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Homoleptic Crown N-Heterocyclic Carbene Complexes**

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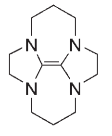
Since the first crystal structure, reported by Arduengo et al. in 1991,[1] N-heterocyclic carbenes (NHCs) and their metal complexes have become the subject of intensive study.[2] Their relative ease of synthesis from readily accessible precursors, together with their favorable donor properties, have made them the ligand of choice in many applications. Mono- and bidentate NHC ligands are common, and hybrid NHC ligands with pyridine, oxazoline, phosphine, and other pendant donors are also known.[3]

Our interest is in generating a convenient and easily adapted route to metal complexes in which the metals are complexed exclusively by macrocyclic NHC ligands; such complexes are likely to have unique reactivity profiles that could be attractive in synthesis and in coordination chemistry and are likely to have interesting electrochemical properties compared with known types of complexes.

Surprisingly, to date only a small handful of metal complexes with cyclic poly-NHC ligands are known. The majority of such complexes contain cyclic dicarbenes, generated either from activated alkenes such as **1**[4] or from bisimidazolium cyclophanes **2**.[5] However, in these species the ligands coordinate to *cis* coordination sites on the metal center and act more like classical bidentate ligands rather than encapsulating the metal in the manner typically observed with macrocyclic ligands. Only one example (**3**) of a tetradentate macrocyclic ligand with two imidazolium-derived NHC donors containing a metal ion within the macrocyclic cavity has been reported.[6] Very recently, the first example of a homoleptic platinum(II) complex of a tetrakis NHC macrocycle has been obtained (**4**). This species was synthesized not from an imidazolium precursor but rather by an elegant, multistep metal-templated cyclization of 2-azidophenylisocyanide.[7] It is, however, unlikely that this procedure will be widely adopted by coordination chemists in its present form, since the use of platinum salts on a multigram scale will be prohibitively expensive. In addition, removal of platinum from the macrocycle to yield free carbene ligand is likely to be problematic.



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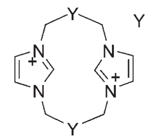

Y = o-C_6H_4
m-C_6H_4
2,6-pyridyl

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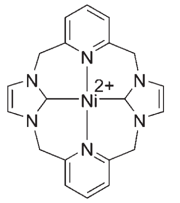

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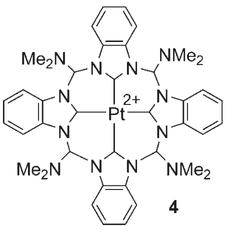

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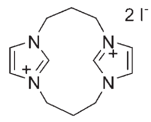
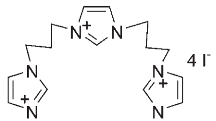


$(\mathbf{5}H_2)^{2+}(I^-)_2$



$(\mathbf{6}H_4)^{4+}(I^-)_4$

Our approach is different, involving the synthesis of a preformed macrocycle bearing multiple imidazolium salts as precursors of NHCs. Appropriate choice of macrocycle should allow adaptive binding to different metals.

The most easily accessible imidazolium macrocycle is the bis-imidazolium salt $(\mathbf{5}H_2)^{2+}(I^-)_2$, easily formed from imidazole and 1,3-diiodopropane;[8a] however, we have adapted the synthesis to afford its tetrameric homologue $(\mathbf{6}H_4)^{4+}(I^-)_4$ in multigram quantities (Scheme 1).[14] An alternative and more lengthy route to $(\mathbf{6}H_4)^{4+}(PF_6^-)_4$ has been developed independently by Beer and co-workers,[8b] but for different purposes. The ^1H and ^{13}C NMR spectra of the tetramer $(\mathbf{6}H_4)^{4+}$ are very simple, thus attesting to the high degree of symmetry present; the formulation is supported by mass spectrometry. The parent ion is observed, together with ions corresponding to the association of one, two, and three iodide anions. We have confirmed the formulation by X-ray crystallography,[15] which indicates a tetracationic species with four iodide counterions, one of which interacts strongly with the cation through both imidazolium and alkyl C–H···I contacts (Figure 1). The potential of this salt as a precursor to a range of previously inaccessible macrocyclic NHC ligand complexes was immediately recognized, and we have proceeded to investigate this aspect of their chemistry. The widespread use of silver carbene complexes as ligand transfer agents[9] prompted us to attempt the synthesis of a silver complex from our cyclic proligand. Thus, reaction of $(\mathbf{6}H_4)^{4+}(I^-)_4$ with Ag_2O in DMSO in the presence of sodium acetate results in the formation of a white solid that is sparingly soluble in polar solvents.[14] Mass spectrometry suggests the presence of two silver cations per ligand, while once more the NMR spectra are very simple, thus indicating the equivalence of the four imidazole groups. X-ray crystallography (Figure 2)[15] confirms that two silver(I) cations are complexed by a single ligand, each having linear two-

