Facile Synthesis of Silver(I)−Carbene Complexes. Useful Carbene Transfer Agents

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[Ag(Et$_2$-Bimy)$_2$][AgBr$_2$] (**1**; Et$_2$-Bimy = diethylbenzimidazol-2-ylidene) was obtained readily from the reaction of [Et$_2$-BimyH]Br with Ag$_2$O. Compound **2**, [Ag(Et$_2$-Bimy)$_2$]PF$_6$, was prepared by the reaction of [Et$_2$-Bimy]PF$_6$ with Ag$_2$O under basic phase transfer catalysis conditions. Both compounds **1** and **2** are good carbene transfer agents. Thus, Pd(Et$_2$-Bimy)$_2$-Cl$_2$, Au(Et$_2$-Bimy)Br, and [Au(Et$_2$-Bimy)$_2$]PF$_6$ were obtained in high yields using **1** and **2** as carbene sources. The byproduct AgBr or AgCl can be reused to generate **1** under basic phase transfer catalysis conditions. The crystal structure of compound **1** revealed that linear [Ag-(Et$_2$-Bimy)$_2$]$^+$ and [AgBr$_2$]$^-$ groups were associated through a short Ag^I−Ag^I contact (2.956 Å). FAB/mass spectrometry and molar conductivity measurements indicate the existence of ligand-unsupported Ag^I−Ag^I interactions in the gas phase and acetonitrile solution. ^{13}C NMR studies suggest that the two Bimy ligands in **1** are fluxional in solution.

Introduction

Metal complexes of carbenes derived from imidazolium salts have recently received much attention.[1−3] The renaissance of this type of metal−carbene complex began after the isolation of free stable carbenes[4,5] and their subsequent use as catalysts for reactions such as the Heck olefination of haloarenes and the asymmetric hydrosilylation of acetophenone.[6] In the past few years, we have been interested in the molecular recognition of coinage metal complexes.[7] We thus reported the molecular association of annular digold(I) compounds with diphosphine and dithiolate ligands,[7a−c] and a series of thermally stable liquid crystalline Au(I) compounds of imidazol-2-ylidene (Imy).[7d] While attempting to look for the possible ligand-unsupported Ag^I−Ag^I interactions in Ag^I−Imy compounds, we uncovered a convenient method for preparing metal-Imy complexes. Although numerous metal−Imy compounds are known, examples of Ag^I−Imy complexes are relatively rare.[8]

Results and Discussion

Metal complexes of Imy are normally prepared under an atmosphere of dry nitrogen, and solvents have to be dried and deoxygenated.[1−3, 9] Here, we report not only a simple method for the synthesis of Ag(I) complexes of 1,3-diethylbenzimidazol-2-ylidene (Et$_2$-Bimy) in high yield but also the use of these complexes as good precursors for the synthesis of other transition-metal−carbene complexes. In this reaction, the AgCl byproduct can be reused to prepare silver−carbene complexes under basic PTC (phase transfer catalyst) conditions. Thus, silver(I) is, in a sense, a catalyst for the synthesis of other metal−carbene complexes. Although group 8 carbene complexes have been reported as carbene transfer agents,[10] regenerating the group 8 carbene complexes has not yet been reported. In our typical reaction (Scheme 1) 1,3-diethylbenzimidazolium bromide ([Et$_2$-Bimy]Br; 310 mg, 1.22 mmol) was added to a Ag$_2$O (141 mg, 0.61 mmol) suspension in CH$_2$Cl$_2$ (30 mL) in a 2:1 ratio. When it was stirred, the solid suspension gradually disappeared to give [Ag(Et$_2$-Bimy)$_2$]-[AgBr$_2$] (**1**) in a 96% yield after workup. Alternatively, compound **1** was obtained in 94% yield by the reaction of [Et$_2$-Bimy]Br with AgCl or AgBr in a 1:1 molar ratio under PTC/OH$^-$ conditions. To have a compound free of [AgBr$_2$]$^-$ anion, [Et$_2$-Bimy]PF$_6$ was allowed to react with Ag$_2$O in a 4:1 ratio under basic PTC conditions to give [Ag(Et$_2$-Bimy)$_2$]PF$_6$ (**2**) in 89% yield. In these reactions solvent pretreatments were not required and a simple base, NaOH, was used.

