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Well-defined N-heterocyclic carbene silver halides of 1-cyclohexyl-3-arylmethylimidazolylidenes: synthesis, structure and catalysis in A³-reaction of aldehydes, amines and alkynes[†]

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Structurally well-defined N-heterocyclic carbene silver chlorides and bromides supported by 1-cyclohexyl-3-benzylimidazolylidene (CyBn-NHC) or 1-cyclohexyl-3-naphthalen-2ylmethylimidazolylidene (CyNaph-NHC) were synthesized by reaction of the corresponding imidazolium halides with silver(I) oxide while cationic bis(CyBn-NHC) silver nitrate was isolated under similar conditions using imidazolium iodide in the presence of sodium nitrate. Single-crystal X-ray diffraction revealed a dimeric structure through a nonpolar weak-hydrogen-bond supported Ag-Ag bond for 1-cyclohexyl-3-benzylimidazolylidene silver halides [(CyBn-NHC)AgX]₂ (X = Cl, 1; Br, 2) but a monomeric structure for N-heterocyclic carbene silver halides with the more sterically demanding 1-cyclohexyl-3-naphthalen-2-ylmethylimidazolylidene ligand (CyNaph-NHC)AgX (X = Cl, 4; Br, 5). Cationic biscarbene silver nitrate [(CyBn-NHC)₂Ag]⁺NO₃⁻ 3 assumed a *cis* orientation with respect to the two carbene ligands. The monomeric complexes (CyNaph-NHC)AgX 4 and 5 showed higher catalytic activity than the dimeric [(CyBn-NHC)AgX]₂ 1 and 2 as well as the cationic biscarbene silver nitrate 3 in the model three component reaction of 3-phenylpropionaldehyde, phenylacetylene and piperidine with chloride 4 performing best and giving product in almost quantitative yield within 2 h at 100 °C. An explanation for the structure-activity relationship in N-heterocyclic carbene silver halide catalyzed three component reaction is given based on a slightly modified mechanism from the one in literature.

Introduction

N-Heterocyclic carbene (NHC) silver complexes have attracted increasing interests due to their structural diversity, wide applications as carbene transfer reagent and their antimicrobial and anticancer properties¹ since Arduengo and co-workers² isolated the first NHC silver complex in 1993. However, the NHC silver complexes have found few applications in silver catalyzed organic transformations³ except for scattered examples, such as diboration of alkynes and alkenes,4 carbomagnesiation of terminal alkynes5 and reaction of aldehydes, amines and alkynes (A³).⁶ In fact, the features of structural diversity, especially the polynuclear or cluster structures, and good carbene transfer property of NHC silver complexes are undesirable in transition metal catalysis because the former could hamper identification of the true catalytic species while the later would lead to decomposition of the corresponding catalysts. Therefore, structurally well-defined stable NHC silver complexes, especially the single site ones, are highly required

to explore the catalytic chemistry of NHC silver complexes. However, even for the most common silver chloride, structurally characterized single site two coordinate NHC complexes (NHC)AgCl still remain rare, except for a handful of examples supported by very sterically demanding NHC ligands.^{1,7,8} Herein we report synthesis and structure of well-defined N-heterocyclic carbene silver halides, including single site two coordinate silver halides (NHC)AgX supported by readily available 1-cyclohexyl-3-arylmethyl imidazolylidenes and their catalytic activities in the A³-reaction of aldehydes, amines and alkynes.

Results and discussion

1-Cyclohexyl-3-benzylimidazolylidene silver complexes

The NHC silver halides, 1-cyclohexyl-3-benzylimidazolylidene (CyBn-NHC) silver chloride (1) and bromide (2) were synthesized by reaction of the corresponding 1-cyclohexyl-3-benzylimidazolium salts with silver oxide (Ag₂O) in CH₂Cl₂ following a procedure reported in literature (Scheme 1).⁹

However, reaction of 1-cyclohexyl-3-benzylimidazolium iodide with Ag_2O under the otherwise identical conditions led to the formation of NHC silver chloride complex 1 in CH_2Cl_2 , through

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Scheme 1 Synthesis of NHC silver halides 1 and 2.

