# An iodide/anion exchange route to benzimidazolylidene silver complexes from benzimidazolium iodide: Crystal structures of N,N′-dibutylbenzimidazolylidene silver chloride, bromide, cyanide and nitrate

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## Abstract

Syntheses of N,N′-dibutylbenzimidazolylidene silver complexes having chloride, nitrate or cyanide as an anion part through an iodide/anion exchange from N,N′-dibutylbenzimidazolium iodide are described, representing a practical route to benzimidazolylidene silver complexes from readily accessible benzimidazolium iodide. The crystal structures of N,N′-dibutylbenzimidazolylidene silver chloride, bromide, cyanide and nitrate have been determined, showing a close ligand-unsupported Ag–Ag interaction in $[(NHC)_2]Ag^+[AgX_2]^-$ and a "T" shape geometry about the silver(I) cation in complexes of chloride, bromide and cyanide, but a nearly linear shape in the bis(N,N′-dibutylbenzimidazolylidene) silver complex $[(NHC)_2Ag]^+NO_3^-$ with non-coordinating nitrate anion.
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*Keywords:* Silver; N-heterocyclic carbene; Benzimidazolylidene; Anion exchange; Crystal structure

## 1. Introduction

N-heterocyclic carbene silver complexes have recently attracted many attentions owing to their structure diversity as well as utility as carbene transfer reagents for access to a diversity of transition metal N-heterocyclic carbene complexes [1–3]. Although several sorts of N-heterocyclic carbenes have been reported, imidazolylidenes have dominated the field of N-heterocyclic carbene chemistry partly due to the wide applications of imidazolylidenes as supporting ligands in transition metal catalysts [4]. Recently, benzimi-

dazolylidene-supported transition metal complexes have been reported to display some properties remarkably different from the corresponding imidazolylidene ones as both homogeneous catalysts and materials [5–12]. Unlike the imidazolylidenes, free benzimidazolylidenes are not stable enough to be isolated unless their dimerization is sterically blocked [13–16]. Therefore, benzimidazolylidene silver halides represent a reliable and practical benzimidazolylidene source in preparation of N-heterocyclic carbene transition metal complexes of benzimidazolylidenes. Although the first benzimidazolylidene silver bromide, N,N′-diethyl-benzimidazolylidene silver bromide, was reported in 1998 among the earliest structurally characterized N-heterocyclic carbene silver complexes [17], few benzimidazolylidene silver complexes have been characterized crystallographically [1]. Herein we report the syntheses and crystal struc-
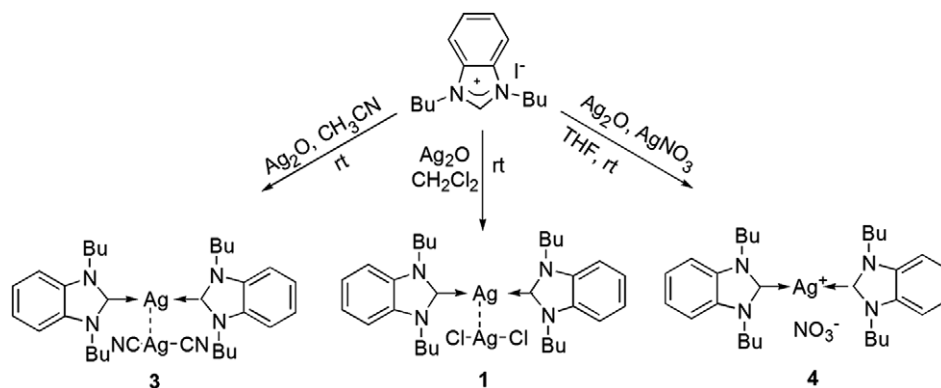
tures of N,N′-dibutylbenzimidazolylidene silver complexes of chloride, bromide, cyanide and nitrate as well as iodide/chloride, iodide/cyanide or iodide/nitrate exchanges in the reaction of N,N′-dibutylbenzimidazolium iodide with silver(I) oxide in CH₂Cl₂, CH₃CN or THF in the presence of $NO_3^-$ anion, respectively.

