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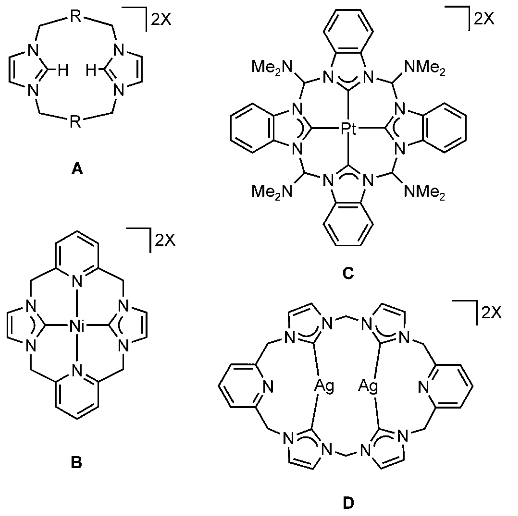
Metal-Dependent Coordination Modes Displayed by Macrocyclic Polycarbene Ligands

Christian Radloff,[a] Han-Yuan Gong,[b] Christian Schulte to Brinke,[a] Tania Pape,[a] Vincent M. Lynch,[b] Jonathan L. Sessler,*[b, c] and F. Ekkehardt Hahn*[a]

Macrocyclic polymidazolium salts have attracted considerable attention in recent years. On the one hand, these systems have been studied with respect to their function as anion receptors, and several cyclophane-like polyimidazolium cations have been shown to bind anions inside the ring cavity.[1] Alternatively, cyclic polyimidazolium cations have been explored as precursors for cyclic poly(NHC) ligands and their metal complexes.[2]

Metal complexes bearing cyclic di(NHC) ligands, for example, have been generated from cyclophanes-like diazolium salts such as **A** (Scheme 1). These dicarbene ligands, however, are coordinated to square-planar metal centers such as Pd^{II} with the NHC donor groups bound in a *cis*-fashion.[3] As such, they act as classical bidentate ligands rather than encapsulating the metal in a manner typical for macrocyclic ligands. Similar observations have been made for cyclic tetraimidazolium cations, which upon deprotonation and coordination to d^8 transition-metal ions fold around, rather than encapsulate, the metal ion in the center of the macrocycle.[4]



Scheme 1. Diimidazolium salt **A** and complexes with poly(NHC) ligands.

Alternatively, cyclophane-like diimidazolim salts react with linearly coordinated metal ions such as silver(I) under formation of dinuclear complexes. Normally, the dicarbene ligands obtained from cyclic diimidazolium salts of type **A** cannot accommodate a linearly coordinated metal center within the cycle. In this situation the carbene donors rotate out of the plane of the macrocycle and form dinuclear complexes in which two linearly coordinated metal centers are sandwiched between two cyclic dicarbene ligands. Examples for this coordination mode have been described for lutidine-[5] and xylene-bridged[6] cyclophane-like diimidazolium cations.[7]

Only one cyclic tetradentate diamine/dicarbene ligand has been reported to form the saddle-shaped macrocyclic complex **B** with nickel(II).[8] A complex with the macrocyclic tetracarbene ligand **C**[9] has been obtained in a template-controlled reaction from the isocyanide complex.[10] Related template-controlled reactions have been used to generate complexes with *facially* coordinated [11]ane-P_2C^{NHC}[11] and macrocyclic [16]ane-$P_2C^{NHC}_2$ ligands.[12]

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[a] Dr. C. Radloff, Dipl.-Chem. C. Schulte to Brinke, T. Pape,
Prof. Dr. F. E. Hahn
Institut für Anorganische und Analytische Chemie
Westfälische Wilhelms-Universität Münster
Corrensstrasse 30, 48149 Münster (Germany)
Fax: (+49) 251-833-3293
E-mail: fehahn@uni-muenster.de

[b] Dr. H.-Y. Gong, V. M. Lynch, Prof. Dr. J. L. Sessler
The University of Texas at Austin
Department of Chemistry and Biochemistry
1 University Station, A5300
Austin, TX 78712-0165 (USA)
Fax: (+1) 512-471-7550
E-mail: sessler@mail.utexas.edu

[c] Prof. Dr. J. L. Sessler
Yonsei University
Seoul 120-749 (South Korea)

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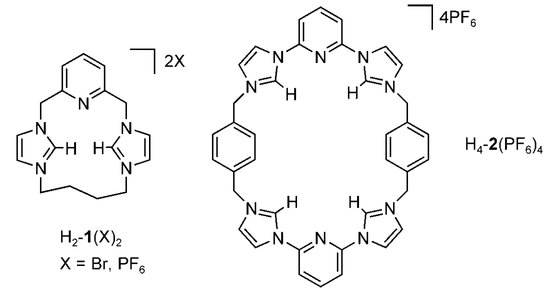
More recently, a lutidine-bridged cyclophane-like tetraimidazolium cation, intially developed as an anion receptor,[13] has been metallated with silver oxide[14] leading to the disilver complex **D**.[15] Transmetallation of **D** to give the digold complex has also been demonstrated.