an I/Cl exchange.^{9,10} In chloride-free solvents THF or methanol, a structurally unidentified white solid formed but almost insoluble in common organic solvents. Elemental analyses indicated the solid consisted of one NHC ligand with seven silver iodide molecules. A rationale for the failure in isolating the corresponding CyBn-NHC silver iodide possibly lies in the stronger interaction (soft acid-soft base interaction) of silver ion with iodide than NHCs, which makes silver iodide form cluster itself rather than be supported by NHCs. In other words, if the coordination of an anion to silver is much weaker than a NHC, then NHC-supported silver cations $[(NHC)_2Ag]^+$ would be likely to form. To test this, one equivalent sodium nitrate was deliberately added to the reaction mixture of 1-cyclohexyl-3-benzylimidazolium iodide and silver(1) oxide in THF to supply a weakly coordinating anion and a biscarbene silver nitrate $[(CyBn-NHC)_2Ag]^+NO_3^-3$ was obtained in 37% yield.

Spectra and elemental analyses provided little information on the molecular structure of these NHC silver complexes. Thus, single crystals of the NHC silver complexes **1**, **2** and **3** were grown by slow evaporation of their acetonitrile solutions and X-ray diffraction analysis was performed. A dimeric structure through a ligand-unsupported nonpolar Ag–Ag bond having crystallogrphically imposed twofold symmetry, thus a *trans* conformation, was found for NHC silver chloride **1** (Fig. 1) and bromide **2** while the two NHC ligands assume a *cis* orientation in cationic biscarbene silver nitrate complex **3** (Fig. 2). Complexes **1** and **2** are isomorphous, thus structure of **2** is not shown. The selected bond lengths and angles of complexes **1**, **2** and **3** are compiled in Table 1.

The lengths of the coordination bonds between the CyBn-NHC ligand and silver ion, C(1)-Ag(1) in 1 (2.079 Å) and 2 (2.085 Å), are close to the values observed in NHC silver chlorides with similar structure, such as 1,3-dialkyl imidazolylidene silver chlorides [(EtEt-NHC)AgCl]₂ (2.064 Å),¹¹ [(ⁱBuⁱBu-NHC)AgCl]₂,

Table 1 Selected bond lengths (Å) and angles (°) for complexes 1, 2 and 3 $\,$

Bond	1	2	3
C(1)–Ag	2.079(4)	2.085(7)	2.071(2), 2.077(2)
Ag–X	2.3296(11)	2.4045(12)	
Ag–Ag	2.8886(7)	2.8564(12)	
C(1)–Åg–X ^a	169.00(11)	166.6(2)	177.96(8)
Ag-C(1)-N(1)	132.5(3)	134.3(5)	128.36(16), 127.89(16)
Ag-C(1)-N(2)	123.4(3)	122.7(5)	127.42(17), 128.05(15)
Ag–Ag–X	82.74(4)	80.74(3)	
Ag-Ag-C(1)	101.44(11)	103.61(19)	
^{<i>a</i>} C–Ag–C for 3 .			



Fig. 1 Crystal structure (30% probability) of [(CyBn-NHC)AgCl]₂ 1.



Fig. 2 Crystal structure (30% probability) of $[(CyBn-NHC)_2Ag]^+NO_3^- 3$ (anion omitted).

(2.060–2.087 Å), [(CyCy-NHC)AgCl]₂ (2.075–2.096 Å)⁸ and biscarbene silver cation [Ag(NHC)₂]⁺ with non-coordinating anions (2.073–2.089 Å),¹² as well as the average value observed in [Ag(NHC)₂]⁺[AgX₂]⁻(2.08 Å).¹ However, the Ag–Ag distances in the dimeric CyBn-NHC silver complexes 1 (2.8886 Å) and 2 (2.8564 Å) are not only significantly shorter than sum (3.44 Å) of the van der Waals radii of silver,¹³ but also compared to the metal-metal distances in the open-shell metallic silver (2.889 Å), indicating a genuine attractive interaction between silver atoms.¹⁴ The Ag–Ag distances in the dimeric complexes of 1 and 2 are also shorter than those typically observed for ligand-unsupported polar Ag–Ag interaction, such as in [(MeMe-NHC)₂Ag]⁺[AgX₂]⁻ of *N*,*N'*-dimethylimidazolylidene silver chloride (3.188 Å) and bromide (3.2082 Å)⁹ although longer than a C_{carbene}-supported Ag–Ag interaction (2.705 Å)¹⁵ in (NHC)Ag⁺(µ-NHC)Ag⁺(DMSO)_m.