## 2. Results and discussion

We previously reported a preparation of bis(N,N′-dibutylbenzimidazolylidene) palladium chloride in low yield by reaction of the corresponding benzimidazolylidene silver bromide generated *in situ* with palladium chloride [18]. The low yield was obviously due to the use of benzimidazolylidene silver bromide with palladium chloride, which unavoidably led to a mixture of benzimidazolylidene palladium bromide and chloride. However, the reaction of N-butylbenzimidazole with 1-chlorobutane to prepare the benzimidazolylidene precursor, N,N′-dibutylbenzimidazolium chloride, was found to be very sluggish giving only 8% yield after heating a mixture of N-butylbenzimidazole and 1-chlorobutane (excess) in acetonitrile at reflux for 48 h while the reactions of N-butylbenzimidazole and 1-bromobutane or 1-iodobutane completed in 6 or 2 h, respectively, under the similar conditions. We noticed some reports in the literature that imidazolylidene silver chlorides were obtained by reaction of the corresponding imidazolium iodides with Ag₂O in CH₂Cl₂, namely, an iodide/chloride anion exchange occurred in the formation of imidazolylidene silver halides in chlorinated solvents [1,19,20]. However, this iodide/chloride exchange is not always observed and no investigation has been performed to evaluate if the iodide/chloride exchange would represent a synthetic route to imidazolylidene silver chlorides. When N,N′-dibutylbenzimidazolium iodide was subjected to Ag₂O (2.0 equiv.) in CH₂Cl₂ at room temperature, N,N′-dibutylbenzimidazolylidene silver chloride 1 was isolated in 49% yield according to the elemental analyses, EI-MS and X-ray crystal structure determination (see below) although the "normal" product, N,N′-dibutylbenzimidazolylidene silver bromide 2, was isolated in 76% yield using

N,N′-dibutylbenzimidazolium bromide as the carbene precursor. The observation of iodide/chloride but no bromide/chloride exchanges had been tentatively attributed to the poorer solubility of benzimidazolylidene silver iodide in CH₂Cl₂ than its bromide and chloride analogs considering that the largest silver dihalogen anion $[AgI_2]^-$ typically shows poor solubility in organic solvents [21]. To test this hypothesis, the reaction of N,N′-dibutylbenzimidazolium iodide with Ag₂O was switched to polar non-chlorosolvents, such as CH₃CN, CH₃OH and THF. In the case of acetonitrile, N,N′-dibutylbenzimidazolylidene silver cyanide 3 was obtained in 37% yield and no NHC silver iodide was isolated from the reaction solution. When the reaction was carried out in CH₃OH or THF under the otherwise identical conditions, bis(N,N′-dibutylbenzimidazolylidene) silver nitrate 4 was obtained in about 17% yield from the reaction solution, possibly due to the residue of $NO_3^-$ in Ag₂O that was prepared from AgNO₃. In deed, the yield of nitrate 4 increased to 63% if 0.5 equiv. AgNO₃ was deliberately added to the reaction mixture (Scheme 1).

The failures in isolation of N,N′-dibutylbenzimidazolylidene silver iodide by reaction of N,N′-dibutylbenzimidazolium iodide with Ag₂O in various solvents implied that instability of benzimidazolylidene silver iodide is more likely to be responsible for the iodide/anion exchange in the formation of benzimidazolylidene silver complexes from benzimidazolium iodide. The rationale for the instability of benzimidazolylidene silver iodide may lie in a confliction of the well-known strong σ-donating property of both NHC carbene and iodide. The stronger σ-donating property of iodide anion than chloride and bromide ones leads to an electron-richer silver species AgI or $[AgI_2]^-$, which would be reluctant to attract another strong σ-donating NHC carbene ligand or the corresponding biscarbene silver species $[(NHC)_2Ag]^+$. Therefore, the reaction of readily available benzimidazolium iodides with Ag₂O should represent a practical route to the benzimidazolylidene silver complexes having a non-iodide anion part, especially when the corresponding benzimidazolium salts are not easy to access, such as the chloride, cyanide and nitrate.



