A new chiral N-heterocyclic carbene silver(I) cylinder: synthesis, crystal structure and catalytic properties†

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Received 12th January 2010, Accepted 4th May 2010
First published as an Advance Article on the web 20th May 2010
DOI: 10.1039/c000793e

A new chiral cyclic trimidazoline salt and its chiral N-heterocyclic carbene trisilver(I) cylinder-like cage was prepared via self-assembly, with size-selective catalytic performance for the cyanosilylation of several Schiff-base compounds.

The coordination paradigm pioneered by Lehn and Sauvage,1 and as developed in the groups of Stang, Fujita, Raymond and others for closed systems, has allowed the synthesis of an enormous number and variety of discrete, isolable structures featuring well-defined nanoscale cavities.2 These capsules are invariably comprised of many metal–ligand components, which often self-assemble rapidly and in high yield into a single gigantic species—sometimes even protein-size. Like natural enzyme pockets,3 such nanovessels provide a very specific environment in terms of size, shape, and chemical properties around a bound guest, which not only dictates the selectivity of guest binding, but can also be exploited to control the structure or the chemical reactivity of encapsulated species.4 Accordingly, the incorporation of chiral organometallic precursors as building blocks for the creation of optical active metalorganic polyhedrons will lead to stereochemical selective catalytic performance within.5

On the other hand, the field of metal complexes of N-heterocyclic carbene (NHC) has grown explosively in the last two decades and numerous studies have been reported owing to their applications in homogeneous and asymmetric catalyses.6 For example, Grubbs’ second generation catalyst is well known to display an incredible application in olefin metathesis, which is a powerful tool in organic synthesis and polymer chemistry.7 Au(i), Rh(i), Ir(i), Cu(i), Pd(ii), Ni(ii) complexes of NHC as high-efficiency catalysts have also been reported.8,9 Silver NHC complexes have played an important role in the development of metal-carbene systems.8 But few reports have explored the applications of silver NHCs in asymmetric catalysis.10

As a continuation of our research work on the imidazoline-based robust crypt and metal-tunable nanocages,1 we report here the synthesis, crystal structure and catalytic properties of a novel chiral N-heterocyclic carbene silver(I) cage Ag–CNHC assembled from a newly positively charged chiral macrocycle trimidazoline salt (CNHC)(BF4)3 (Scheme 1).† The bowl-shaped chiral CNHC was synthesized from the chiral reactant R,R,1,2-diaminohexane.11 H NMR spectrum of CNHC exhibited only one set of signals corresponding to imidazoline protons at about 9.15 ppm,12 indicating the presence of only one configuration of the three imidazoline groups. API-MS spectrum showed intense peaks at 227.4, 384.4 and 855.4, corresponding to the [CNHC]+, [CNHC(BF4)]2+ and [CNHC(BF4)2]2+ species, respectively. X-ray structure analysis had unequivocally confirmed the existence of a tricationic imidazolidinium. The macrocycle trimidazoline salt crystallized in a chiral P63 space group. One-third of the imidazoline cation, one BF4− anion, as well as one-third of a water molecule and one third of an acetonitrile molecule were found in an asymmetry unit. The CNHC cation had a crystallographic C3 axis across the centre of the cyclic cation. The three cationic imidazoline units were symmetrically related and consequently all of these optical active carbon atoms were present in a R-configuration. An imidazoline N–C bond length of 1.31 Å on average and N–C–N angle of 113.5(4)° were consistent with those in related compounds.13 The upper-rim of the CNHC cation was composed of three active imidazoline protons, whereas the lower-rim of the cage was composed by three cyclohexanes. The diameters of the upper and bottom rims were 0.74 nm and 0.62 nm, respectively.

Further reaction of the chiral macrocycle trimidazoline salt with 3 equivalents of Ag2O in DMSO solution afforded the complex Ag3(CNHC)2(BF4) in a good yield.1 H NMR spectrum of the complex revealed the absence of the imidazolidine protons in the CNHC compound during the reaction. Single crystal structural analysis revealed the silver N-heterocyclic carbene cylinder consisted of a trisilver(I) chiral cationic cage. The cylinder also crystallized in a chiral P63 space group. An asymmetry unit was comprised of one-third of the cationic cage, one BF4− anion, one lattice water molecule and two-third of lattice dichloromethane molecules. The two CNHC N-heterocyclic carbene ligands with the same geometrical

![Scheme 1](image-url)

**Scheme 1** Synthetic procedure of the chiral macrocycle trimidazoline salt CHNC and its silver cage Ag–CNHC.
conformation were joined together by three silver atoms to consolidate the cage, and the \([\text{Ag}_3(\text{CNHC})_3]^{3+}\) cation positioned at a crystallographic \(C\) axis with the centres of the two cyclic tricarbene ligands both positioned on the same axis. Each silver atom coordinated to two carbene donors from two ligands with the Ag–C distances ranging from 2.078(6) to 2.118(7) Å, quite close to those in several related complexes.\(^{14}\) The C–Ag–C bond angle of 176.0(2) suggested the three atoms were approximately positioned in a line and the cage thus was described as a cylinder. The N–C bond length of the carbene group was 1.39 Å on average, which was obviously longer than those in its imidazoline form. Since the two chiral carbene group was 1.39 Å on average, which was obviously longer than those in its imidazoline form. Since the two chiral 

The three silver atoms are positioned in the three vertexes of an equilateral triangle with a Ag···Ag separation of 8.26 Å. Whereas the two ligands located above or beneath of the triangle plane. The cylinder had a diameter of about 1 nm (9.5 Å) and a height calculated from the two parallel to the triangle plane. The cylinder had a diameter of about 1 nm (9.5 Å) and a height calculated from the two 

Molecular structure of the chiral Ag_3(CNHC)_2 cation showing the cylinder geometry. The anions, solvent molecules and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)–C(1) 2.078(6), Ag(1)–C(16) 2.118(7), N(1)–C(1) 1.392(6), N(2)–C(1) 1.396(6), N(3)–C(16) 1.399(7), N(4)–C(16) 1.395(7) and C(1)–Ag(1)–C(16) 176.40(2).