Compared with the NHC silver halides having ligandunsupported nonpolar Ag-Ag interaction similar to 1 and 2, such as 1,3-dialkylimidazolylidene silver chlorides [(ⁱBuⁱBu-NHC)AgCl]₂, (3.108 Å, 3.124 Å), [(CyCy-NHC)AgCl]₂ (3.0650 Å, 3.0181 Å),⁸ [(EtEt-NHC)AgCl]₂ (3.0553 Å),¹¹ 1,3,4,5-tetramethyl imidazolylidene silver chloride [(meNHC)AgCl]₂ (3.0673 Å)⁸ and complex [(2,6-bis(n-butylcarbenemethyl)-pyridine)AgCl]₂ (3.269 Å),¹⁶ the Ag-Ag interaction in 1 and 2 is also obviously stronger. The strong nonpolar Ag-Ag interaction and trans conformation implied that the Ag-Ag interaction in complexes 1 and 2 could not be truly unsupported. In fact, a couple of intraand intermolecular Csp^3 -H–A and Csp^2 -H–A (A = Cl, Br, Ag) weak hydrogen bonds17 could be identified in the crystal packing diagram of complexes 1 and 2. Further, these weak hydrogen bonds appeared not only to provide supports for the conformation and the nonpolar Ag-Ag interaction in dimeric structure of 1 and 2, but also to drive the dimer to self-assembly into a supramolecular architecture in crystal (Fig. 3).



Fig. 3 A weak-hydrogen-bond supported supramolecular architecture of 1 and 2 in crystal. Bond lengths (Å) and angles (°): C4–H4B–X, 2.88(2.88), 164.5(168.5); C4–H4B–Ag 3.07(3.09), 115.9(115.6); C7–H7–Ag 3.02(3.12), 111.6(107.2); C8–H8–Cl 3.14(3.09), 136.6(140.3); C11–H11–Ag 2.65(2.64), 125.2(125.1); C16–H16A–Cl 2.84(2.88), 163.9(164.0).

1-Cyclohexyl-3-naphthalen-2-ylmethylimidazolylidene silver halides

Generally, weak hydrogen bonds C–H–A are readily destroyed by a slight change of the molecular structure. Breaking the weakhydrogen-bond net in the dimeric structure of complexes 1 and 2 could lead to disassembly of the (NHC)AgX dimers.

Table 2Selected bond lengths (Å) and angles (°) for complexes 4 and 5

Bond	4	5
C(1)–Ag	2.090(8)	2.090(5)
Ag–X	2.3824(16)	2.4331(7)
C(1)–Ag–X	166.5(2)	174.18(12)
Ag-C(1)-N(1)	130.3(6)	126.4(3)
Ag-C(1)-N(2)	126.0(5)	128.6(3)

And more, Nolan *et al.*⁸ has shown that replacement of the isobutyl or cyclohexyl groups on the N-heterocyclic carbene ligands with more sterically demanding isopropyl groups in the 1,3-bialkylimidazolylidene silver chlorides made them change from dimers through a ligand-unsupported Ag–Ag bond to monomeric complexes (NHC)AgCl. Inspired by these, a more sterically demanding ligand 1-cyclohexyl-3-naphthalen-2-ylmethylimidazolylidene was designed to support monomeric NHC silver halides.

Similar to complexes 1 and 2, 1-cvclohexvl-3-naphthalen-2ylmethylimidazolylidene silver chloride 4 was synthesized by reaction of 1-cyclohexyl-3-naphthalen-2-ylmethyl imidazolium chloride with Ag₂O in CH₂Cl₂ in 64% yield. However, reaction of 1-cyclohexyl-3-naphthalen-2-ylmethylimidazolium bromide with Ag₂O under the otherwise identical conditions led to the formation of chloride 4, through an unexpected Br/Cl exchange, implying 1-cyclohexyl-3-naphthalen-2-ylmethylimidazolylidene silver chloride is more thermally stable than its bromide analogue. The desired bromide 5 had to be prepared by conduction of the reaction in acetonitrile to prevent the Br/Cl exchange from taking place. Single-crystal X-ray diffraction analysis on complexes 4 and 5 revealed the desired monomeric structure with a two coordinate silver ion (CyNaph-NHC)AgX for 4 (Fig. 4) and 5. The structure of 5 is essentially identical to 4, thus being omitted. The selected bond lengths and angles of complexes 4 and 5 are compiled in Table 2.



