

# Silver Complexes of a Novel Tripodal N-Heterocyclic Carbene Ligand: Evidence for Significant Metal–Carbene $\pi$ -Interaction

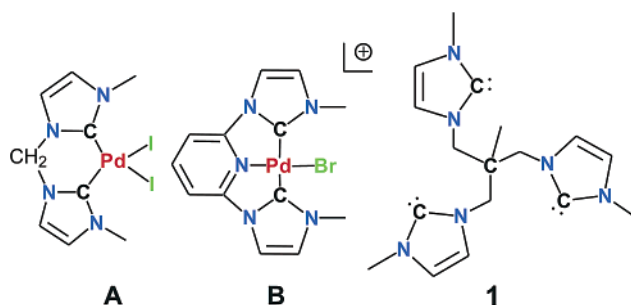
Xile Hu, Yongjun Tang, Peter Gantzel, and Karsten Meyer\*

Department of Chemistry and Biochemistry, Mail Code 0358, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093-0358

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**Summary:** A novel N-heterocyclic tridentate polycarbene ligand has been synthesized and stabilized as its corresponding silver complex. An electronic structure investigation reveals significant  $\pi$ -bonding interactions within the Ag–carbene unit of the  $[(\text{TIME}^{\text{Me}})_2\text{Ag}_3]^{3+}$  cation.

Compounds containing divalent carbon centers have sparked the interest of organic,<sup>1,2</sup> inorganic,<sup>3,4</sup> and theoretical chemists<sup>5</sup> like no other single class of molecules in chemistry. This is probably due to their fascinating molecular and electronic structures,<sup>6</sup> challenging syntheses,<sup>7</sup> and versatile properties, varying from nucleophilic to electrophilic and even ambiphilic character.<sup>8</sup> The study of carbene compounds has proven to be rewarding for material scientists as well as preparative chemists and has resulted in promising materials, such as single-molecule magnets,<sup>9</sup> liquid crystals,<sup>10</sup> and a new generation of catalysts for organic synthesis. The usefulness of the last group is especially true for metal complexes of imidazol-2-ylidenes. These N-heterocyclic carbenes (NHC) derived from the imidazolium and pyrazolium salts by deprotonation are important ligands in organometallic chemistry. Chelating NHC ligands of the pincer type (Figure 1) reportedly yield especially stable complexes and, thus, have many advantages over conventional catalysts.<sup>11,12</sup> The increased stability of compounds of type **A** and **B** is likely due to the chelating effect of the bidentate ligand, yet only very few chelating bis(carbene) ligands have been reported in the literature; known examples include linkage by a pyridine or simple  $\text{CH}_2$  unit.<sup>11,13,14</sup> Macro-



**Figure 1.** Structural representatives of palladium catalysts supported with bidentate carbene chelators (**A**, **B**) and a structural diagram of the tridentate free percarbene ligand **1**.

cyclic percarbene ligands remain elusive.<sup>15</sup> The synthesis of chelating multidentate carbene ligands and their corresponding metal complexes could make available the many valuable properties of carbene-based ligand systems.

Much of our research has focused on the synthesis and coordination chemistry of tridentate percarbene ligands anchored to either a single atom such as boron,<sup>16</sup> carbon,<sup>17</sup> and nitrogen or a trifunctionalized arene moiety.<sup>18</sup> We present here an unprecedented tripodal N-heterocyclic carbene ligand system with a carbon anchor and important silver precursors that give access to synthetic routes for the isolation of a new generation of potentially catalytically active metal–carbene complexes. Traditionally, NHC ligands almost exclusively are referred to as pure  $\sigma$ -donors when coordinated to metal ions.<sup>2</sup> Only a few theoretical studies on transition-metal NHC complexes have been reported.<sup>19–21</sup> In some cases, the existence of metal to ligand  $\pi$ -back-bonding was suggested but the magnitudes of such interactions were reported to be minimal.<sup>19,20</sup> Recently however, on the basis of structural information, nonnegligible  $\pi$ -in-

\* To whom correspondence should be addressed. Fax: (+1) 858-534-5383. E-mail: kmeyer@ucsd.edu

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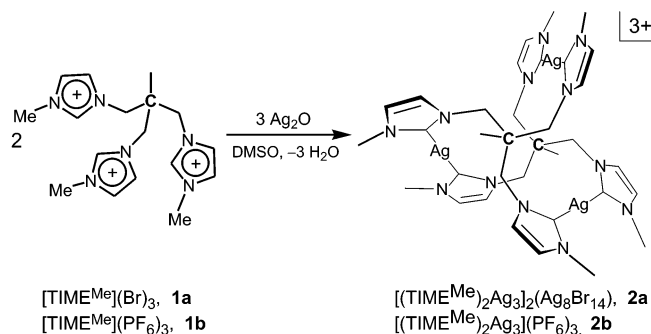
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**Scheme 1. Synthesis of Silver–Carbene Complexes  $[\text{Ag}_3(\text{TIME}^{\text{Me}})_2]^{3+}$**



teraction between group 11 metals and carbene ligands was suggested.<sup>22,23</sup> The recent development of modern density functional theories and corresponding computer programs allows the calculation of entire molecules at a quantum-mechanical level. Taking advantage of this progress, we have computed the electronic structure of the newly synthesized, highly symmetrical silver(I) carbene complexes. The analysis of the molecular orbitals reveals interesting bonding features in the linear, coplanar carbene–metal–carbene entities.

