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# A Unique Three-Dimensional Coordination Cluster Based on a Silver Carbene Complex

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S *Supporting Information*

**ABSTRACT:** In an attempt to perform a simple anion-exchange reaction on a pincer-carbene-ligated nickel complex using $AgNO_3$, we instead obtained an unexpected three-dimensional (3D) $Ag_7$ cluster containing a $[Ag_6]$ core in a twisted-bowtie geometry. The reverse-transmetalation reaction by which the carbene is transferred from nickel to silver is virtually unprecedented. The CNC pincer-carbene ligands exhibit unusual bridging modes of ligand bonding for all three donor atoms. Another unique feature is that the final structure exhibits a 3D structure brought about by the connection of two-dimensional layers of the $[Ag_6]$ core via a seventh Ag ion.

During the past several years, there has been intense interest within the inorganic and organometallic literature concerning the synthesis and characterization of new multidentate ligands, as well as the coordination chemistry of these ligands. While precise reasons for this interest vary depending on the ultimate applications of the complexes, enhanced levels of thermal stability and improvements in air and moisture stabilities are often highly desired properties. One unique subset of multidentate ligands is the so-called pincer family of ligands, where a trans-spanning, tridentate ligand is complexed to a metal ion to yield a relatively rigid, stable coordination complex.[1] Pincer ligands have shown a rich reaction chemistry, with a range of transition-metal, main-group, and lanthanide complexes known. Unique stabilities are seen when these pincers are complexed with electron-rich, late-transition-metal ions,[2] and this area is of particular interest to our research groups[3−5] and others[1,6,7] because these late-transition-metal pincer complexes have found use in a variety of catalytic and organometallic applications.[8,9] These pincer ligands can be systematically modified to offer a variety of ligand frameworks containing specific donor atoms. In this submission, we restrict ourselves to a class of pyridine-based pincer ligands containing N-heterocyclic carbene (NHC) donors, the neutral CNC ligands. The naming of these ligands as "CNC" follows the accepted convention of creating an abbreviation from the atoms that designate the points of attachment to the metal ion. Even more specifically, we are interested in neutral CNC ligands with NHC groups directly attached in a meta orientation on the pyridine ring (A), which will permit a more rigid framework to be formed when compared to those NHCs containing a methylene bridge (B) (Figure 1). The precursor salts for both of these classes of CNC ligands have been previously synthesized.[10,11]

Concurrently, there has also been increasing attention paid to silver-based clusters that can be used in various applications, including recent literature reports of uses in photoluminescence,[12,13] in the preparation of novel nanomaterials,[14] and in molecular cylinders.[15] However, solid-state structures for these clusters are rare, and computational studies can be required to determine the structures of the clusters.[16]

When these two areas of research are combined, silver(I)-containing carbene complexes have gained special attention, with applications as diverse as synthetic carbene-transfer reagents[17] to antimicrobial pharmaceuticals.[18,19] Again, depending on the ultimate purpose, the chemical properties of the silver(I) carbene complex can be greatly controlled. In a search of the Cambridge Structural Database (CSD; Nov 2010 update),[20] we find that there is an unexpectedly small number of CNC-containing silver(I) complexes that have been structurally characterized. Of these complexes, the vast majority assume well-behaved monomeric or dimeric solid-state structures, while only one is found as a linear polymer, utilizing the bridging nature of the NHC ligand to link multiple $Ag^I$ ions.[19]

In an attempt to perform a simple anion exchange using a type A CNC−Ni halide salt, we surprisingly observed a transmetalation reaction that instead produced a novel Ag(CNC)-containing cluster. In order to effect the $Br^-/NO_3^-$ exchange, a 7-fold excess of $AgNO_3$ was added at 25 °C to a suspension of $[(^{Me}CNC)NiBr]^+Br^-$ in methanol (Scheme 1).[21] The solution was allowed to stir for 2 h and then filtered to remove excess $AgNO_3$. After filtration, the solution was concentrated by the removal of methanol and allowed to crystallize under an inert atmosphere. Two types of crystal morphologies were obtained and could be physically separated. Product **2** was obtained as large, colorless crystals suitable for single-crystal X-ray analysis (vide infra). Product **3** precipitated as a microcrystalline colorless material that diffracted poorly and was unsuitable for X-ray study. However, **3** had an elemental analysis corresponding to an overall molecular formula of $(^{Me}CNC)AgNO_3$. Nickel appears to have been lost as $NiBr_2$. We found **2** and **3** to be largely insoluble in most solvents. As such, the $^1H$ NMR data obtained were not particularly informative because only broad signals were observed in the NMR spectrum. The IR spectrum of **2** in a Nujol mull indicated the presence of metal-coordinated $NO_3^-$ groups in the