Fig. 4 Crystal structure (30% probability) of (CyNaph-NHC)AgCl 4.

The C(_{carbene})-Ag bond lengths (2.090 Å) in complexes 4 and 5 are slightly longer than those reported for some monomeric two-coordinate (NHC)AgCl complexes of sterically demanding NHCs, such as in 1,3-dimesimidazolylidene silver chloride (2.056 Å), 1,3-di(2,6-4-tolyl)imidazolylidene silver chloride (2.062 Å) and 1,3-didodecylimidazolylidene silver chloride (2.067 Å), but close to those in highly sterically demanding NHC

supported silver chlorides, such as 1,3-di(2-phenyl)imidazolylidene silver chloride (2.079 Å), 1,3-di(2,6-bis(diphenylmethyl)-4methylphenyl) imidazolylidene silver chloride (2.081 Å) and 1.3diadamantylimidazolylidene silver chloride (2.094 Å), while the Ag-Cl bond length (2.3824 Å) in 4 is slightly longer than all in the above sterically demanding NHC supported silver chloride (2.314–2.345 Å),^{7,8} indicating the 1-cyclohexyl-3-naphthalen-2ylmethylimidazolylidene is rather sterically demanding. The C(1)-Ag and Ag-X bond lengths in 4 and 5 are also comparable to, if not longer than, those observed in [(CyBn-NHC)AgX]₂ 1 and 2 (Table 1) which have a more crowded environment around silver ion, consistent with the more sterically demanding property of 1-cyclohexyl-3-naphthalen-2-ylmethyl imidazolylidene than 1cyclohexyl-3-benzylimidazolylidene. All the NHC silver halides 1, 2, 4 and 5 have a near linear C-Ag-X geometry with bond angles from 166-174°, falling into the ranges reported for the NHC silver halides.1

Catalysis

Propargylamines are important skeletons or synthetically versatile building blocks for the preparation of many nitrogen-containing biologically active compounds.18 In 2003, Li et al. reported the first silver catalyzed three-component A3 reaction of aldehydes, amines and alkynes in water to efficiently provide propargylamines.¹⁹ Owning to the importance of propargylamines and the high synthetic efficiency of the A³ reaction, many efforts have been made to improve the three-component reaction by use of silver nanoparticles²⁰ and supported silver salt (Ag^I) catalysts,²¹ as well as development of alternative transition-metal based catalysts such as copper,²² gold,²³ iridium²⁴ and zinc²⁵ etc.. Recently, N-heterocyclic carbene silver halides have been reported to show high catalytic activity in the A3 reaction,6 in which in situ-generated polymer-supported complexes were claimed to be more active than the parent NHC silver halides. However, the intrinsic nature of the in situ-generated polymer-supported complexes hampers elucidation of the true catalytic species. With the structurally well-defined NHC silver complexes 1-5 in hands, we investigated the structure-activity relationship of NHC silver-based catalysts in the A³ reaction. The reaction of 3-phenylpropionaldehyde, phenylacetylene and piperidine was chosen as the model. Using NHC silver halides 1, 2, 4 or 5 as the catalyst or combining the corresponding imidazolium halides with silver(I) oxide to generate catalysts in situ, the model A³ reaction occurred very slowly adapting the conditions reported by Wang et al.⁶ and only trace amount of product could be detected by TLC in 12 h at room temperature in CH₂Cl₂ although the reaction proceeded significantly faster in refluxing CH₂Cl₂.[‡] Considering most of metal-catalyzed A³ reactions were run at elevated temperature (~100 °C) and to avoid the possible Br/Cl exchange of the NHC silver bromide in chloride solvents, dioxane was chosen as the solvent for the model reaction (Table 3).