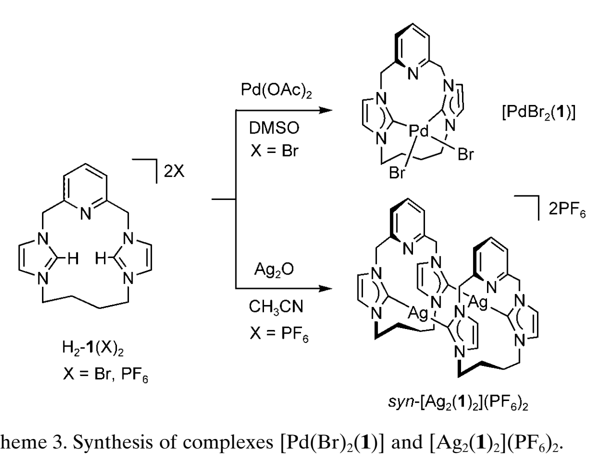
Since the preparation of complexes of type **C** in template-controlled reactions is generally cumbersome, we became interested in the use of cyclic polyimidazolium salts for the preparation of complexes with macrocyclic poly(NHC) ligands. In this contribution we describe the use of the diimidazolium salts H_2-**1**$(X)_2$ and H_4-**2**$(PF_6)_4$ (Scheme 2) for the preparation of carbene complexes that are found to differ in their topology and nuclearity depending on the metal ion used for carbene complex synthesis.



Scheme 2. Di and tetraimidazolium salts H_2-**1**$(X)_2$ and H_4-**2**$(PF_6)_4$.

Upon deprotonation of H_2-**1**$(X)_2$ the resulting dicarbene **1** potentially can act as a tridentate pincer ligand coordinating with two NHC-*C* and the lutidine-*N* donor groups to a square-planar metal center such as Pd^{II}.[16] This type of coordination is, however, obstructed by the cyclic topology of ligand **1**, which prevents the simultaneous coordination of all three donor groups. In this situation, exclusive coordination of the carbene donors to a square-planar metal center in *cis*-positions is expected, as has been reported for related ligands.[3a–d]

In fact, diimidazolium salt H_2-**1**$(Br)_2$ reacts with $Pd(OAc)_2$ in DMSO to form the complex $[Pd(Br)_2($**1**$)]$ (Scheme 3, top). Evidence for formation of this carbene complex came from ^{1}H NMR spectroscopy. Only one set of signals was detected in the ^{1}H NMR spectrum, a finding that is consistent with the formation of only one compound and no isomeric by-products. The resonance for the imidazolium protons of H_2-**1**$(Br)_2$ ($\delta = 9.13$ ppm) disappears upon complex formation. In addition, the N-CH_2-C_{Ar} methylene resonance of the diimidazolium cation was detected as a singlet in H_2-**1**$(X)_2$, while these protons become diastereotopic in the carbene complex and give rise to a doublet for each proton (AA' spin system). The imidazolium N-CH-N resonance of H_2-**1**$(Br)_2$ ($\delta = 136.4$ ppm) is absent in the ^{13}C NMR spectrum of $[PdBr_2($**1**$)]$ and the resonance for the carbene-carbon atom was observed at $\delta = 161.0$ ppm. HR-ESI mass spectrometry revealed a signal at *m*/*z* 479.98 corresponding to the cation $[PdBr($**1**$)]^+$.



Scheme 3. Synthesis of complexes $[Pd(Br)_2($**1**$)]$ and $[Ag_2($**1**$)_2](PF_6)_2$.