A novel imidazolium precursor, [1,1,1-tris(3-methylimidazolium-1-yl)methyl]ethane tribromide ( $[\text{TIME}^{\text{Me}}](\text{Br})_3$ , **1a**), for the neopentane-based tripodal carbene system **1** was synthesized by quaternization of *N*-methylimidazole with 1,1,1-tris(bromomethyl)ethane in high yield (>85%). Treatment of a methanolic solution of **1a** with ammonium hexafluorophosphate effected complete substitution of bromide and the formation of  $[\text{TIME}^{\text{Me}}](\text{PF}_6)_3$  (**1b**). Chemical shifts of the resonances in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1a** and **1b** are similar and consistent with those of other reported imidazolium salts.<sup>24</sup> The solid-state structure of **1a** was established by X-ray crystallography.<sup>25</sup>

Reaction of both imidazolium salts, **1a** and **1b**, with  $\text{Ag}_2\text{O}$  in DMSO at 75 °C yielded the corresponding silver carbene complexes [1,1,1-tris((3-methylimidazol-2-ylidene)methyl)ethane]silver bromide,  $[(\text{TIME}^{\text{Me}})_2\text{Ag}_3]_2(\text{Ag}_8\text{Br}_{14})$  (**2a**), and [1,1,1-tris((3-methylimidazol-2-ylidene)methyl)ethane]silver hexafluorophosphate,  $[(\text{TIME}^{\text{Me}})_2\text{Ag}_3](\text{PF}_6)_3$  (**2b**) (Scheme 1).<sup>26</sup> Recrystallization from DMSO solution delivered **2a** as colorless, highly light-sensitive crystals of **2a**·5DMSO, while diffusion of ether into an acetonitrile solution of **2b** afforded hexagonal, light-stable crystals of **2b**. The formation of the metal carbene complexes was confirmed

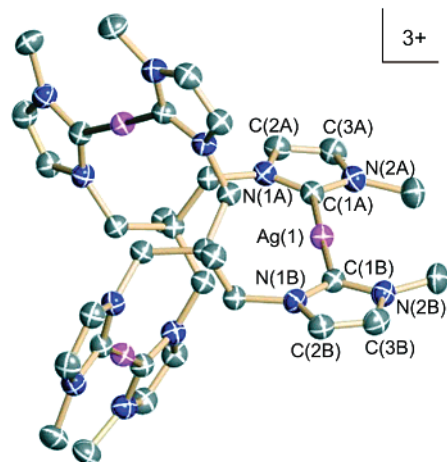
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(26)  $[(\text{TIME}^{\text{Me}})_2\text{Ag}_3](\text{PF}_6)_3$  (**2b**): 1.08 g (1.44 mmol) of **1b** was dissolved in 100 mL of DMSO, and then 0.52 g of  $\text{Ag}_2\text{O}$  (2.24 mmol) was added. The mixture was heated at 75 °C for 12 h. The resulting suspension was then filtered through Celite, and an equal amount of water was added to the filtrate to give a white powder. The precipitate was filtered, washed with ether, and dried under vacuum (0.67 g, yield 67%). <sup>1</sup>H NMR (400 MHz,  $[\text{D}_6]\text{DMSO}$ , 20 °C):  $\delta$  7.55 (s, 3H), 7.49 (s, 3H), 4.44 (s, br, 3H), 4.20 (s, br, 3H), 3.90 (s, 9H), 1.24 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz,  $[\text{D}_6]\text{DMSO}$ , 20 °C):  $\delta$  182.5, 123.6, 123.2, 59.0, 40.4, 38.2, 18.1 ppm. Anal. Calcd for  $\text{C}_{34}\text{H}_{48}\text{N}_{12}\text{Ag}_3\text{P}_3\text{F}_{18}$ : C, 29.52; H, 3.50; N, 12.15. Found: C, 29.26; H, 3.46; N, 11.77.