All the NHC silver halides and nitrate 1-5 could efficiently catalyze the A³ reaction giving the desired product in good to excellent yields in dioxane at 100 °C in air. The activities of

Table 3 Catalytic activity of NHC silver complexes 1–5 in A³ reaction

R^{1} -CHO + N + H - R^{2} $\frac{3 \text{mol}\%}{\text{dioxane}}$ N R^{2}						
Entry	Cat.	R ¹	\mathbb{R}^2	T∕°C	t/h	Yield (%) ^a
1	1	PhCH ₂ CH ₂	Ph	100	2	79
2	2	PhCH ₂ CH ₂		100	2	61
3	3	PhCH ₂ CH ₂		100	2	77
4	4	PhCH ₂ CH ₂		100	2	99
5	5	PhCH ₂ CH ₂		100	2	84
6	AgCl	PhCH ₂ CH ₂		100	2	80
7	AgBr	PhCH ₂ CH ₂		100	2	64
8	AgI	PhCH ₂ CH ₂		100	2	49
9	AgNO ₃	PhCH ₂ CH ₂		100	2	61
10	Ag ₂ O	PhCH ₂ CH ₂		100	2	78
11	4	PhCH ₂ CH ₂	Ph	50	12	81
12	4	PhCH ₂ CH ₂	Ph	r.t.	72	69
13	4	PhCH ₂ CH ₂	Ph	100	12	31 ^b
14	4	PhCH ₂ CH ₂	$n-C_6H_{13}$	100	6	64
15	4	4-ClC ₆ H ₄	Ph	100	12	77
16	4	Piperonyl	Ph	100	12	49
" Isolated yield. ^b Run in water.						

NHC silver halides 1 and 2 were just comparable to the simple inorganic silver halides of AgCl and AgBr (Table 3, entries 1, 2, 6 and 7). However, the more sterically demanding NHC, 1-cyclohexyl-3-naphthalen-2-ylmethylimidazolylidene, supported monomeric silver halides 4 and 5 displayed remarkably higher activities than simple silver halides AgX as well as the dimeric NHC silver halides 1 and 2 supported by the less sterically demanding 1-cyclohexyl-3-benzylimidazolylidene (Table 3, entries 4 and 5). In fact, the reaction catalyzed by complex 4, (CyNaph-NHC)AgCl, completed in 2 h giving the product in an almost quantitative yield. It was reported that cationic or high oxidation state metal compouds, thus strong Lewis acids, showed high activities in the A3 reaction.23 However, the cationic biscarbene silver nitrate 3 did not display better performance than the silver halides possibly due to steric hindrance of the silver in the biscarbene cation [(NHC)₂Ag]⁺, thus implying the importance of accessible coordination of silver to catalyze the A³ reaction. The reaction proceeded rather slowly at low temperature (Table 3, entries 11 and 12). Alkyl alkynes, such as octyne, and aromatic aldehydes, both electron-rich and -deficient ones, also reacted, albeit slowly, under similar conditions (Table 3, entries 14-16). Unlike the reaction in water,¹⁹ the catalytic activities of both NHC supported and simple silver halides AgX decreased from chloride to bromide or iodide in dioxane and even nitrate and oxide gave better performance than silver iodide (Table 3, entries 1–10).

The fact of higher catalytic activity of chloride **4** than the corresponding bromide **5** and the cationic biscarbene silver $[(NHC)_2Ag]^+$ nitrate **3** along with the formation of **4** from the precursor imidazolium bromide for **5** in CH₂Cl₂ during synthesis indicated the true catalytic species in the NHC silver-catalyzed A³ reaction would be a structurally stable and coordinatively unsaturated N-heterocyclic carbene silver halide (NHC)AgX rather than a silver cation. A slightly modified mechanism from the originally proposed one by Li¹⁹ is shown in Scheme 2 to explain the observed structure–activity relationship in the NHC silver halide catalyzed A³ reaction.

[‡] We could not repeat the results reported in ref. 6 at room temperature using 1,3-dibenzylimidazolylidene silver chloride as catalyst. When the reaction was conducted in refluxing CH_2Cl_2 for 12 h (~50 °C bath temperature), the desired product was isolated in 55% yield.



Scheme 2 A plausible mechanism for (NHC)AgX catalyzed A³ reaction.

The catalyst (NHC)AgX reacts with alkyne and amine to form the silver alkynide and the amine hydrogen halide salt at first. The latter then condenses with aldehyde to generate iminium halide, which reacts with the previously generated silver alkynide to afford the desired product and regenerate the catalyst (NHC)AgX. The structural stability and coordinative accessibility of silver ion in NHC silver halides appeared to play a crucial role in the catalysis. Based on this, it is easy to explain the highest catalytic activity of chloride **4** (CyNaph-NHC)AgCl among these investigated silver compounds since it posses the most stable structure yet with open coordination environment around silver ion.