Scheme 1. The iodide/anion exchange route to benzimidazolylidene silver complexes.
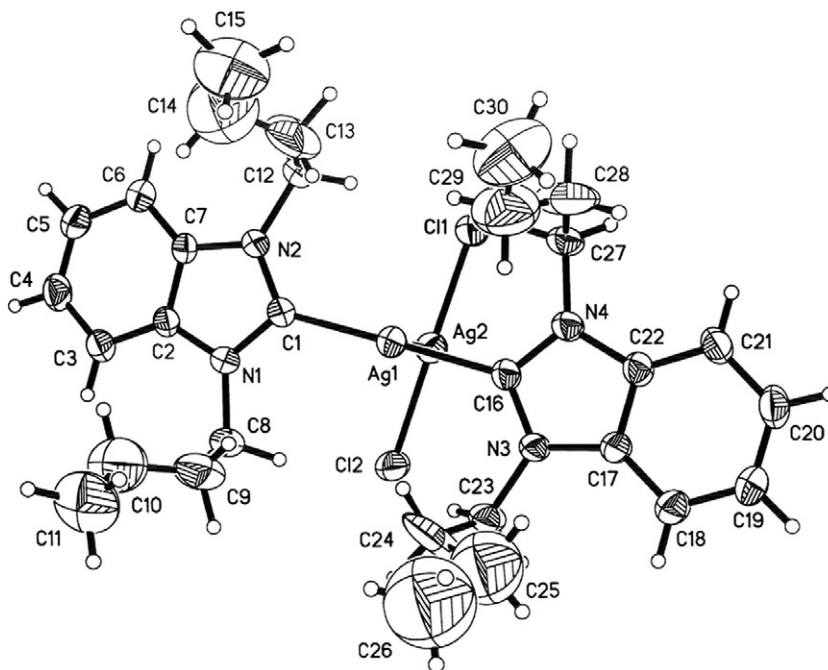
Fig. 1. ORTEP drawing (30% thermal ellipsoids) of N,N'-dibutylbenzimidazolylidene silver chloride **1**.

It is not clear at present how the iodide/anion exchanges exactly occurred. A possible route is formation of AgX at first, followed by coordination of benzimidazolylidene generated *in situ* or from the decomposition of benzimidazolylidene silver iodides. A possible source of anions X⁻ might be the HX residues in the solvents of $CH_2Cl_2$ and $CH_3CN$. However, use of $CH_2Cl_2$ and $CH_3CN$ distilled from $K_2CO_3$ as the solvents, complexes **1** and **3** were still the sole NHC silver complexes isolated from the reaction, respectively, indicating the anions X⁻ should alternatively originate

from the solvents themselves $CH_2Cl_2$ or $CH_3CN$ by cleavage of C–X (X = Cl, CN) bonds [22].

ORTEP drawings of the X-ray crystal structures of the NHC silver complexes **1**, **3** and **4** are shown in Figs. 1–3, respectively. The structure of **2** is essentially identical to **1**, thus being omitted. The selected bond lengths and angles of **1–4** are compiled in Table 1.
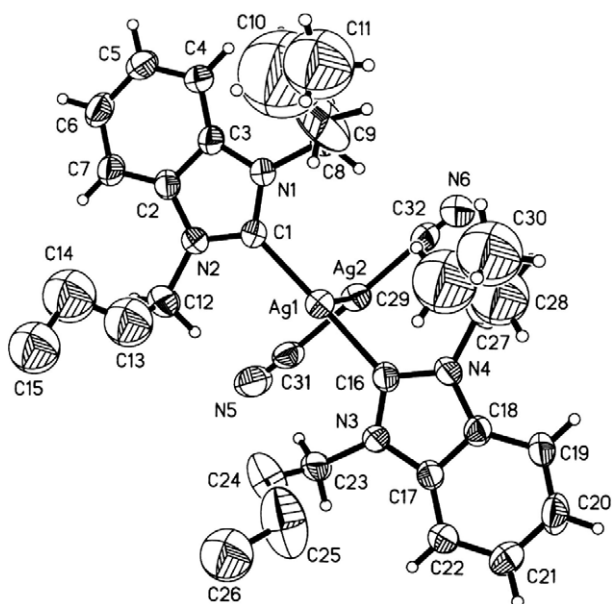


