs (see Scheme 2). The bis(MIC) structure of 7 ([AgL][Br])<sup>30</sup> was confirmed by high-resolution mass spectrometry, which gave an m/z of 745.3148, corresponding to  $[AgMIC_2]^+$ . In addition, the formation of complex 7 was accompanied by clean loss of the triazole C-H peak at 8.98 ppm, present in the <sup>1</sup>H NMR spectrum of ligand precursor 2. The  ${}^{13}C{}^{1}H$  NMR spectrum of 7 displays a characteristic resonance at 172 ppm corresponding to the Ag-C moiety.<sup>31</sup> Similarly, the formation of complex 8 was accompanied by clean loss of the triazole C-H peak at 8.77 ppm, present in the <sup>1</sup>H NMR spectrum of 6, along with the formation of a characteristic resonance at 172 ppm in the  ${}^{13}C{}^{1}H$  NMR spectrum, corresponding to the Ag–C moiety. As full conversion of 6 could be observed by  ${}^{1}H$ NMR of 8, the lower isolated yield of 8 relative to 7 may indicate the presence of insoluble, oligomeric Ag-MIC species that are removed during filtration.

The structure of complex **8** was unambiguously determined by single-crystal X-ray diffraction after crystallization by slow diffusion of hexanes into a concentrated solution of **8** in CH<sub>2</sub>Cl<sub>2</sub>. The solid-state molecular structure of complex **8** is depicted in Figure 1. Complex **8** crystallizes with a 2:2 (Ag:L) molecular ratio with a molecular formula of  $[Ag_2L_2][Ag_2Br_4]$ , exhibiting a nearly planar geometry around each silver atom. The two ligands are nearly parallel to each other and are interconnected by two silver atoms. The two bridging phenyl rings have no  $\pi$ - $\pi$  interactions with each other, at a separation distance of 5.891 Å. Each of the triazole rings is tilted with



#### Scheme 2. Synthesis of Ag-MIC Complexes 7 and 8





Figure 1. Crystallographically determined structure of  $[Ag_2L_2]$ - $(Ag_2Br_4)\cdot 3CH_2Cl_2$  (8) displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms, counteranion  $(Ag_2Br_4)$ , and solvent  $(CH_2Cl_2)$  are omitted for clarity. There is  $^{1}/_{4}$  of a molecule of complex 8 per asymmetric unit. Selected interatomic distances [Å] and angles [deg]: Ag(1)-C(6), 2.075(7); N(2)-N(3), 1.340(8); N(1)-N(2), 1.321(9); N(3)-C(6), 1.350(8); N(1)-C(7), 1.477(9); C(6)-Ag(1)-C(6B), 173.9(3).

respect to the plane of the central phenyl ring with an angle of 46.15°. Each Dipp wingtip group is nearly perpendicular with respect to the triazole rings, both displaying dihedral angles of 89.60°. The Ag– $C_{\rm MIC}$  bond is 2.075(7)Å, which is nearly identical to that in the Ag-MIC complex reported by Bielaweski (2.074(4)Å),<sup>11a</sup> and similar to that in related Ag-NHC complexes.<sup>32</sup> To the best of our knowledge, this is the first structurally characterized example of a cationic 2:2 (Ag:L) silver triazole MIC complex.

**Transmetalation to Rhodium.** Both complexes 7 and 8 were investigated for their ability to transfer their MIC ligands to rhodium. The transmetalation of complex 8 to rhodium was investigated at room temperature by the addition of 8 to stoichiometric quantities (per potential MIC ligand) of [Rh- $(COD)_2$ ]BF<sub>4</sub> in MeCN. This resulted in the near immediate formation of a white precipitate. After 3 h, the <sup>1</sup>H NMR spectrum of the resulting mixture showed the complete disappearance of 8, along with the formation of a new complex 9 (see Scheme 3). The <sup>1</sup>H NMR spectrum of 9 also indicated a

highly symmetrical species, consistent with the formation of only one isomer. This differs from a related neutral bimetallic rhodium NHC complex reported by Hollis, which exists as two interconverting diastereomeric complexes.<sup>19</sup> In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, the Ag–C resonance at 172 ppm disappeared, and in its place, a new downfield resonance at 166 ppm was observed, corresponding to the Rh–C<sub>MIC</sub>. The relatively large <sup>103</sup>Rh–<sup>13</sup>C coupling constant of <sup>1</sup>J<sub>Rh–C</sub> = 47 Hz suggests a strong Rh–C<sub>MIC</sub> bond.<sup>8a</sup> X-ray quality single crystals were grown by slow diffusion of hexanes into a concentrated CH<sub>2</sub>Cl<sub>2</sub>–THF solution of **9**.

X-ray crystallographic analysis unambiguously confirms the bimetallic nature of complex **9** with a metal-to-ligand ratio of 2:1 (Figure 2A). The remaining coordination sites on the rhodium are occupied by one COD ligand, and one acetonitrile. The two triazole rings are twisted  $53.51^{\circ}$  in opposite directions with respect to the bridging phenyl ring. This conformation is likely caused by the steric hindrance provided by the COD groups. This hindrance is further observed in the Dipp wingtip groups, which are tilted with respect to their corresponding triazole rings with dihedral angles of  $77.71^{\circ}$ .