Conclusions

Structurally well-defined N-heterocyclic carbene silver chlorides, bromides and nitrate supported by 1-cyclohexyl-3-arylmethyl imidazolylidene have been synthesized and crystallographically characterized. The structures of the 1-cyclohexyl-3-arylmethyl imidazolylidene silver halides have been tuned from dimer [(NHC)AgX]₂ through non-polar silver-silver interaction to monomer (NHC)AgX with a two coordinate silver ion by replacement of benzyl group on the imidazole moiety to more sterically demanding naphthalene-2-ylmethyl group. The catalytic activities of these structurally well-defined N-heterocyclic carbene silver complexes in the model three-component reaction of 3phenylpropionaldehyde, phenylacetylene and piperidine indicated that both the structural stability and accessible coordination to silver of the NHC silver catalyst played key roles in the NHC silver catalyzed A³ reaction. Further work on these structurally welldefined N-heterocyclic carbene silver halides and applications of readily available sterically demanding 1-cyclohexyl-3-naphthalen-2-ylmethylimidazolylidene ligand in transition metal catalysis is in progress in our laboratory.

Experimental

General

1-Cyclohexylimidazole,²⁶ 2-(chloromethyl)naphthalene and 2-(bromomethyl)naphthalene²⁷ were prepared according to the previously reported procedures. All the other chemicals were commercially available and were used as received. Melting points were recorded on a SWG[®]X-4 capillary melting point apparatus. ¹H and ¹³CNMR spectra were recorded on a Bruker Avance Spectrometer. Elemental analyses and mass spectra were performed at the Center for Analysis, ECUST.

1-Cyclohexyl-3-benzylimidazolylidene silver chloride (1)

To a solution of 1-cyclohexyl imidazole (1.5 g, 10 mmol) in 20 mL toluene was added benzyl chloride (1.5 g, 12 mmol). The resulting mixture was heated to reflux until 1-cyclohexyl imidazole was completely consumed. The salt separated upon cooling was washed with toluene until free of benzyl chloride to provide 1-cyclohexyl-3-benzylimidazolium chloride quantitatively, which was dissolved in 50 mL CH₂Cl₂ and subjected to Ag₂O (3.5 g, 15 mmol) at room temperature. The resulting mixture was stirred for 24 h in dark. Then, the solid materials were filtered off and the filtrate was concentrated under reduced pressure. The residue was washed with ether and recrystallized in acetonitrile to provide 1 as colorless crystals, 1.77 g (46%). M.p.: 157–159 °C. ¹HNMR (CDCl₃, 500 MHz, 25 °C), δ (ppm): 7.40–7.47 (m, 3H), 7.35 (d, J = 5.5 Hz, 2H), 7.05 (d, J = 2.0 Hz, 1H), 6.90 (d, J = 1.5 Hz, 1H), 5.30 (s, 2H), 4.26–4.31 (m, 1H), 2.05–1.20 (m, 10H). Anal. for 1: Calcd for C₁₆H₂₀N₂ClAg (%): C, 50.09; H, 5.25; N, 7.30. Found (%): C, 50.46; H, 5.41; N, 6.97.

1-Cyclohexyl-3-benzylimidazolylidene silver bromide (2)

A procedure similar to the synthesis of **1** was adapted with benzyl bromide (2.1 g, 12 mmol) to afford **2** as colorless crystals (2.23 g, 52%). M.p.: 108–111 °C. ¹HNMR (CDCl₃, 500 MHz, 25 °C), δ (ppm): 7.42–7.48 (m, 3H), 7.30 (d, J = 6.0 Hz, 2H), 7.00 (d, J = 2.0 Hz, 1H), 6.90 (d, J = 1.5 Hz, 1H), 5.35 (s, 2H), 4.28–32 (m, 1H), 2.05–1.20 (m, 10H). Anal. for **2**: Calcd for C₁₆H₂₀N₂BrAg (%): C, 44.89; H, 4.71; N, 6.54. Found (%): C, 45.26; H, 4.70; N, 6.27.