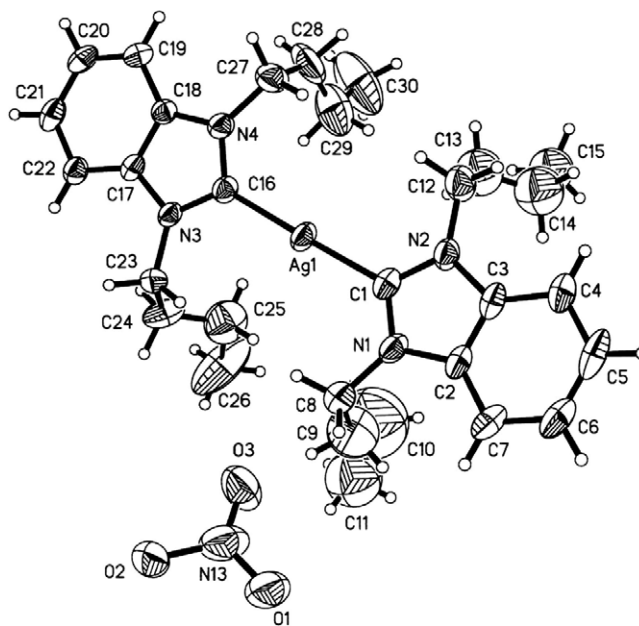Fig. 2. ORTEP drawing (30% thermal ellipsoids) of N,N'-dibutylbenzimidazolylidene silver cyanide **3**.



Fig. 3. ORTEP drawing (30% thermal ellipsoids) of bis(N,N'-dibutyl-benzimidazolylidene) silver nitrate **4** (one of the three similar but discrete molecules in the unit cell).

Table 1
Selected bond lengths (Å) and angles (°) for complexes **1**–**4**

|  | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Ag(1)–C(1) | 2.096(4) | 2.098(10) | 2.081(5) | 2.077(5) |
| Ag(1)–C(16) | 2.091(4) | 2.105(10) | 2.090(5) | 2.086(5) |
| Ag(1)–Ag(2) | 2.9342(7) | 2.9516(15) | 2.9693(9) | – |
| Ag(2)–X(1) | 2.3311(14) | 2.4271(15) | 2.068(8) | – |
| Ag(2)–X(2) | 2.3288(13) | 2.4280(15) | 2.096(8) | – |
| C(1)–N(1) | 1.344(5) | 1.363(11) | 1.341(6) | 1.331(7) |
| C(1)–N(2) | 1.342(5) | 1.388(11) | 1.339(6) | 1.355(7) |
| C(16)–N(3) | 1.341(5) | 1.338(11) | 1.330(7) | 1.348(6) |
| C(16)–N(4) | 1.355(5) | 1.355(11) | 1.359(6) | 1.354(6) |
| C(1)–Ag(1)–C(16) | 177.94(18) | 179.0(4) | 178.8(2) | 178.2(2) |
| C(1)–Ag(1)–Ag(2) | 88.32(13) | 91.6(4) | 88.97(16) | – |
| C(16)–Ag(1)–Ag(2) | 89.83(12) | 87.8(3) | 90.59(17) | – |
| X(1)–Ag(2)–Ag(1) | 93.25(4) | 89.63(5) | 88.6(2) | – |
| X(2)–Ag(2)–Ag(1) | 89.85(4) | 94.74(5) | 93.0(3) | – |
| X(1)–Ag(2)–X(2) | 176.89(6) | 175.60(7) | 178.3(3) | – |

