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

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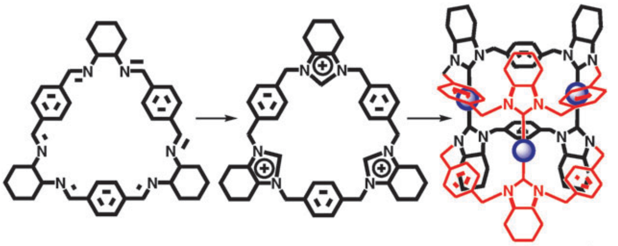
A new chiral cyclic triimidazoline salt and its chiral N-heterocyclic carbene trisilver(I) cylinder-like cage was prepared *via* self-assembly, with size-selective catalytic performance for the cyanosilylation of several Schiff-base compounds.

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 metallorganic polyhedrons will lead to stereochemical selective catalytic performance within.[5]

On the other hand, the field of metal complexes of N-heterocyclic carbenes (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.[6b,8] Silver NHC complexes have played an important role in the development of metal-carbene systems.[9] 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,[11] 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 new positively charged chiral macrocycle triimidazoline salt (**CNHC**)(BF_4)$_3$ (Scheme 1).‡ The bowl-shaped chiral **CNHC** was synthesized from the chiral reactant *R*,*R*-1,2-diamino hexane. ^{1}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**]$^{3+}$, [(**CNHC**)(BF_4)]$^{2+}$ and [(**CNHC**)(BF_4)$_2$]$^+$ species, respectively. X-ray structure analysis had unequivocally confirmed the existence of a tricationic imidazolidinium. The macrocycle triimidazoline salt crystallized in a chiral $P6_3$ space group. One-third of the imidazoline cation, one BF_4^- 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 C_3 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 by 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 triimidazoline salt with 3 equivalents of Ag_2O in DMSO solution afforded the complex Ag_3(**CNHC**)$_2$(BF_4)$_3$ 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 $P6_3$ space group. An asymmetry unit was comprised of one-third of the cationic cage, one BF_4^- anion, one lattice water molecule and two-third of lattice dichloromethane molecules. The two **CNHC** *N*-heterocyclic carbene ligands with the same geometrical



1 **CNHC** **Ag_3(CNHC)$_2$**

Scheme 1 Synthetic procedure of the chiral macrocycle triimidazoline salt **CHNC** and its silver cage **Ag–CNHC**.

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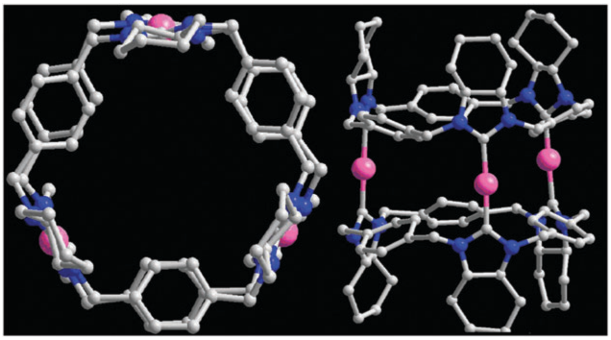

Fig. 1 Molecular structure of the chiral Ag_3(**CNHC**)$_2$ cation showing the cylinder geometry. The anions, solvent molecules and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)–C(1) 2.078(6), Ag(1)–C(16) 2.118(7), N(1)–C(1) 1.392(6), N(2)–C(1) 1.396(6), N(3)–C(16)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

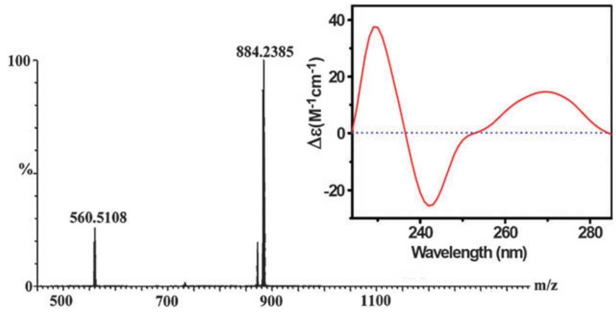

Fig. 2 ESI-MS and CD spectra of the Ag_3(**CNHC**)$_2$(BF_4)$_3$ complex in CH_2Cl_2 solution.

conformation were joined together by three silver atoms to consolidate the cage, and the [Ag_3(**CNHC**)$_2$]$^{3+}$ cation positioned at a crystallographic C_3 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 *N*-heterocyclic carbene moieties coordinated to one silver ion had the same chirality, and these optical active carbon atoms were *R*-configurations, accordingly, all the optical carbon atoms in the cylinder were present in a homochiral fashion (Fig. 1).