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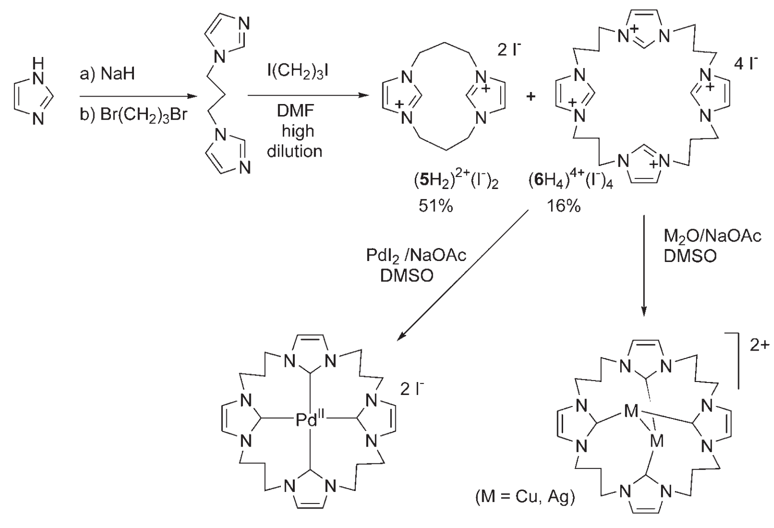
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Synthesis of cyclic imidazolium salts and crown carbene complexes.

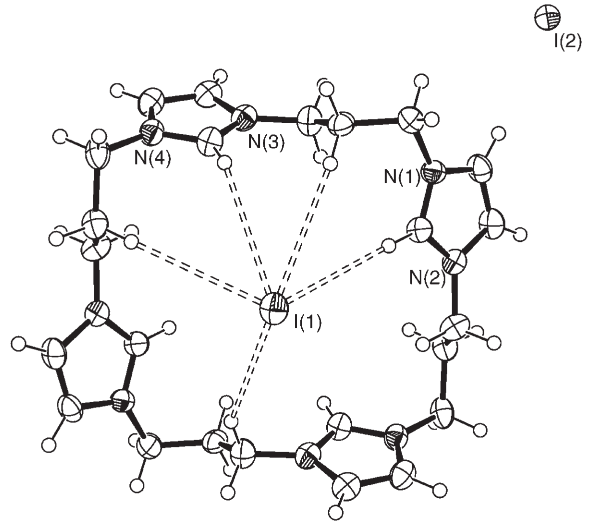


Figure 1. X-ray crystal structure of the macrocyclic tetraimidazolium salt $(\mathbf{6}H_4)^{4+}(I^-)_4$ showing C–H···I distances of less than 3.4 Å. Thermal ellipsoids are drawn at the 50% level.

coordinate geometry. The silver centers are coordinated to alternate NHC donors in the macrocycle, which results in a mutually orthogonal orientation of the two L-M-L units (C-Ag-Ag-C torsion angles, e.g. C(1)-Ag(1)-Ag(2)-C(7), lie in the range 88.8–91.5°). The flexibility of the ligand allows the incorporation of two metal ions into the macrocycle cavity and apparently also constrains them in close proximity; the ligand geometry dictates that a Ag–Ag interaction (d(Ag–Ag) = 2.8349(6) Å) is present. This distance is somewhat shorter than the average Ag–Ag separation (3.056 Å) extracted from the Cambridge Crystallographic Database.[10] While linear $\{Ag^I(NHC)_2\}$ units are reasonably common,[11] in the cases where these form Ag–Ag interactions, they invariably bond to AgX_2 units (X = halide, CN). Our silver complex is the first compound to exhibit strong argentophilic interactions between two $\{Ag(NHC)_2\}$ units. The extended structure in the crystal is also of interest, since the cations assemble into infinite, one-dimensional chains via intermolecular contacts between silver ions and the carbene carbon atoms in the neighboring molecules. It is tempting to describe these assemblies as insulated molecular wires with chains of silver ions sheathed by the macrocyclic ligands. In this case, the association is relatively weak, but the generation of a more robust linkage between the units could be envisaged, thus leading to 1D coordination polymers.