Similar to the reported *N,N′*-diethylbenzimidazolylidene silver bromide [17], complexes **1**–**3** crystallize in *P*2(1)/*n* group showing a structure consisting of cationic [(NHC)$_2$Ag]$^+$ and anionic [AgX$_2$]$^-$ with a close ligand-unsupported Ag–Ag interaction while complex **4** crystallizes in *P*$\bar{1}$ group with three similar but discrete molecules in the unit cell showing a mononuclear ionic structure consisting of a silver cation supported by two NHC ligands, [(NHC)$_2$Ag]$^+$ and a nitrate anion. The geometry around silver in complexes **1**–**3** is the common "T" shape for a three-coordinate silver atom. The Ag–Ag bonds in complexes **1**–**3** are nearly perpendicular (87.8–93.2°) to both the linear NHC–Ag–NHC with C(1)–Ag(1)–C(16) bond angles of 177.9–179.0° and the linear X–Ag–X with X(1)–Ag(2)–X(2) bond angles of 175.6–178.3°. In complex **4**, the silver cation is linearly bonded by two NHC carbenes with C(1)–Ag(1)–C(16) bond angle of 178.2°. The nitrate anion does not directly interact with the silver cation, instead, forms O–H–O hydrogen bonds with the incorporated water molecules in the crystal.

The distances of Ag–Ag in complexes **1**–**3**, 2.9342, 2.9516 and 2.9693 Å, respectively, are at the low end of the known ligand-unsupported Ag–Ag interaction (2.80–3.30 Å) [20], comparable to that in *N,N′*-diethylbenzimidazolylidene silver bromide (2.954 Å), but significantly shorter than those in the imidazolylidene analogs [Ag(NHC)$_2$]$^+$[AgX$_2$]$^-$ of *N,N′*-dimethylimidazolylidene silver chloride (3.188 Å) and bromide (3.2082 Å). The lengths of the coordination bonds between NHC carbene and silver ion, C(1)/C(16)–Ag(1) in complexes **1**–**4**, are 2.077–2.105 Å slightly longer than those observed in [Ag(NHC)$_2$]$^+$[AgBr$_2$]$^-$ of *N,N′*-diethylbenzimidazolylidene silver bromide (2.05–2.07 Å), but close to those in *N,N′*-dimethylimidazolylidene silver chloride (2.096 Å) and bromide (2.084 Å) as well as the average value of 2.087 Å in the biscarbene silver cation with non-coordinating anions ranging from 2.06 to 2.117 Å [1]. The Ag–Cl bond lengths, 2.3311 and 2.3288 Å in [AgCl$_2$]$^-$ anion of complex **1**, are close to that in *N,N′*-dimethylimidazolylidene silver chlo-

ride 2.335 Å. Similarly, the Ag–Br bond lengths, 2.4271 and 2.4280 Å in [AgBr$_2$]$^-$ anion of complex **2**, are close to those in *N,N′*-diethylbenzimidazolylidene silver bromide (2.448 Å) and *N,N′*-dimethylimidazolylidene silver bromide (2.4390 Å). The Ag–CN bond lengths in [Ag(CN)$_2$]$^-$ anion of complex **3**, 2.068 and 2.096 Å, also fall in the range reported in the literature for the anion, such as 2.06–2.10 Å in TlAg(CN)$_2$ [23], 2.052–2.062 Å in (CH$_3$CN)$_2$LiAg(CN)$_2$ [24] and 2.074–2.055 Å in [R$_3$Te][Ag(CN)$_2$] (R = CH$_3$, Ph) [25].

