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

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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 \([\text{TIME}^\text{Me}_2\text{Ag}]_3^+\) cation.

Compounds containing divalent carbon centers have sparked the interest of organic, inorganic, and theoretical chemists like no other single class of molecules in chemistry. This is probably due to their fascinating molecular and electronic structures, challenging syntheses, and versatile properties, varying from nucleophilic to electrophilic and even amphiphilic character. 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, liquid crystals, and a new generation of catalysts for organic synthesis. The usefulness of the last group is especially true for metal complexes of imidazol-2-ylidene. These N-heterocyclic carbene (NHC) derived from the imidazolium and pyrazolium salts by deprotonation are N-heterocyclic carbenes (NHC) derived from the imidazolium and pyrazolium salts by deprotonation are N-heterocyclic carbenes (NHC) derived from the imidazolium and pyrazolium salts by deprotonation are N-heterocyclic carbenes (NHC) derived from the imidazolium and pyrazolium salts by deprotonation.

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 CH2 unit.11,13,14 Macroyclic percarbene ligands remain elusive.15 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, carbon,16 and nitrogen or a trifunctionalized arene moiety.18 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 \( \pi \)-donors when coordinated to metal ions.2 Only a few theoretical studies on transition-metal NHC complexes have been reported.19–21 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.19,20 Recently however, on the basis of structural information, nonnegligible \( \pi \)-in...
The formation of the metal carbene complexes was confirmed. 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-methylimidazol-1-yl)-methyl]ethanebromide ([TIME]MeBr)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 [TIME]Me(Me)PF6 1b. Chemical shifts of the resonances in the 1H and 13C NMR spectra of 1a and 1b are similar and consistent with those of other reported imidazolium salts. Recrystallization from DMSO solution delivered 1a as colorless, highly light-sensitive crystals of 1b. The solid-state structure of 1a was established by X-ray crystallography.

Reaction of both imidazolium salts, 1a and 1b, with AgO in DMSO at 75 °C yielded the corresponding silver carbene complexes [1,1,1-tris(3-methylimidazol-2-ylidene)methyl]ethanesilver bromide, ([TIME]MeAg)3Br (2a), and [1,1,1-tris(3-methylimidazol-2-ylidene)methyl]ethanesilver hexafluorophosphate, ([TIME]MeAg)(PF6)3 (2b) (Scheme 1). Recrystallization from DMSO solution delivered 2a as colorless, highly light-sensitive crystals of 2a-DMSO, 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 by 1H and 13C NMR spectroscopy. Single-crystal X-ray diffraction studies were carried out for complexes 2a and 2b. In the solid-state structure of 2a, two structurally equivalent ([TIME]MeAg)3+ fragments, linked by an unprecedented [Ag8Br14]12+ 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 D3 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 TIME 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. 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 imidazolylamine [TIME]Me[Br] (1a), the five-membered rings of the coordinated carbene 2b display elongated N–Caryl bonds, a smaller N–Caryl–N angle, and a decrease in C=C bond distance. These results are consistent with an increase of p character at the carbene carbon and a decrease in π-delocalization in the imidazole rings.

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

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**Scheme 1. Synthetic of Silver—Carbene Complexes [Ag3(TIMEMe)2]3+**

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**Figure 2.** Solid-state molecular structure of [Ag3(TIMEMe)2]3+ in crystals of 2b. Hydrogen atoms are omitted for clarity; thermal ellipsoids are shown at 50% probability.
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 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 interactions of 2b are in accord with others reported for Pd(0) and Pt(0) bis(carbene) complexes.21

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 NH complexed. To further investigate bonding interactions in NH 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 ((CH3)2S)AuCl, for instance, to yield the analogous metal complexes [(TIMEMe)2M3]^+ (M = Cu(I), Au(I)). Accordingly, the copper and gold TIMEMe 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 (TIMEMe) 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 reagents32 for the, otherwise unstable, free percarbene (TIME Me). We envision these air- and moisture-stable silver complexes to offer a convenient entry into the coordination chemistry of 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.

(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.

(31) The term symbols in this paper are referred to D_3h symmetry.  