Bis(1-cyclohexyl-3-benzylimidazolylidene) silver nitrate (3)

A procedure similar to the synthesis of **1** was adapted with benzyl iodide (2.6 g, 12 mmol), Ag₂O (3.5 g, 15 mmole) and NaNO₃ (0.9 g) but using THF in placement of CH₂Cl₂ to afford **3** (1.24 g, 37%). as a pale crystal. M.p.: 149 °C (dec.) ¹HNMR (CDCl₃, 500 M Hz, 25 °C), δ (ppm): 7.43–7.50 (m, 6H), 7.30 (d, *J* = 6.1 Hz, 4H), 7.00 (d, *J* = 2.0 Hz, 2H), 6.90 (d, *J* = 1.6 Hz, 2H), 5.40 (s, 4H), 4.27–4.31 (m, 2H), 2.00–1.20 (m, 20H). Anal. for **3**: Calcd for C₃₂H₄₀N₅O₃Ag·H₂O (%):C, 57.49; H, 6.33; N, 10.48. Found (%): C, 57.92; H, 6.20; N, 10.39.

1-Cyclohexyl-3-naphthalen-2-ylmethylimidazolylidene silver chloride (4)

A procedure similar to the synthesis of **1** was adapted with 2-(chloromethyl)naphthalene (2.1 g, 12 mmol) to afford **4** as colorless crystals (2.77 g, 64%). M.p.:178–180 °C. ¹HNMR (CDCl₃, 500 MHz, 25 °C), δ (ppm): 7.84–7.82 (m, 3H), 7.73 (s, 1H), 7.52–7.50 (m, 2H), 7.34 (dd, $J_1 = 2.5$ Hz, $J_2 = 2.0$ Hz, 1H), 7.01 (d, J = 2.5 Hz, 1H), 6.94 (d, J = 2.0 Hz, 1H), 5.41 (s, 2H), 4.34–4.28 (m, 1H), 2.08–1.44 (m, 10H). Anal. for **4**: Calcd for C₂₀H₂₃N₂ClAg (%): C, 55.38; H, 5.11; N, 6.46. Found (%): C, 55.01; H, 5.23; N,6.56.

1-Cyclohexyl-3-naphthalen-2-ylmethylimidazolylidene silver bromide (5)

A procedure similar to the synthesis of 1 was adapted but using CH_3CN in placement of CH_2Cl_2 with

 Table 4
 Crystal data for N-cyclohexyl-N'-arylmethylimidazolylidene silver complexes

	1	2	3	4	5
Formula	$C_{32}H_{40}Ag_2Cl_2N_4$	$C_{32}H_{40}Ag_2Br_2N_4$	$C_{32}H_{42}AgN_5O_4$	C ₂₀ H ₂₂ AgClN ₂	C ₂₀ H ₂₂ AgBrN ₂
Formula weight	767.32	856.24	668.58	433.72	478.18
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	C2/c	C2/c	$P\bar{1}$	$P\overline{1}$	$P\overline{1}$
a/Å	10.1326(10)	10.2059(10)	10.4641(7)	8.6763(10)	9.5958(14)
b/Å	16.0862(16)	16.0854(16)	13.1306(9)	9.2220(11)	10.0014(14)
c/Å	19.984(2)	19.955(2)	13.3806(9)	12.2495(15)	10.5225(15)
α (°)	90	90	67.602(1)	91.356(2)	78.320(2)
β (°)	94.549(2)	95.573(2)	71.583(1)	105.679(2)	68.860(2)
γ (°)	90	90	76.576(1)	97.504(2)	84.966(2)
V/Å ³	3247.0(6)	3262.5(6)	1599.59(19)	933.78(19)	922.3(2)
Ζ	4	4	2	2	2
F(000)	1552	1696	696	440	476
No of reflns	3523	3696	6768	3428	3548
No of reflns gt	2781	2445	5977	2885	3023
No of params	182	181	387	217	218
Goodness of fit	1.099	1.041	0.993	1.069	1.023
Final R, $R_{w}(I > 2\sigma(I))$	0.0501, 0.1380	0.0721, 0.2378	0.0340, 0.0813	0.0773, 0.2171	0.0539, 0.1375
$\Delta ho_{ m max,min}$ / e Å ⁻³	0.001, 0.000	0.001, 0.000	0.002, 0.000	0.000, 0.000	0.000, 0.000