**Figure 2.** Solid-state molecular structure of  $[\text{Ag}_3(\text{TIME}^{\text{Me}})_2]^{3+}$  in crystals of **2b**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (deg):  $\text{Ag}(1)\text{--C}(1\text{A}) = 2.082(2)$ ,  $\text{C}(1\text{A})\text{--N}(1\text{A}) = 1.359(3)$ ,  $\text{C}(1\text{A})\text{--N}(2\text{A}) = 1.347(3)$ ,  $\text{C}(2\text{A})\text{--C}(3\text{A}) = 1.341(4)$ ;  $\text{C}(1\text{A})\text{--Ag}(1)\text{--C}(1\text{B}) = 178.56(13)$ ,  $\text{N}(1\text{A})\text{--C}(1\text{A})\text{--N}(2\text{A}) = 104.3(2)$ .

by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Single-crystal X-ray diffraction studies were carried out for complexes **2a** and **2b**.<sup>27</sup> In the solid-state structure of **2a**, two structurally equivalent  $[(\text{TIME}^{\text{Me}})_2\text{Ag}_3]^{3+}$  fragments, linked by an unprecedented  $[\text{Ag}_8\text{Br}_{14}]^{6-}$  cluster through two bridging bromide atoms, were found. For the silver cluster, the Ag–Br distances range between 2.5802(15) and 2.7712(16) Å and the Ag–Ag distances between 2.9300 and 3.1369(14) Å.

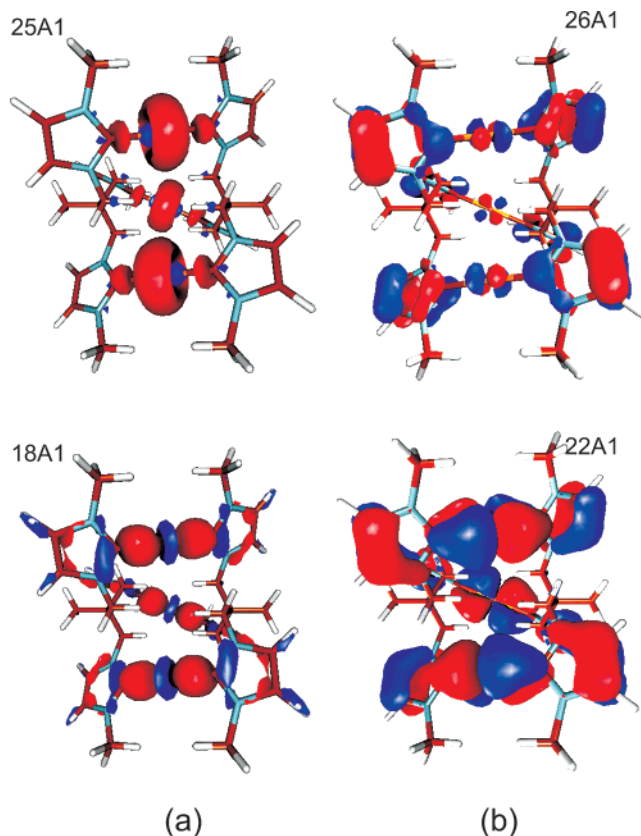
The structure of **2b** exhibits  $D_3$  symmetry with the 3-fold axis passing through the anchoring C atoms of the two ligands. In the solid-state structure, three silver atoms bridge two  $\text{TIME}^{\text{Me}}$  ligands through each of the three pendant arms (Figure 2). Each silver atom is two-coordinate, and the silver–carbene bond distance is 2.082(2) Å, which is comparable to those found in known Ag–NHC complexes.<sup>28,29</sup> The carbene–silver units are nearly linear, with a C–Ag–C' angle of 178.56(13)°. In comparison to the structural parameters of the imidazolium salt  $[\text{TIME}^{\text{Me}}](\text{Br})_3$  (**1a**), the five-membered rings of the coordinated carbene **2b** display elongated N–C<sub>carbene</sub> bonds, a smaller N–C<sub>carbene</sub>–N angle, and a decrease in C=C bond distance. These results are consistent with an increase of p character at the carbene carbon<sup>6</sup> and a decrease in  $\pi$ -delocalization in the imidazole rings.<sup>24</sup>

To elucidate the electronic structure of our newly synthesized silver complexes, density functional calculations (BY86/TZP with relativistic effects accounted for by ZORA) were performed on the tricationic portion of **2b** (for details see the Supporting Information).<sup>30</sup> The optimized structural parameters are in good agreement

(27) An ORTEP plot of **2a** and crystallographic details for **2a**·5DMSO can be found in the Supporting Information. Crystallographic details for **2b** ( $\text{C}_{34}\text{H}_{48}\text{Ag}_3\text{F}_{18}\text{N}_{12}\text{P}_3$ ): colorless colorless hexagonal crystals,  $0.15 \times 0.14 \times 0.10 \text{ mm}^3$ , space group  $R\bar{3}c$ , rhombohedral,  $a = 18.5021(10)$  Å,  $c = 23.672(3)$  Å,  $V = 7017.8(10) \text{ \AA}^3$ ,  $Z = 6$ ,  $\rho_{\text{calcd}} = 1.964 \text{ mg/m}^3$ ,  $F(000) = 4104$ ,  $R(F) = 0.0277$ ,  $R_w(F^2) = 0.0700$ ,  $\text{GOF} = 1.078$  ( $I > 2\sigma(I)$ ).