### 3. Conclusion

In conclusion, *N,N′*-dibutylbenzimidazolylidene silver complexes of chloride, cyanide and nitrate have been synthesized by reaction of *N,N′*-dibutylbenzimidazolium iodide with Ag$_2$O through abstracting Cl$^-$ and CN$^-$ anions from solvents CH$_2$Cl$_2$ and CH$_3$CN, respectively, or in the presence of NO$_3^-$ anion in reaction mixture. Crystal structures of *N,N′*-dibutylbenzimidazolylidene silver chloride, bromide, cyanide and nitrate were determined, unmistakably confirming the iodide/anion exchanges. The possible rationale for the iodide/anion exchanges lies in the instability of benzimidazolylidene silver iodides. The iodide/anion exchange route possibly represents a practical route to prepare a diversity of benzimidazolylidene silver complexes with a non-iodide anion part from readily available benzimidazolium iodides and silver(I) oxide, especially when the benzimidazolium salts are difficult to access.

### 4. Experimental

#### 4.1. General

All manipulations were performed in air unless otherwise indicated. All the commercially available chemicals were used as received. *N*-butylbenzimidazole and *N,N′*-dibutylbenzimidazolium bromide were prepared according to our previously reported procedure [18]. ^{1}H NMR spectra

were recorded on a Bruker 500 spectrometer using the residue of deuterated solvents as the internal standard. EI-MS and elemental analyses were performed at the Center for Analysis and Structure Determination of ECNU.

## 4.2. Preparation of silver(I) oxide

To a rigorously stirred stock NaOH(aq.) solution (1.0 M, 110 mL, 110 mmol) was added dropwise a freshly prepared aqueous solution of AgNO₃ (17 g, 100 mmol in 100 mL H₂O) at room temperature. A fine brown precipitate formed immediately upon addition. The precipitate was filtered, washed with deionized water (3 × 100 mL) and dried in suction at room temperature for 10 h. A fine brown powder (10.6 g, 92%) was obtained and used in the following experiments.

## 4.3. Synthesis of N,N′-dibutylbenzimidazolium iodide

To an acetonitrile (20 mL) solution of *N*-butylbenzimidazole (1.74 g, 10 mmol) was added 4 equiv. *n*-Iodobutane (7.4 g, 40 mmol) at room temperature under N₂. The resulting mixture was refluxed for 2 h before cooling to room temperature. Then toluene (20 mL) was added to the reaction mixture to precipitate a pale yellow powder, which was separated by filtration and washed with ether (3 × 10 mL) to provide *N,N′*-dibutylbenzimidazolium iodide 3.42 g, (96%). m.p.: 107–108° C. Anal. Calc. for $C_{15}H_{23}N_2I \cdot 0.5H_2O$: C, 49.01; H, 6.59; N, 7.62. Found: C, 48.86; H, 6.48; N, 7.52%. $^1H$ NMR (CDCl₃, 25 °C), δ, ppm: 11.2 (1H, s), 7.75–7.80 (2H, m, Ar), 7.65–7.70 (m, Ar, 2H), 4.67 (4H, t, *J* = 7.0 Hz, NCH₂), 2.05–2.10 (4H, m, CH₂), 1.45–1.55 (4H, m, CH₂), 0.95–1.05 (6H, t, *J* = 7.0 Hz, CH₃).

## 4.4. Synthesis of N,N′-dibutylbenzimidazolylidene silver chloride (1)

To a CH₂Cl₂ (20 mL) solution of *N,N′*-dibutylbenzimidazolium iodide (0.358 g, 1.0 mmol) was added 2 equiv. Ag₂O (0.464 g, 2 mmol) at room temperature. A plenty of off-white precipitate formed and the resulting mixture was stirred in dark for 48 h. Most of the off-white precipitate disappeared and the insoluble brown solid (excess Ag₂O) was filtered off with the aid of celite. The filtrate was concentrated to about 5 mL and some hexane was carefully added to reach a cloudy point. The resulting cloudy solution was allowed to stand overnight to precipitate the NHC silver complex **1** as fine colorless crystals 0.184 g (49%). m.p.: 179–181 °C. Anal. Calc. for $C_{30}H_{44}Ag_2Cl_2N_4$: C, 48.21; H, 5.93; N, 7.50. Found: C, 48.67; H, 5.66; N, 7.83. $^1H$ NMR (CDCl₃, 25 °C), δ, ppm: 7.50–7.54 (4H, m, Ar), 7.28–7.46 (4H, m, Ar), 4.40 (8H, t, *J* = 7.4 Hz, NCH₂), 1.81–1.84 (8H, m, CH₂), 1.30–1.41(8H, m, CH₂), 0.98–1.01(12H, t, *J* = 7.4 Hz, CH₃). EI-MS (70 equiv., based on Ag¹⁰⁷): *m/z* (relative intensity): 514 (1%) [M−NHC]⁺, 337 (38%) [M−AgCl₂−NHC]⁺, 265 (12%), 230 (100%) [NHC]⁺.