Finally, the adventitious $[Ag_4I_8]^{4-}$ anion is a fourth, previously unreported, structural isomer of this anion. The three crystallographically characterized structures in the literature include a linear diiodo-bridged species $[I\{Ag(\mu_2\text{-}I)_2\}_3AgI]^{4-}$, (**7**),[12a] a $\{Ag_4I_4\}$ cubane with an additional terminal iodide on each silver center (**8**),[12b] and a structure based on a silver rhombus with terminal,

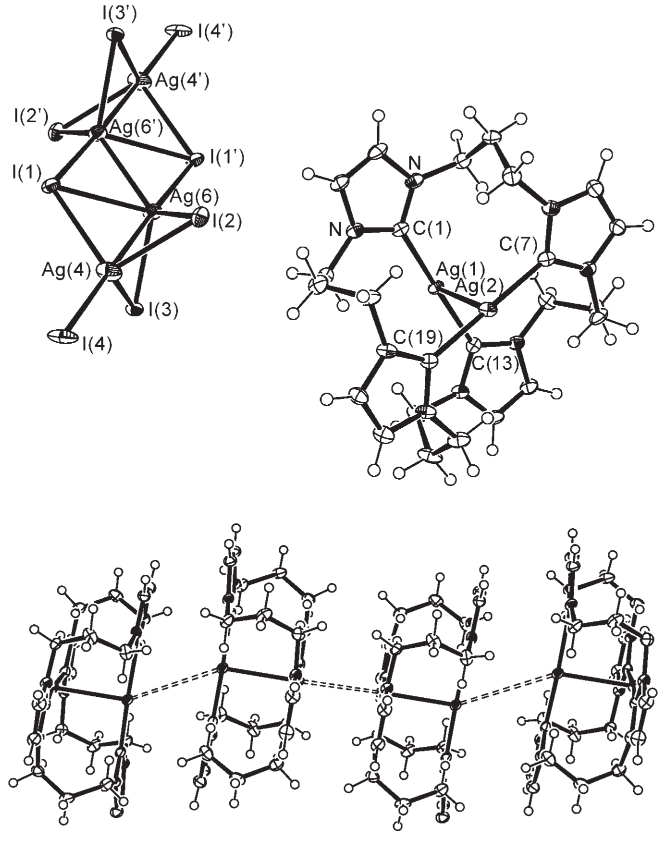
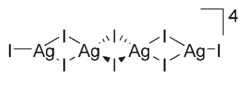


Figure 2. The X-ray crystal structure of the $[Ag_2(\mathbf{6})]^{2+}$ cation and its counteranion $[Ag_4I_8]^{4-}$ (top), and the long-range association of the $[Ag_2(\mathbf{6})]^{2+}$ cations in $[Ag_2(\mathbf{6})]_2[Ag_4I_8]$ (bottom). Thermal ellipsoids are drawn at the 50% probability level.

di- and tri-bridged iodide ions (**9**).[12c] In our complex, a planar $\{Ag_4I_4\}$ raft is doubly bridged along the external Ag–Ag bonds by iodide ions (**10**). It is clear that these structures lie on a shallow potential energy surface, with the synthesis and



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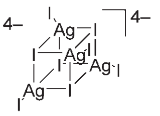

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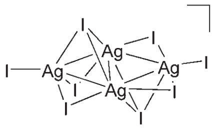

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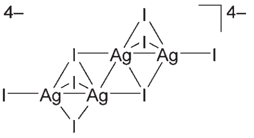

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crystallization conditions strongly influencing the structural outcome.

The copper complex $[Cu_2(\mathbf{6})]^{2+}$ is prepared similarly to its silver analogue by reaction of Cu_2O with the cyclic imidazolium salt in DMSO in the presence of acetate ions;[14] it crystallizes as the simple diiodide salt. The cation is isostructural with the silver analogue (Figure 3),[15]and once more the metal–metal distance (2.553(2) Å) is substantially shorter than the mean value (2.751(4) Å) determined from the Cambridge Crystallographic Database.[10] Short, unbridged copper–copper interactions in NHC complexes are unprecedented. In the copper complex, there is no association of cations to form coordination polymers.