Crystals of $[PdBr_2($**1**$)]\cdot 2\,DMSO$ were grown from a DMSO solution of the complex. The X-ray diffraction analysis of $[PdBr_2($**1**$)]\cdot 2\,DMSO$ confirmed the conclusions drawn from the NMR and mass spectra. The palladium cation is coordinated outside of the cavity of the macrocyclic ligand by two carbene-carbon atoms in *cis*-fashion (Figure 1). Although the ligand itself is potentially tridentate, no coordination of the pyridine-nitrogen atom to the palladium atom was observed. The coordination geometry of the palladium center is slightly distorted square planar with values of 98.01(12)° for the C-Pd-C angle and 95.016(13)° for the Br-Pd-Br angle. While preventing the formation of a pincer complex, the long (butenyl or lutidinyl) spacer group between the carbene donors allows them to adopt an orientation that is almost perpendicular to the $PdBr_2C_2$ coordination plane. This geometrical feature has been observed previously for related complexes bearing *cis*-coordinated dicarbene or two mondentate carbene ligands.[17] It is, however, uncommon for dicarbene ligands with short spacers between the carbene donors. In this instance, a more coplanar orientation of the carbene donor with the coordination plane of the metal center is normally observed.[9,17c] The Pd–C and

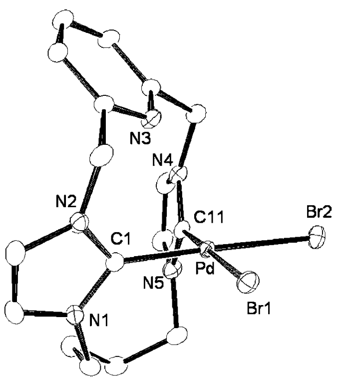


Figure 1. Molecular structure of $[PdBr_2($**1**$)]$ in $[PdBr_2($**1**$)]\cdot 2\,DMSO$. Selected bond lengths [Å] and angles [°]: Pd–Br1 2.5112(4), Pd–Br2 2.4969(4) Pd–C1 2.011(3), Pd–C11 2.006(3); Br1-Pd-Br2 95.016(13), Br1-Pd-C1 84.07(8), Br1-Pd-C11 176.86(8), Br2-Pd-C1 178.16(8), Br2-Pd-C11 82.84(8), C1-Pd-C11 98.01(12).

Pd–Br bond lengths in [$PdBr_2$(**1**)] fall in the range previously reported for related complexes of the type *cis*-[$PdBr_2$(NHC)$_2$].[3a,c]

For the preparation of the silver complex with ligand **1**, the bromo anions in H_2-**1**(Br)$_2$ were exchanged for hexafluorophosphate anions. This gave H_2-**1**(PF_6)$_2$, a species that is freely soluble in acetonitrile but insoluble in water. Dimidazolium salt H_2-**1**(PF_6)$_2$ was allowed to react with an equimolar amount of Ag_2O in acetonitrile as previously described.[14] Given the similarities between ligand **1** and the ligand used to generate complex **C** (Scheme 1), the formation of a mononuclear, linear dicarbene silver complex could be expected. The reaction led, however, to dinuclear carbene complexes of type [Ag_2(**1**)$_2$](PF_6)$_2$ in a yield of about 89 % (Scheme 3, bottom). Owing to the exocyclic nature of the coordination, two isomeric complexes can form. In fact, the dinuclear complex [Ag_2(**1**)$_2$](PF_6)$_2$ was isolated as a 2:1 mixture of *syn*-[Ag_2(**1**)$_2$](PF_6)$_2$ (major component) and *anti*-[Ag_2(**1**)$_2$](PF_6)$_2$ (minor component) isomers. The complexes proved stable towards light and under aerobic conditions. The NMR spectra of this mixture revealed a set of signals for each isomer (see the Supporting Information). The assignment of the signal sets to a particular isomer was made on the basis of ROESY (rotating frame nuclear overhauser effect spectroscopy) NMR experiments.

The major isomer was crystallized as *syn*-[Ag_2(**1**)$_2$](PF_6)$_2$·4 CH_3CN by diffusion of diethyl ether into an acetonitrile solution of the isomer mixture [Ag_2(**1**)$_2$](PF_6)$_2$. The X-ray diffraction analysis confirmed the formation of the dinuclear complex (Figure 2), revealing a molecular structure quite different from that of the palladium complex [$PdBr_2$(**1**)] described above.