## 4.5. Synthesis of N,N′-dibutylbenzimidazolylidene silver bromide (2)

A similar procedure to the synthesis of *N,N′*-dibutylbenzimidazolylidene silver chloride was adopted with *N,N′*-dibutylbenzimidazolium bromide (0.311 g, 1.0 mmol) to provide **2** as colorless crystals (0.318 g, 76%). m.p.: 175–177°C. Anal. Calc. for $C_{30}H_{44}Ag_2Br_2N_4$: C, 43.09; H, 5.30; N, 6.70. Found: C, 43.57; H, 5.46; N, 6.73%. $^1H$ NMR (CDCl₃, 25 °C), δ, ppm: 7.49–7.52 (4H, m, Ar–H), 7.28–7.47 (4H, m, Ar–H), 4.41 (8H, t, *J* = 7.3 Hz, N–CH₂), 1.81–1.83 (8H, m, CH₂), 1.31–1.43(8H, m, CH₂), 0.98–1.01(12H, t, *J* = 7.4 Hz, CH₃). EI-MS (70 equiv., based on Ag¹⁰⁷): *m/z* (relative intensity): 416 (14%) 1/2[M]⁺, 337 (70%) [1/2M−Br]⁺, 309 (16%), 229 (50%) [NHC−1]⁺, 188 (100%).

## 4.6. Synthesis of N,N′-dibutylbenzimidazolylidene silver cyanide (3)

A similar procedure to the synthesis of *N,N′*-dibutylbenzimidazolylidene silver chloride but using CH₃CN as solvent was adopted with *N,N′*-dibutylbenzimidazolium iodide (0.359 g, 1.0 mmol) to provide **3** as pale yellow crystals (0.14 g, 37%). m.p.: 198–200 °C. Anal. Calc. for $C_{32}H_{44}Ag_2N_6 \cdot H_2O$: C, 51.46; H, 6.16; N, 11.26. Found : C, 51.99; H, 6.07; N, 11.24% $^1H$ NMR (CDCl₃, 25 °C), δ, ppm: 7.52–7.57 (4H, m, Ar–H), 7.45–7.49 (4H, m, Ar–H), 4.50 (8H, t, *J* = 7.4 Hz, N–CH₂), 1.95–2.00 (8H, m, CH₂), 1.45–1.49 (8H, m, CH₂), 0.98–1.02 (12H, t, *J* = 7.0 Hz, CH₃). EI-MS (70 equiv., based on Ag¹⁰⁷): *m/z* (relative intensity): 363 (8%) 1/2[M]⁺, 337 (70%) [1/2M−CN]⁺, 258 (20%), 230 (72%) [NHC]⁺, 189 (100%).