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**Figure 3.** (a) Representative  $\sigma$ -type orbitals of **2b**: 18A1 (bottom) and 25A1 (top). (b) Representative  $\pi$ -type orbitals of **2b**: 22A1 (bottom) and 26A1 (top).

with the crystallographically established values. Analysis of the frontier orbitals reveals the nature of the silver–carbene bonding interaction (Figure 3; a more detailed orbital diagram is depicted in Figure S3, Supporting Information). The bonding orbitals<sup>31</sup> involving the carbene lone pairs and the silver hybrid ( $d(z^2) + s$ ) closely approach 3-fold degeneracy (18A1, 31E1,  $\Delta(18A1-31E1) = 2.7$  kJ/mol) and can be found 430.8 kJ/mol below HOMO 49E1 (Figure 3a, bottom). The interaction between the carbene lone pairs with the silver  $p(z)$  orbitals (23A2, 44E1,  $\Delta(23A2-44E1) = -2.2$  kJ/mol) is less favorable, having a calculated value of 153.3 kJ/mol below the HOMO. Finally, the quasi-antibonding interaction between the carbene lone pair and the silver hybrid (25A1, 47E1,  $\Delta(25A1-47E1) = 2.1$  kJ/mol) is shown in Figure 3a (top), 34.1 kJ/mol below the HOMO. Overall, our results on the  $\sigma$ -bonding

(30) We herein report the analysis of the frontier orbitals in **2b**. A detailed study containing an extended discussion on the calculation of the entire series of group 11 metal NHC complexes as well as closely related species will be given in a more specialized paper.

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interactions of **2b** are in accord with others reported for Pd(0) and Pt(0) bis(carbene) complexes.<sup>21</sup>

Most importantly, however, our calculations also reveal significant  $\pi$ -interaction between the carbene ligands and the silver ions. Two representative molecular orbitals involved in  $\pi$ -bonding are shown in Figure 3b. These orbitals can be regarded as linear combinations of the carbene  $p-\pi$  orbitals and the metal  $d(xz)/d(yz)$  orbitals. The orbital 22A1 has apparent bonding character, while orbital 26A1 is quasi-antibonding in nature. Visual inspection of the shape of the molecular orbitals reveals a considerable overlap between the metal  $d$  and the carbene  $p-\pi$  type orbitals, indicating significant  $\pi$  interaction in this complex. We therefore conclude that, under certain structural and electronic conditions, both  $\sigma$ - and  $\pi$ -type interactions exist in NHC complexes. To further investigate bonding interactions in NHC complexes, we are currently performing calculations on other complexes synthesized in our laboratory as well as on compounds reported in the literature. Complexes **2a** and **2b** readily react with CuBr and  $((\text{CH}_3)_2\text{S})\text{AuCl}$ , for instance, to yield the analogous metal complexes  $[(\text{TIME}^{\text{Me}})_2\text{M}_3]^{3+}$  ( $\text{M} = \text{Cu}(\text{I}), \text{Au}(\text{I})$ ). Accordingly, the copper and gold  $\text{TIME}^{\text{Me}}$  carbene complexes were prepared and isolated. Our preliminary spectroscopic and crystallographic studies indicate isostructural geometries for the group 11 analogues. Details for these complexes will be reported elsewhere.

In summary, we have synthesized a new tripodal carbene ligand system ( $\text{TIME}^{\text{Me}}$ ) and its corresponding silver complexes. The molecular and electronic structures of these complexes are described. For the first time,  $\pi$ -bonding between metal ions and  $p-\pi$  orbitals of an N-heterocyclic carbene ligand system was established unambiguously by computational analysis.

Silver complexes **2a** and **2b** have proven to be potent ligand transfer reagents<sup>32</sup> for the, otherwise unstable, free percarbene ( $\text{TIME}^{\text{Me}}$ ). We envision these air- and moisture-stable silver complexes to offer a convenient entry into the coordination chemistry of  $\text{TIME}$ -type complexes of Pd and Pt.

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**Supporting Information Available:** Text giving synthetic details and spectroscopic data for new compounds, an ORTEP plots of **1a** and **2a**, a calculated orbital diagram and DFT input file for **2b**, and complete listings of structural parameters for **1a**, **2a**, and **2b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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