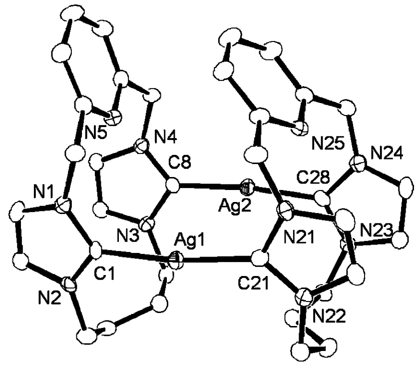


Figure 2. Molecular structure of *syn*-[Ag_2(**1**)$_2$]$^{2+}$ in *syn*-[Ag_2(**1**)$_2$](PF_6)$_2$·4MeCN. Selected bond lengths [Å] and angles [°]: Ag1–C1 2.095(11), Ag1–C21 2.084(11), Ag2–C8 2.082(12), Ag2–C28 2.073(12), Ag1···Ag 2.4.6636(7); C1-Ag1-C21 171.7(3), C8-Ag2-C28 172.5(4).

Specifically, a metal-linked dimeric species was seen like the ones obtained from related cyclophane-like di-NHC ligands.[5–7] Both silver atoms in cation [Ag_2(**1**)$_2$]$^{2+}$ are coordinated by two carbene donors from two different ligands **1**. To achieve this type of coordination the carbene donors must rotate out of the plane of the macrocycle. As a result of this rotation, the carbene donors can coordinate to just one square-planar metal center in *cis*-configuration as seen for [$PdBr_2$(**1**)]. However, they cannot accommodate in an intramolecular fashion a metal center requiring linear coordination, such as silver(I). Consequently, each of the carbene donors of one ligand **1** coordinates to a different silver(I) cation. Each silver cation then completes its linear coordination environment by binding to a carbene donor from a second ligand **1**. This leads to a dinuclear complex in which the two silver cations are sandwiched in between two dicarbene ligands.

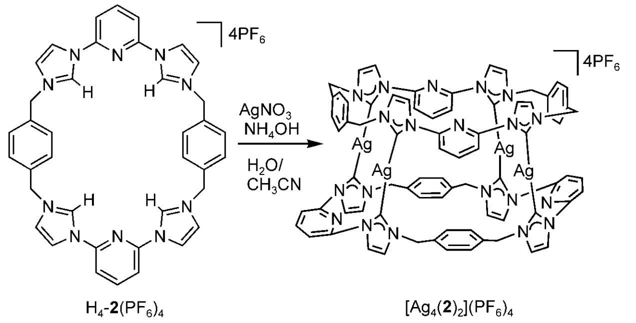
Others[5–7] and we have previously observed this kind of inter-receptor binding mode in the case of a cyclic polycarbene ligand. In one previous example, a derivative of the tetraimidazolium–dilutidine macrocycle used for the preparation of complex **D**, namely the hexaimidazolium–trilutidine hexacation, was found to react with three equivalents of Ag_2O. This leads to the formation of a similar sandwich compound composed of an Ag_6 hexagon between two hexa(NHC) ligands.[15] In this complex, and contrary to the situation in **D**, the NHC donors are also rotated out of the plane of the macrocycle. Presumably, this permits formation of the sandwich complex by the stabilization of six almost linear $C_{carbene}$-Ag-$C_{carbene}$ bonds involving NHC donors from two different hexacarbene ligands. Very recently, a macrocyclic trisimidazolium salt has also been shown to form a sandwich compound featuring three silver(I) cations sandwiched between two tricarbene ligands.[18]

The coordination chemistry of cyclic polycarbene ligands of type **1** is apparently determined by the coordination chemistry of the metal ion. With complexes [$PdBr_2$(**1**)] and [Ag_2(**1**)$_2$](PF_6)$_2$ we observed a mononuclear complex with coordination of the dicarbene ligand **1** in *cis*-fashion to a square-planar metal center and the formation of a dinuclear sandwich complex featuring two ligands **1** and two linearly coordinated metal centers, respectively. From this observation it appears that cyclic polycarbenes are suitable ligands for the generation of metallosupramolecular structures provided that the proper metal ions are selected. In fact, some metallosupramolecular structures built up from polycarbene ligands, namely a molecular rectangle[19] and cylindrical structures featuring two tri- or tetracarbene ligands and linearly di(NHC) coordinated silver(I) or gold(I) ions[20] have been described recently.

To investigate further the suitability of cyclic polycarbene ligands for the synthesis of metallosupramolecular structures based on M–$C_{carbene}$ bonds, we have studied the coordination chemistry of a cyclic tetraimidazolium ligand after deprotonation to the tetracarbene. Compound H_4-**2**(PF_6)$_4$ was initially developed as a molecular box that forms an anion-induced supramolecular necklace,[21] but also appears as a suitable precursor for the preparation of a cyclic tetracarbene ligand.