## 4.7. Synthesis of N,N′-dibutylbenzimidazolylidene silver nitrate (4)

A similar procedure to the synthesis of *N,N′*-dibutylbenzimidazolylidene silver chloride using THF as solvent was adopted with *N,N′*-dibutylbenzimidazolium iodide (0.359 g, 1.0 mmol), 2 equiv. Ag₂O (0.464 g, 2 mmol) and AgNO₃ (0.085 g, 0.5 mmol) to provide **4** as pale yellow crystals (0.20 g, 63%). m.p.: 120–123 °C (dec.). Anal. Calc. for $C_{30}H_{44}N_5O_3Ag \cdot 1.5H_2O$: C, 54.74; H, 7.15; N, 10.64. Found: C, 54.27 H, 7.05; N, 10.29. $^1H$ NMR (CDCl₃, 25 °C), δ, ppm: 7.55–7.62 (4H, m, Ar), 7.42–7.78 (4H, m, Ar), 4.50 (8H, t, 7.5 Hz, NCH₂), 1.98 (8H, m, CH₂), 1.45 (8H, m, CH₂), 1.02 (12H, m, CH₃). EI-MS (70 equiv., based on Ag¹⁰⁷): *m/z* (relative intensity): 232 (25%) [NHC+2]⁺, 189 (99%), 132 (100%).

## 4.8. X-ray crystal structure determination

The single crystals of complexes **1**–**4** suitable for X-ray diffraction study were grown from CH₂Cl₂ (**1** and **2**), CH₃CN (**3** and **4**). The X-ray diffraction intensity data of **1**–**4** were collected with a Bruker Smart diffractometer at

Table 2
Crystal data and refinements for complexes **1**–**4**

| Entry | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Formula | $C_{30}H_{44}Ag_2Cl_2N_4$ | $C_{30}H_{44}Ag_2Br_2N_4$ | $C_{32}H_{44}Ag_2N_6$ | $C_{90}H_{142}Ag_3N_{15}O_{14}$ |
| Formula weight | 747.33 | 836.25 | 728.47 | 1981.80 |
| Crystal size (mm) | $0.50 \times 0.43 \times 0.21$ | $0.52 \times 0.39 \times 0.12$ | $0.49 \times 0.47 \times 0.21$ | $0.5 \times 0.39 \times 0.28$ |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Triclininc |
| Space group | $P2(1)/n$ | $P2(1)/n$ | $P2(1)/n$ | $P\bar{1}$ |
| $a$ (Å) | 11.7939(8) | 11.7259(17) | 11.5708(8) | 16.7782(12) |
| $b$ (Å) | 16.6950(11) | 16.902(3) | 17.0068(12) | 19.1889(13) |
| $c$ (Å) | 17.4605(12) | 17.858(3) | 17.8225(13) | 20.0486(14) |
| $\alpha$ (°) | 90 | 90 | 90 | 103.0530(10) |
| $\beta$ (°) | 108.0320(10) | 106.986(3) | 105.0110(10) | 106.8820(10) |
| $\gamma$ (°) | 90 | 90 | 90 | 110.3820(10) |
| $V$ (Å$^3$) | 3269.1(4) | 3384.9(9) | 3387.5(4) | 5391.4(7) |
| $Z$ | 4 | 4 | 4 | 2 |
| $D_{cald}$ (Mg/m$^3$) | 1.518 | 1.641 | 1.428 | 1.221 |
| $F(000)$ | 1520 | 1664 | 1488 | 2080 |
| Number of reflections collected | 19002 | 19424 | 19797 | 30803 |
| Unique reflections | 7088 | 7305 | 7383 | 21838 |
| Number of parameters | 333 | 297 | 330 | 1112 |
| Goodness-of-fit | 1.008 | 0.881 | 0.972 | 0.916 |
| Final $R$, $wR_2$ | 0.0577, 0.1595 | 0.0870, 0.2470 | 0.0670, 0.1980 | 0.0767, 0.2359 |
| $\Delta\rho_{max}$, $\Delta\rho min$ (e Å$^{-3}$) | 0.987, −0.605 | 1.530, −1.186 | 0.829, −0.563 | 1.914, −0.689 |

20 °C using Mo Kα radiation with an $\omega$–$2\theta$ scan mode. Crystallographic data and details of the procedures used for data collection and reduction information are compiled in Table 2.

## Acknowledgement

## Appendix A. Supplementary material

CCDC 631860, 631861, 631862 and 631863 contain the supplementary crystallographic data for **1**, **2**, **3**, and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.05.019.

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