Inorganic Chemistry
Communication
pubs.acs.org/IC

# Application of Open Chain Tetraimidazolium Salts as Precursors for the Synthesis of Silver Tetra(NHC) Complexes

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Ⓢ *Supporting Information*

**ABSTRACT:** The synthesis of 3-((1H-imidazol-1-yl)-methyl)-1-methyl-1H-imidazol-3-ium iodide **1** for the synthesis of multidentate tetra-N-heterocyclic carbene (NHC) structures is described. Two acyclic open chain tetra(NHC) precursors are synthesized together with their corresponding silver complexes. On the basis of nuclear magnetic resonance (NMR) spectroscopy and single crystal X-ray diffraction (XRD) data, the coordination geometry of the silver complexes is discussed. Dependent on the length of the alkyl bridge of the tetradentate ligand either a double helix structure with four linear-coordinated silver cations or a twisted geometry with two linear-coordinated silver cations is obtained.

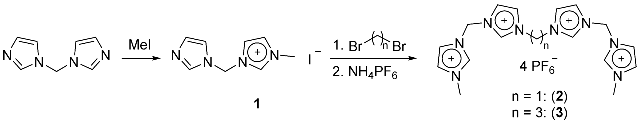
N-heterocyclic carbenes (NHC) are well known as versatile $\sigma$-donor ligands to transition metals.[1] The ability to easily tune steric and electronic properties by modifying substituents makes them a powerful tool for target-oriented catalyst design. The introduction of chelating di- and tricarbene ligands in transition metal chemistry led to a plethora of new structures and applications in homogeneous catalysis and medicinal chemistry.[2] However, only a small number of multidentate carbene ligands with four or more NHC moieties have been described so far. After an initial report of a macrocyclic tetra(NHC) ligand by Hahn et al. in 2005,[3] the most common approach to access macrocyclic tetra(NHC) ligands was presented by Murphy et al.[4] in 2007. To date, a few structural variations have been reported including the modification of the alkyl bridges and the imidazolium backbone.[5] All literature-known mononuclear tetracarbene complexes are based on cyclic tetracarbene ligands. They exhibit a square-planar coordination for metals such as Ni, Pd, and Pt,[5c,6] a tetrahedral or square-pyramidal coordination for Co complexes,[6b,7] and an octahedral coordination for Fe and Cr.[6b,8] In the latter case, both axial coordination sites are typically occupied by either solvent molecules or halides.

While macrocyclic carbene ligands have received a lot of interest, little work has been done on acyclic ligands featuring more than three NHC units. Hahn et al.[9] were again the first to isolate and characterize acyclic tetracarbene complexes. Only very recently have other groups reported on similar structural motifs containing up to six NHC units.[10] Jenkins et al.[6b] described transmetalation from silver complexes as an easy and versatile approach for the syntheses of various transition metal complexes with tetradentate NHC ligands. The most promising approach toward acyclic chelating tetracarbene ligand precursors has been published in 2005 by Kang et al.[11] Tetra(NHC) ligands are promising tools for stabilization and isolation of unusual high-valent intermediates as shown by both Jenkins and Meyer, who isolated an iron(IV) imide and an iron(IV) oxo species, respectively.[8a,12] However, due to the rigid cyclic structure of the macrocylic ligands applied, possible coordination modes are limited. Although acyclic tetradentate ligands with flexible linkers could overcome such limitations, no examples of respective mononuclear transition metal complexes are reported so far. Therefore, the aim of this work is the introduction of flexible linear tetraimidazolium structures and their application as multidentate ligands.

For ligand synthesis, preparation of compound **1** is based on a modified approach for the synthesis of asymmetrically substituted diimidazolium salts.[11] Using alkyl dihalides as reaction partner for **1**, various new tetraimidazolium salts can be accessed, which is demonstrated by two examples. Previously, we and others have shown that the choice of the alkane as linker for tetradentate ligand systems influences the coordination mode to a metal center, showing significant differences between methylene and propylene bridges.[13] Hence, dibromomethane and 1,3-dibromopropane were chosen as reaction partners for **1**, resulting in tetraimidazolium salts **2** and **3**. For both ligand precursors, the respective silver complexes were synthesized and characterized.