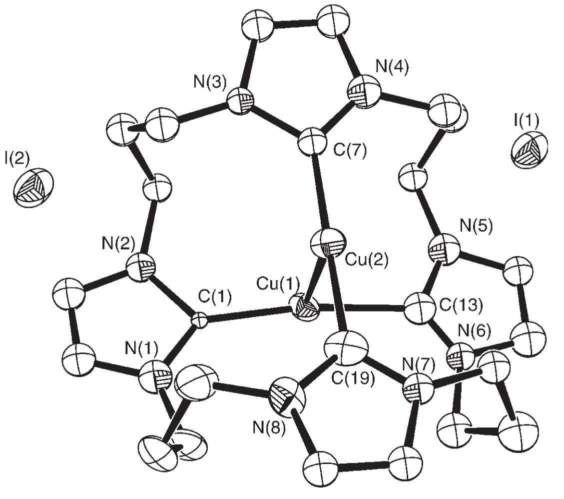

Figure 3. The X-ray crystal structure of $[Cu_2(\mathbf{6})]I_2$ with thermal ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

Treatment of $(\mathbf{6}H_4)^{4+}(I^-)_4$ with PdI_2 and NaOAc in DMSO solution[14] results in the formation of a stable white solid, which once more has spectroscopic properties consistent with high symmetry. X-ray crystallography[15] indicates that this complex has the formulation $[Pd(\mathbf{6})]I_2$, and that the metal ion is tetracoordinated by the macrocyclic ligand in a square-planar geometry (Figure 4). The complex broadly resembles a palladium complex bearing four monodentate NHCs reported by Fehlhammer et al.[13]

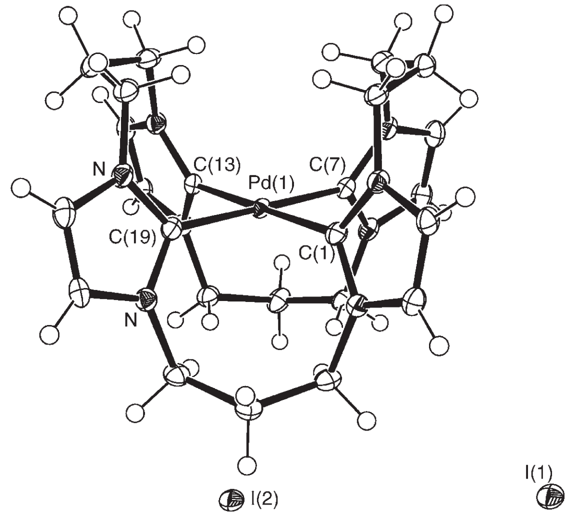

Figure 4. The X-ray crystal structure of $[Pd(\mathbf{6})]I_2$ with thermal ellipsoids drawn at the 50% probability level.

The contrast between the structures of the copper and silver complexes and that of the palladium complex is marked. Two very different ligand conformations are observed. In the Group 11 complexes, the $\{M(NHC)_2\}$ units form mutually parallel planes, which are linked by the propylene spacers, thus resulting in a lanternlike structure that is remarkably compact and can readily stack end-to-end in the solid state. By contrast, in the palladium complex the ligand adopts a conformation topologically equivalent to the seams on a tennis ball. The consequence of this arrangement is that the vacant coordination sites at the palladium center are located in protected pockets formed by the propylene linkers between the heterocycles. It will be of interest to explore the extent to which small ligands (substrates) can infiltrate these pockets.

The conjunction of NHC and macrocyclic ligand types generates an important new class of ligands. This first foray into their chemistry with transition metals indicates a remarkable flexibility of coordination mode, with the ability to form both mono- and dinuclear complexes, presaging a rich and varied coordination chemistry from this and related systems.

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[14] Complete experimental details, a summary of the crystallographic data, and spectroscopic characterization are available in the Supporting Information.

[15] CCDC-644573 (Ag complex), CCDC-644574 (tetraimidazolium salt), CCDC-644575 (Cu complex) and CCDC-644576 (Pd complex) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.