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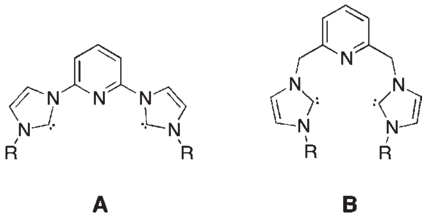
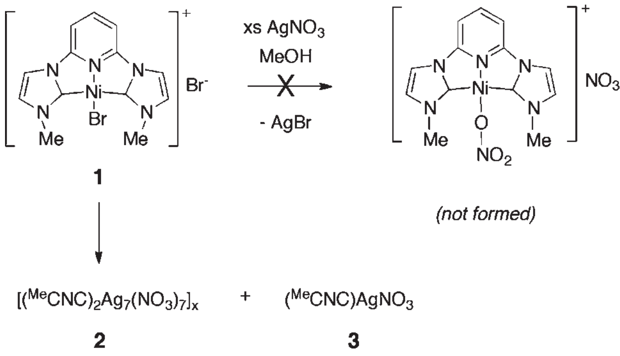


**Figure 1.** CNC ligands either with NHCs directly attached (A) or with NHCs attached via a bridging $-CH_2-$ group (B).

**Scheme 1. Syntheses of Complexes 2 and 3**



product, with characteristic absorptions at 1400, 814, and 723 cm$^{-1}$.[22] However, the elemental analysis and X-ray data for **2** indicated that the product was not the expected anion-exchanged $[(^{Me}CNC)NiONO_2]^+NO_3^-$ salt.

To determine the structure of **2** with certainty, a single-crystal X-ray diffraction analysis was performed, and the results showed that the $^{Me}$CNC pincer ligands were no longer bound to Ni$^{II}$ ions but rather to Ag$^{I}$ ions. Compound **2** crystallizes in the monoclinic crystal system, space group $P2(1)/n$. A formulation with the overall stoichiometry of $[(^{Me}CNC)_2Ag_7(NO_3)_7(H_2O)_{0.5}]_x$ could be assigned for **2**, indicating that a virtually unprecedented reverse-transmetalation reaction had occurred to transfer $^{Me}$CNC *from* nickel *to* silver. To our knowledge, the only prior instance of a reverse transmetalation of nickel and silver is a single example using large 2,6-diisopropylphenyl ligands over a 24 h reaction time reported by Pugh et al.[23] While this transfer to silver(I) was most unexpected, what is also of interest is that the solid-state structure of **2** is a three-dimensional (3D) polymer in which two-dimensional (2D) networks of $[Ag]_6$ clusters are linked by a seventh Ag ion to form an extended coordination structure. We speculate that the formation of the insoluble **2** upon crystallization acts as the major driving force for this reverse-transmetalation reaction.

Figure 2 highlights the core $Ag_6$ cluster that crystallizes in a twisted-bowtie geometry. While this bowtie arrangement is unknown for silver, it has been seen previously by Furuya and Gladfelter in a mixed $[Fe_4Ru_2]$ cluster.[24] While the seven Ag−Ag bonds vary significantly in length from 2.726 to 3.349 Å, all are within the range for Ag−Ag bond lengths reported in the CSD.[25] Also shown are the two $^{Me}$CNC ligands, which bind to all six Ag ions of the bowtie in a crisscross (X) (see the Supporting Information for more views) fashion (C4−N3−C12 and C17−N8−C25 define the attachment points to Ag for the two CNC ligands). The imidazole rings of the carbenes $\pi$-stack with one other, at a centroid···centroid distance of 3.87 Å for the C4/C25 rings and of 4.19 Å for C12/C17.[26] Most

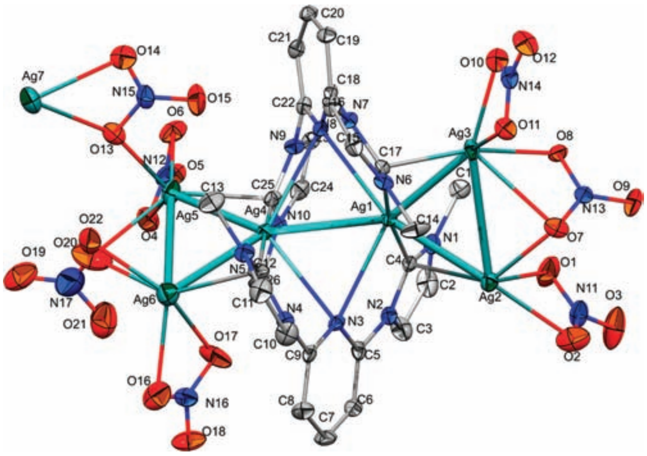


**Figure 2.** Asymmetric unit of **2** with a twisted-bowtie configuration of the $[Ag]_6$ cluster highlighted (50% ellipsoids). H atoms are not shown.