Reaction of H_4-**2**(PF_6)$_4$ with silver nitrate in the presence of NH_4OH in a water/acetonitrile solvent mixture gave the metallosupramolecular complex [Ag_4(**2**)$_2$](PF_6)$_4$. This species was formed in 60 % yield as the main reaction product.

(Scheme 4). The complex is stable towards light and can be handled under aerobic conditions. As above, initial evidence for formation of the carbene complex $[Ag_4(\mathbf{2})_2](PF_6)_4$ came from ^{1}H NMR spectroscopic analysis. Only one set of signals was detected, as would be expected given the proposed formation of a highly symmetrical compound free of isomeric by-products. The resonance for the imidazolium protons of H_4-$\mathbf{2}(PF_6)_4$ ($\delta = 9.53$ ppm) is no longer detectable after complex formation as befits the formation of a C–Ag bond. In addition, the methylene proton signals, originally a singlet in the starting tetraimidazolium salt, were observed as an AA' spin system (doublet for each proton), leading us to conclude that these protons are diastereotopic in the carbene complex.



Scheme 4. Preparation of the tetranuclear cylinder-like cage complex $[Ag_4(\mathbf{2})_2](PF_6)_4$.

An X-ray diffraction analysis with single crystals of $[Ag_4(\mathbf{2})_2](PF_6)_4{\cdot}5\,DMF{\cdot}H_2O$ revealed a boxlike structure that was fully consistent with the conclusions drawn from the NMR spectroscopic analysis (Figure 3). Specifically, this structure revealed that four silver cations are coordinated by two NHC donor groups from to different tetracarbene ligands. The net result is a well-defined, cagelike species that consists of two macrocyclic NHC ligands bridged by four silver atoms.

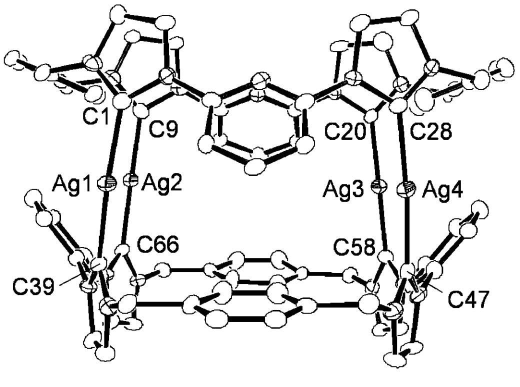


Figure 3. Molecular structure of the cation $[Ag_4(\mathbf{2})_2]^{4+}$ in $[Ag_4(\mathbf{2})_2](PF_6)_4{\cdot}5\,C_3H_6O{\cdot}H_2O$ viewed parallel to the Ag_4 rectangle. Solvent molecules and cations have been omitted for clarity. Selected bond lengths [Å] and angles [°]: range Ag–C 2.084(5)–2.103(6), range C-Ag-C 175.05(14)–176.45(15).

Tetracarbene macrocycle **2** thus exists in a totally different form than it does either as the hexafluorophosphate salt, H_4-$\mathbf{2}(PF_6)_4$, wherein bent geometries are seen, or when it is complexed to an interpenetrated monoterphthalate anion.[21] This observation underscores the versatility of this relatively large receptor system and the power of metal carbene chemistry in terms of controlling the structure in the case of appropriately chosen ligands.

The present work serves to highlight further the utility of imidazolium macrocycles, not just as receptors for anions, but also as precursors for the formation of poly(NHC) ligands and their metal complexes. In the particular case of ligands **1** and **2** that are the subject of this report, boxlike dimeric structures are formed in the case of the linear di or tetrasilver complexes, whereas a monomeric species is formed in the case of **1** and Pd^{II}. While both polynuclear and mononuclear complexes have been previously observed with cyclic polycarbene ligands depending on the metal ion used (linear Ag^I or square planar Pd^{II}), we described here both types of complexes obtained from the same ligand. In no cases are purely endocyclic or within-plane macrocyclic metal complexes observed. On the other hand, the specifics of the structure as well as the conformation of the ligand in the complexes are seen to be dependent on the choice of metal. Such findings lead us to propose that the use of carbene coordination could be employed to control the formation of a variety of novel structures that might be difficult to access by alternative approaches.

Experimental Section

Experimental details (synthesis protocols, compound characterization data, crystallographic data, and CCDC numbers are given in the Supporting Information.

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