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 with the benzene rings in each ligand were almost parallel to the triangle plane. The cylinder had a diameter of about 1 nm (9.5 Å) and a height calculated from the two cyclohexanes linked by one silver atom of about 13.4 Å. The inner volume of the cylinder was estimated to be about 450 Å^3, which was large enough for encapsulation of small substrates. One of the BF_4^- ions was encapsulated in the center of the cylinder through the weak F···Ag interactions (the separation of 3.49 Å). Consequently, these coordinatively unsaturated silver atoms were well positioned within the inner surface of the cylinder, which could interact with guest molecules that enter the cavity of the cylinder. These silver ions might serve as potential weak Lewis acids, thus the trisilver cylinder had the potential to function as active homogeneous catalyst for acid promoted reactions.[15]

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 {[Ag_3(**CNHC**)$_2$]BF_4}$^{2+}$ and [Ag_3(**CNHC**)$_2$]$^{3+}$, respectively in solution (Fig. 2). While in its MALDI-Tof spectrum, the peak at m/z = 1855.59 was assignable to the molecular ion {[Ag_3(CNHC)$_2$](BF_4)$_2$}$^+$ (Fig. S2).† Circular dichroism (CD) studies of the silver cage in CH_2Cl_2 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 [Ag_3(**CNHC**)$_2$]$^{3+}$ 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 α-amino nitriles derivatives, including α-amino alcohols and direct precursors of α-amino acids derivatives, was carried out.[16] 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 Ag_3(**CNHC**)$_2$(BF_4)$_3$ (0.01 mmol) lead to the almost complete conversion of N-benzylidenebenzenamine and N,N-dimethyl-4-((phenylimino)methyl)benzenamine at room temperature, while the blank experiments had average yields lower than 15%. The control reactions by using the **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 **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)-benzenamine 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 acetonitrile derivatives had an enantioselectivity *ee* lower than 30%, which is not larger than those in the case of the **CNHC** to prompt the relative reactions. It seems that the enantioselectivity of the cyano-silylation reaction was mainly controlled by the chirality of the **CNHC** backbone. The absence of additional enantioselectivity of the cylinder-like silver complex was possibly attributed to that the linear coordination mode of

Table 1 Cyanosilylation of imines derivatives with Me_3SiCN catalyzed by **Ag–CNHC**

	$Ar_1CH{=}NAr_2$	Yield(%)[a]	*ee* (%)
1	PhCH=NPh	98	10
2	*p*-$(CH_3)N$–PhCH=NPh	99	28
3	*p*-CH_3–PhN=CHPh	83	27
4	1-Np–NH=CHPh	<5	
5	1-Np–CH=NPh	<5	

[a] Reactions conditions: To a mixture of Me_3SiCN (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.

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 triimidazoline 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 homogeneous catalyses. 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.

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Notes and references

‡ Crystal data of $CNHC{\cdot}3BF_4{\cdot}CH_3CN{\cdot}H_2O$: $C_{47}H_{62}N_7OB_3F_{12}$, Mr = 1001.47, Hexagonal, space group $P6_3$, colorless block, $a = 17.009(1)$, $c = 11.895(1)$ Å, $V = 2980.5(2)$ Å^3, $Z = 2$, $Dc = 1.116$ g cm^{-3}, μ(Mo-Kα) = 0.093 mm^{-1}, $T = 298(2)$ K. 3428 unique reflections [$R_{int} = 0.0666$]. Final R_1 [with $I > 2\sigma(I)$] = 0.0784, wR_2 (all data) = 0.2399. CCDC number 761390. Crystal data of $Ag_3(CNHC)_2{\cdot}3BF4{\cdot}2CH_2Cl_2{\cdot}3H_2O$: $C_{92}H_{118}Ag_3B_3Cl_4$ $F_{12}N_{12}O_3$, $Mr = 2165.82$, Hexagonal, space group $P6_3$, colorless block, $a = 14.539(1)$, $c = 27.762(1)$, $V = 5082.3(3)$, $Z = 2$, $D_c = 1.415$ g cm^{-3}, μ(Mo-Kα) = 0.751 mm^{-1}, $T = 298(2)$ K. 5889 unique reflections [$R_{int} = 0.0702$]. Final R_1 [with $I > 2\sigma(I)$] = 0.0759, wR_2 (all data) = 0.2141, Flack parameter 0.32(7). CCDC number 761389. The structures were solved by direct methods and refined on F^2 using full matrix least-squares methods using SHELXTL version 5.1. Anisotropic thermal parameters were refined for non-hydrogen atoms within the main backbone of the molecules. Except the solvent molecules, hydrogen atoms were localized in their calculated positions and refined using a riding model. For the Ag complex, the adjacent atom distances in the cyclohexane rings, benzene rings and heterocyclic carbene rings were fixed to be the same, respectively. Several lattice molecules were refined disordered.

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