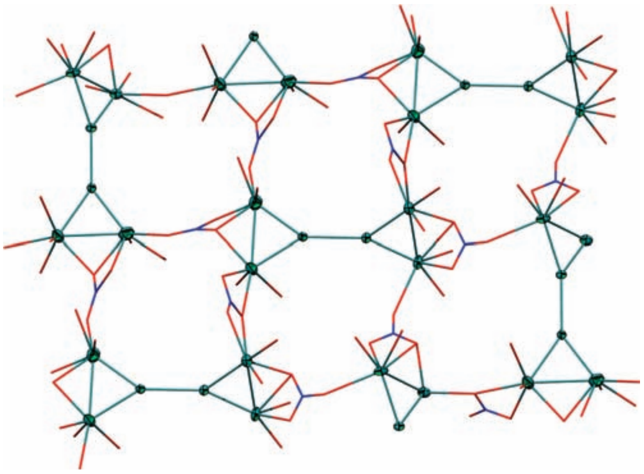


**Figure 3.** 2D layer structure of complex **2** showing the relative position of the $Ag_6$ clusters (shown in green) and the bridging nitrate groups (N atoms shown in blue and O atoms shown in red).

unusual, *all* three of the donor sites in each CNC ligand are bridging in nature (bound to multiple metals), with the pyridyl N atoms bridging the two inner Ag1 and Ag4 atoms, while each of the carbene atoms bridges both an inner Ag atom and an outer Ag atom of the bowtie structure. The Ag−N bonds are relatively long, measuring between 2.714(5) and 2.788(5) Å. The bonds between the carbenes and the inner Ag atoms range from 2.132(6) to 2.174(6) Å, while those to the outer Ag atoms are longer and more varied, from 2.329(6) Å for Ag3−C17 to 2.528(6) Å for Ag2−C4. All are within previously reported values for silver carbenes.[20] That all of the ligands bridge is particularly intriguing because the question of bridging versus terminal (bound to one metal) NHC carbenes has recently been addressed by Hor et al.[27] The other ligands bound to the outer Ag2, Ag3, Ag5, and Ag6 atoms to complete the coordination are nitrate anions.

These $Ag_6$ clusters are coordinated to each other via nitrate anions that serve as bridges to form 2D layers, and this structural feature can be seen in Figure 3. For clarity, the CNC carbene ligands complexed to the bowtie $Ag_6$ cluster are not shown in this view. One can see that the $NO_3^-$ anions are coordinated only to the terminal Ag atoms and the inner Ag atoms (Ag1 and Ag4) are not bound to any nitrate anions.

Lastly, the 2D layers are extended into a 3D network by the seventh Ag ion, Ag7. This Ag7 ion has a coordination number of 8. Of note is that Ag7 is not bound to any CNC ligand fragment but rather only to four nitrate groups. One nitrate group (N17, O19, O20, and O21) is disordered over two positions in a 1:1 ratio. Ag7 serves to act as a bridge to connect the outer Ag ions of the adjacent layers.

In summary, we have prepared a highly unusual 3D coordination complex **2** by a unique and unexpected reverse-transmetalation carbene-transfer reaction from nickel to silver. Compound **2** contains a previously unknown $Ag_6$ twisted-bowtie cluster structure as a core. This core of Ag atoms is bound in an unprecedented bonding pattern in which all CNC donor atoms of each ligand act in a bridging fashion to Ag ions. Bridging nitrate groups allow a 2D-layered structure to form, and a nitrate-bound seventh Ag ion connects the layers into a 3D complex. Well-defined structures of the $Ag_7$ clusters are extremely rare and are of interest. Lastly, we are examining in more detail the unusual reverse-transmetalation reaction that led to the formation of this Ag cluster.

## ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Detailed synthetic procedure resulting in the preparation of **2** and **3**, full characterization data, X-ray crystallographic data for **2** in CIF format, and additional thermal ellipsoid plots and views of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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