Fig. 1

ESI-MS spectra of the silver cage exhibited two intense peaks at \(m/z = 884.24\) and 560.51 with the isotopic distribution patterns separated by 0.50 ± 0.01 and 0.33 ± 0.01 Da, demonstrating the presence of positive charged species \([\text{Ag}_3(\text{CNHC})_2\text{BF}_4]^{2+}\) and \([\text{Ag}_3(\text{CNHC})_3]^{3+}\), respectively in solution (Fig. 2). While in its MALDI-ToF spectrum, the peak at \(m/z = 1855.59\) was assignable to the molecular ion \([\text{Ag}_3(\text{CNHC})_2\text{BF}_4]^{2+}\) (Fig. S2). Circular dichroism (CD) studies of the silver cage in CH₂Cl₂ solution showed bands at 229 and 270 nm with positive Cotton effects and one band at 242 nm with one negative Cotton effect, indicating the homochirality of the carbene moieties in the \([\text{Ag}_3(\text{CNHC})_3]^{3+}\) cation even in solution. These results suggested the possible application of the silver complex in homogeneous enantioselective catalysis.

To further investigate the enantioselective catalysis properties of the chiral cage, cyanosilylation of imines, which is one of the most efficient and general methods for producing optically active \(\alpha\)-amino nitriles derivatives, including \(\alpha\)-amino alcohols and direct precursors of \(\alpha\)-amino acids derivatives, was carried out.\(^{19}\) A variety of chirally modified catalysts have been utilized for the asymmetric transformation, and some of them have achieved high enantioselectivity. However, the development of a suitable chiral catalyst for this reaction still remain a great challenge.\(^{17}\) As shown in Table 1, the loading of only 2% mol ratio of \(\text{Ag}_3(\text{CNHC})_2(\text{BF}_4)_3\) (0.01 mmol) lead to the almost complete conversion of N-benzylidenenbenzamine and N,N-dimethyl-4-((phenylimino)methyl)benzeneamine at room temperature, while the blank experiments had average yields lower than 15%. The control reactions by using the \(\text{CNHC}\) (0.01 mol) as the catalyst under the same experimental conditions gave yields lower than 50%. The significant enhancement of the yield prompting by the silver cage compared with the \(\text{CNHC}\) demonstrated that the silver center had additional catalytic driving forces. Interestingly, only traces of the product were observed when the bulky Schiff-base substrates with larger sizes were used. The lower catalytic activity in entries 4 and 5 is likely due to that the size of the opening within the silver cylinder is too small for N-benzylidenenaphthalen-1-amine 1-naphthaldehyde or N-(naphthalen-1-ylmethylene)-benzeneamine to pass through and access the catalytic sites. The size-selective performance suggested that the reaction occurred within cavities of the silver cylinder.

It should also be noted that the products of phenylamino acetoneitrile derivatives had an enantioselectivity ee lower than 30%, which is not larger than those in the case of the \(\text{CNHC}\) to prompt the relative reactions. It seems that the enantioselectivity of the cyano-silylation reaction was mainly controlled by the chirality of the \(\text{CNHC}\) backbone. The absence of additional enantioselectivity of the cylinder-like silver complex was possibly attributed to that the linear coordination mode of
the silver centers did not provide enough steric hindrance to constrain the spatial of products.

In summary, we have developed a chiral N-heterocyclic carbene silver(i) cage Ag-CNHC assembled from a new positively charged chiral macrocycle trimidazolone salt (CNHC). The catalytic properties based on cyanosilylation of imines reactions demonstrated the size-selectivity catalytic performance, suggesting the possible applications of this kind of carbene silver(i) cage in chiral homogenous catalyse. Work is currently in progress on further investigation of the silver and other metal-CNHC complexes, and on the choosing of suitable auxiliary coordination ligands to improve the efficiency and enantioselectivity of several important catalytic reactions.

This work was supported by the National Natural Science Foundation of China.

Notes and references

Cyanosilylation of imines derivatives with Me3SiCN catalyzed by Ag–CNHC

| Reactions conditions: To a mixture of Me3SiCN (1.2 mmol) and imines derivatives (0.5 mmol) was added Ag–CNHC (0.01 mmol) and the resulting mixture was stirred at rt for seven days. The conversions were determined by 1H NMR, based on starting materials.

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<th>Yield (%)</th>
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<tr>
<td>1</td>
<td>PhCH=NPh</td>
<td>98</td>
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<tr>
<td>2</td>
<td>p-(CH3)2N-PhCH=NPh</td>
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<td>3</td>
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<tr>
<td>5</td>
<td>1-Np=CH=NPh</td>
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"Reactions conditions: To a mixture of Me3SiCN (1.2 mmol) and imines derivatives (0.5 mmol) was added Ag–CNHC (0.01 mmol) and the resulting mixture was stirred at rt for seven days. The conversions were determined by 1H NMR, based on starting materials.