2-(bromomethyl)naphthalene (2.6 g, 12 mmol) to afford **5** as colorless crystals (2.71 g, 57%). M.p.: 150–152 °C. ¹HNMR (CDCl₃, 500 MHz, 25 °C), δ (ppm): 7.84–7.82 (m, 3H), 7.74 (s, 1H), 7.52–7.50 (m, 2H), 7.34 (dd, $J_1 = J_2 = 2.0$ Hz, 1H), 7.01 (d, J = 2.5 Hz, 1H), 6.94 (d, J = 2.5 Hz, 1H), 5.41 (s, 2H), 4.33–4.27 (m, 1H), 2.09–1.20 (m, 10H). Anal. for **5**: Calcd for C₂₀H₂₃N₂BrAg (%): C, 50.24; H, 4.64; N, 5.86. Found (%): C, 50.51; H, 4.33; N, 5.74.

X-Ray crystallography

Single crystals of 1–5 were sealed in thin-walled glass capillaries, and data collection was performed at room temperature on a Bruker SMART diffractometer with grapite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The SMART program package was used to determine the unit-cell parameters. The absorption correction was applied using SADABS. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated without further refinement of the parameters. All calculations were carried out using the SHELXS-97 program. Crystallographic data and refinement for 1–5 are listed in Table 4.

Typical procedure for silver-catalyzed A³ reaction

Aldehyde (1.0 mmol), piperidine (1.2 mmol), alkyne (1.5 mmol) and silver catalyst (3 mol%) were heated in 3 mL dioxane at 100 °C for given time in air. The products were purified directly by flash chromatography with ethyl acetate and hexane as eluents.

1-(1,5-Diphenylpent-1-yn-3-yl)piperidine¹⁹. ¹HNMR (CDCl₃, 400 MHz, 25 °C), δ (ppm): 7.50–7.48 (m, 2H), 7.34–7.22 (m, 8H), 3.51 (dd, $J_1 = 8.0$ Hz, $J_2 = 7.2$ Hz, 1H), 2.96–2.89 (m, 1H), 2.84–2.79 (m, 1H), 2.74–2.70 (m, 2H), 2.53–2.49 (m, 2H), 2.10–2.04 (m, 2H), 1.72–1.61 (m, 4H), 1.51–1.48 (m, 2H).

1-(1-(4-Chlorophenyl)-3-phenylprop-2-ynyl) piperidine²³. ¹HNMR (CDCl₃, 400 MHz, 25 °C), δ (ppm): 7.64–7.63 (m, 2H), 7.57–7.56 (m, 2H), 7.38–7.37 (m, 5H), 4.80 (s, 1H), 2.59 (s, 4H), 1.68–1.58 (m, 4H), 1.51–1.50 (m, 2H).

1-(1-(Benz[1,3]dioxol-5-yl)-3-phenylprop-2-ynyl) piperidine²⁸. ¹HNMR (CDCl₃, 400 MHz, 25 °C), δ (ppm): 7.51–7.49 (m, 2H), 7.33–7.29 (m, 3H), 7.14 (s, 1H), 7.10 (d, J = 8 Hz, 1H), 6.78 (d, J = 8 Hz, 1H), 5.95 (s, 2H), 4.68 (s, 1H), 2.56–2.53 (m, 4H), 1.62–1.55 (m, 4H), 1.44–1.42 (m, 2H).

1-(1-Phenylundec-4-yn-3-yl)piperidine. ¹HNMR (CDCl₃, 500 MHz, 25 °C), *δ* (ppm): 7.28–7.24 (m, 2H), 7.21–7.15 (m, 3H), 3.24 (q, J = 8.0 Hz, 1H), 2.86–2.79 (m, 1H), 2.72–2.66 (m, 1H), 2.60–2.56 (m, 2H), 2.40–2.36 (m, 2H), 2.25–2.22 (m, 2H), 1.97–1.83 (m, 2H), 1.66–1.49 (m, 6H), 1.47–1.42 (m, 4H), 1.35–1.30 (m, 4H), 0.898 (t, J = 8.5 Hz, 3H). ¹CNMR (CDCl₃, 125 MHz, 25 °C), *δ* (ppm): 142.09, 128.60, 128.28, 125.74, 86.02, 77.72, 57.35, 35.41, 33.02, 31.38, 29.15, 28.57, 26.20, 24,66, 22.65, 18.72, 14.10. HREI-MS (70 eV) *m*/*z*: calcd. For C₂₂H₃₃N⁺: 311.2613, Found: 311.2610.

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