Interestingly, multiple weak, noncovalent C–H···F and C– H···Cl interactions are observed between the ligand, the BF<sub>4</sub><sup>-</sup> counterion, and the CH<sub>2</sub>Cl<sub>2</sub> that was incorporated into the crystal lattice (Figure 2B). These contacts may reasonably be considered to be nonclassical C–H···X hydrogen bonds since they are less than the sum of the van der Waals radii (2.67 and 2.95 Å for H···F and H···Cl, respectively.<sup>33</sup> These interactions appear to play a crucial role in the solid-state organization of 9. This complex appears to be the first reported example of a homobimetallic rhodium triazole MIC complex. In an attempt to prepare bidentate versions of 9, we examined the effect of decreasing the ratio of the Rh precursor to carbene complex 8, but in all cases, fewer equivalents of [Rh(COD)<sub>2</sub>]BF<sub>4</sub> resulted in the incomplete transmetalation of 8.

The transmetalation of Ag-MIC complex 7 was performed with  $[Rh(COD)Cl]_2$  in dichloromethane in order to produce the neutral monomeric complex [Rh(MIC)(COD)X] (X = Cl, Br) **10** (Scheme 4). To avoid any halide scrambling, excess KBr (10 equiv) was added. The related Ir complex [Ir(MIC)-(COD)Cl] has been prepared *in situ* by the Bertrand group en

#### Scheme 3. Formation of Rhodium Complex 9 by Transmetalation of Cationic Complex 8 with [Rh(COD)<sub>2</sub>]BF<sub>4</sub>





**Figure 2.** (A) Crystallographically determined structures of  $[Rh_2L_2(COD)_2(MeCN)_2][BF_4]_2CH_2Cl_2$  (9), displaying thermal ellipsoids drawn at the 50% confidence level. There is  $^{1}/_{2}$  of a molecule of complex 9 per asymmetric unit. Hydrogen atoms, counteranion (BF<sub>4</sub>), and solvent (CH<sub>2</sub>Cl<sub>2</sub>) are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Rh(1)–C(6), 2.048(4); Rh(1)–N(4), 2.060(3); C(28)–C(29), 1.459(6); N(2)–N(3), 1.314(4); N(1)–N(2), 1.346(4); N(1)–C(6), 1.361(5); N(3)–C(7), 1.468(4); N(4)–Rh(1)–C(6), 86.70(13). (B) 2D structure of [Rh<sub>2</sub>L<sub>2</sub>(COD)<sub>2</sub>(MeCN)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>CH<sub>2</sub>Cl<sub>2</sub> showing multiple hydrogen C–H…F and C–H…Cl interactions. Non-hydrogen bonding H atoms are omitted for clarity.

route to a biscarbonyl compound employed to assess the donor properties of the MIC derived from 2,<sup>6a</sup> but this compound was not isolated. Thus, the isolation and characterization of **10** by X-ray crystallography also serves as support for the structure of its Ir congener.

Complex 10 exhibits nearly planar geometry around the rhodium atom (Figure 3). A common plane between the aromatic wingtip groups (Ph and Dipp) is not observed, and they lie tilted at different angles from the central triazole ring. The phenyl wingtip group is only slightly twisted with respect to the plane of the triazole ring, at an angle of 33.29°. Likely due to steric considerations, the Dipp wingtip group is much



Figure 3. Crystallographically determined structure of [RhL(COD)-Br] (10), displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Rh(1)–C(1), 2.044(6); Rh(1)–Br(1), 2.4937(10); C(2)–C(16), 1.465(9); N(1)–C(3), 1.436(7); N(1)–C(1), 1.372(8); N(2)–N(3), 1.308(7); N(3)–C(15), 1.483(8); Br(1)–Rh(1)–C(1), 87.54(17).

more tilted with respect to the triazole ring with a dihedral angle of 71.77°. The triazole ring of the carbene unit is completely planar. The Rh– $C_{\rm MIC}$  bond length in **10** (2.044(6) Å) is the same as that of **9** (2.048(4) Å) within error and is nearly identical to the Rh triazole MIC complex reported by Albrecht (2.027(6)Å).<sup>8a</sup> No supramolecular contacts, similar to those of **9**, are observed in **10**, likely due to the overall neutrality of the complex.

In summary, we have investigated the coordination chemistry of triazolium MICs by the formation of silver and rhodium complexes. A novel bridging MIC ligand based on alkylated bis(1,2,3-triazolium salts) was synthesized, and its reactivity toward Ag<sub>2</sub>O was investigated, resulting in the isolation of the first structurally characterized example of a cationic 2:2 (Ag:L) silver triazole MIC complex. This complex was further transmetalated to Rh to give a cationic bimetallic rhodium complex. To the best of our knowledge, this is the first example of a cationic bimetallic mesoionic carbene complex of rhodium reported in the literature.<sup>19–22</sup> In addition, the previously reported monodentate MIC 2 was prepared and reacted with Ag<sub>2</sub>O and then transmetalated to rhodium to give complex 9, which was fully characterized. Complexes 9 and 10 represent some of the first reported and structurally characterized examples of Rh-MIC complexes. We are currently investigating the catalytic activity of complexes 9 and 10, as well as the transmetalation of Ag-MIC complex 8 to other metal sources as

Scheme 4. Formation of Complex 10 by Transmetalation of Ag-MIC Complex 7 with [Rh(COD)Cl]<sub>2</sub>



synthetic routes to pincer complexes, and to prepare other bimetallic complexes.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Synthetic procedures and characterization data for all compounds and selected crystallographic data for compounds 7-10. This material is available free of charge via the Internet at http://pubs.acs.org.

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