The synthesis of chelating acyclic tetraimidazolium ligand precursors **2** and **3** was performed in analogy to the work of Kang et al.[11] In the first step, one imidazole moiety of methylene bisimidazole was protected with a methyl group (Scheme 1). Monomethylated imidazolium salt **1** precipitates from the reaction solution; therefore, formation of the double-substituted diimidazolium salt is not favored. Purification was achieved by repetitive recrystallization from methanol, giving **1** in yields up to 85% on a multigram scale. Compound **1** is an important building block for a new class of NHC ligands. Until now, chelating dicarbene ligands were obtained either by

**Scheme 1. Synthesis of Tetraimidazolium Salts 2 and 3**



**Received:** November 27, 2014
**Published:** December 31, 2014

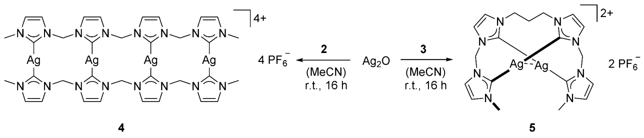
DOI: 10.1021/ic502838x

connecting two imidazole fragments or by symmetric substitution of two previously linked imidazole subunits.

Two molecules of **1** were connected via alkyl bridges, namely, by the reaction with either dibromomethane or 1,3-dibromopropane, giving tetraimidazolium salts **2** and **3**, respectively (Scheme 1). In the case of dibromomethane, the reaction was carried out under neat conditions, as **1** is a liquid and miscible with dibromomethane at the reaction temperature of 100 °C. However, the reaction of **1** with 1,3-dibromopropane requires acetonitrile as solvent and is carried out in a sealed ACE pressure tube. Compounds **2** and **3** are obtained in yields of 70−90% after anion exchange with ammonium hexafluorophosphate.

In order to demonstrate the ability of the tetraimidazolium salts to act as tetradentate NHC ligands, the formation of silver complexes from **2** and **3** was investigated. Typically, silver NHC complexes can be used as transmetalation agents for a variety of transition metals, which makes silver an excellent candidate for further studies.[6b] Silver complexes derived from both **2** and **3** were accessed by literature-known protocols.[14] An excess of silver oxide was reacted with the respective imidazolium salts. The reactions were carried out at room temperature in an acetonitrile solution, and silver complexes **4** and **5** were obtained in high yields (Scheme 2).

**Scheme 2. Synthesis of Silver Tetracarbene Complexes 4 and 5**



Typically, cyclic polycarbene ligands form monomeric complexes when the ligand cavity is large enough for two silver cations.[5a,d,15] For smaller cavities, dimeric structures are preferred with only one silver center within the cavity and two ligands being bridged via additional silver cations coordinated in a linear fashion.[6b] This effect can also be achieved by applying reaction conditions that allow kinetic control of product formation.[5d] If the number of carbenes in the ligand or the cavity size is increased, a molecular box structure is formed, where all silver cations act as bridging atoms between two independent ligands.[5a,15] Rigid acyclic tetracarbene ligands also form such molecular box structures or in one exception a monomeric complex with two silver center in the ligand cavity.[9,10b]

Single crystals of **4** and **5** were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the respective compounds. For both complexes, X-ray diffraction revealed the typical linear coordination of Ag(I) by two carbene units.[14] Complex **4** exhibits a dimeric structure with two ligands forming a double helix around a chain of four silver cations (Figure 1). This structure is neither a molecular box nor similar to cyclic tetracarbene complexes with internal cavities. It is rather uncommon and best comparable to compounds reported by Chen et al.,[13b,16] who described a similar structure for tetradentate biscarbene ligands with helical ligand geometry and metal−metal interactions. However, the terminal silver ions in this example are coordinated in a tripodal fashion with one additional coordinating solvent molecule.

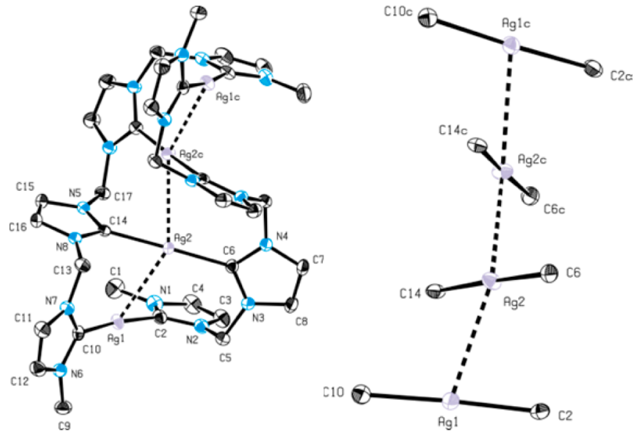


**Figure 1.** (Left) ORTEP view of the cationic fragment of **4** with thermal ellipsoids shown at a 50% probability level. Hydrogen atoms are omitted for clarity. (Right) Simplified representation of the $Ag_4$ core of **4**. Selected bond lengths [Å] and angles [deg]: Ag1−C10 2.093(3), Ag2−C14 2.108(3), Ag1−Ag2 2.9449(3), Ag2−Ag2c 3.0196(4), C10−Ag1−C2 173.49(11), C6−Ag2−C14 177.98(10), and Ag1−Ag2−Ag2c 145.269(11).

All silver cations of compound **4** exhibit an almost linear coordination mode with angles from 173.5° to 178.0°. Ag−$C_{NHC}$ distances are in the range from 2.09 to 2.11 Å, while Ag−Ag distances from 2.945 to 3.020 Å indicate metal−metal interactions comparable to those in the literature.[5a,d,10b,13b,16,17] The Ag1−Ag2−Ag2c angle is around 145°, while the torsion angle of the silver chain is 153°.

In contrast, complex **5** is arranged in a twisted fashion according to X-ray diffraction. Due to the more flexible centered propylene bridge, the ligand is able to wrap around two silver ions, leading to the formation of a dinuclear complex with only one tetradentate ligand (Figure 2). Similar to the geometric parameters of **4**, both Ag centers are coordinated almost linearly with an angle of 173°. Again, a metal−metal interaction is indicated by the Ag1−Ag2 distance of about 3.00 Å. The plains formed by the centered NHC rings are arranged in a nearly parallel fashion but tilted against the silver−silver axis by an angle of 71°.

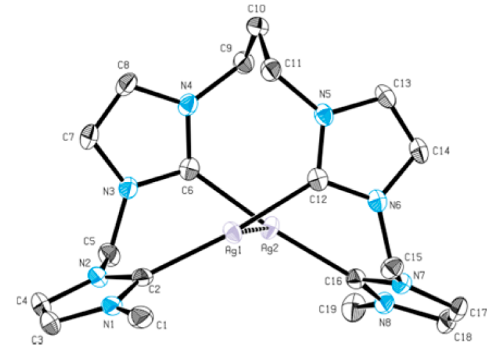


**Figure 2.** ORTEP view of the cationic fragment of **5** with thermal ellipsoids shown at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ag1−C12 2.1065(19), Ag2−C16 2.0939(18), Ag1−Ag2 2.9986(2), C2−Ag1−C12 173.02(7), and C6−Ag2−C16 173.60(7).

Spectroscopic investigations confirm the existence of these structures in solution. Both $^1H$ and $^{13}C$ NMR spectra of **4** display broad signals at room temperature indicating a flexible structure and interconversion of different conformations (Supporting Information, SI). Nevertheless all expected signals for an imidazolium backbone, methylene bridges, and terminal methyl groups are present. Elevated temperature NMR at 75 °C causes the signals to sharpen significantly (SI). Variable temperature NMR spectroscopy of **5** indicates a rigid conformation as no coalescence point is found. A sharp doublet with a coupling constant of 14 Hz for the protons of the methylene bridges is observed. The propylene bridge causes two doublets of triplets at 4.18 and 3.82 ppm and a multiplet at 2.42 ppm in $^1$H NMR. $^{13}$C NMR shows mirror symmetry in the ligand, independent from any temperature influence. The characteristic signals for coordinated $C_{NHC}$ are found at 181.2 and 184.2 ppm. ESI-MS measurements confirmed the dimeric structure of **4** with four silver centers ($m/z$ = 1539) and the dinuclear structure of **5** ($m/z$ = 725).

In summary, the synthesis of open chain tetracarbene ligands and their silver complexes has been achieved. The crucial step is the isolation and purification of monosubstituted imidazolium salt **1**, which is a versatile building block for multicarbene ligands as it facilitates the introduction of dicarbene units. Isolation of methylene-bridged imidazolium salt **2** and propylene-bridged imidazolium salt **3** as ligand precursor could also be achieved. Using literature-known procedures, these imidazolium salts can be easily converted to their respective silver carbene complexes. These silver complexes are found to differ strongly in their structure. While **4** is dimeric, resulting in a double helix structure, complex **5** is found to form a monomeric complex. These complexes might well act as transmetalation agents for transition metal salts of the general type $M^{II}X_2$ (X = halide), thus giving access to a new library of M-tetra(NHC) complexes. Such experiments are currently executed in our laboratories.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details, spectroscopic data, and X-ray crystallographic data of **4** and **5** in CIF format. CCDC 1036475 (**4**) and CCDC 1036476 (**5**) contain crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

D.T.W., S.H., and C.J. gratefully acknowledge support from the TUM Graduate School.

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