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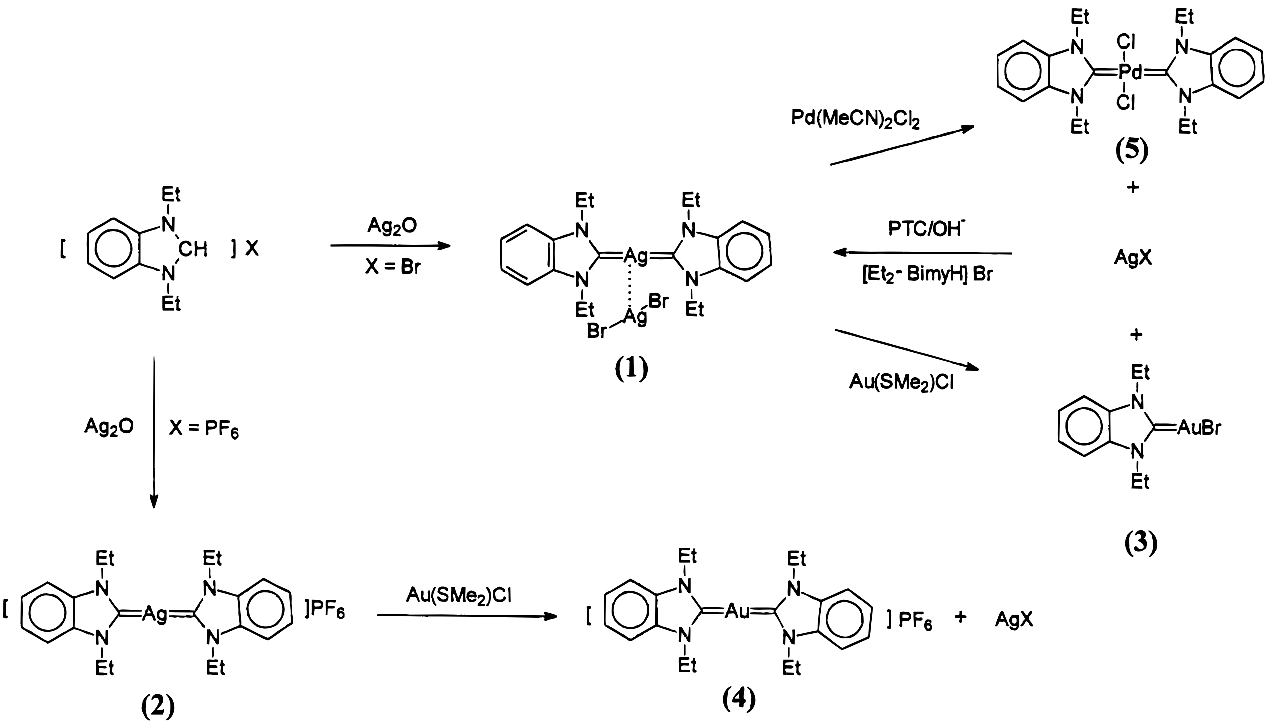
Scheme 1



Compounds **1** and **2** can be used as carbene transfer agents (Scheme 1). For example, the reaction of **1** and **2**, respectively, with Au(SMe$_2$)Cl in a 1:1 molar ratio produces Au(Et$_2$-Bimy)Br (**3**) and [Au(Et$_2$-Bimy)$_2$]PF$_6$ (**4**) in high yield, together with AgCl precipitates. The isolated AgCl can further react with [Et$_2$-Bimy]Br in a 1:1 molar ratio under PTC/OH$^-$ conditions to give **1**. The technique of PTC has been used for the synthesis of liquid-crystalline Au^{I}−Bimy compounds which have long alkyl chains on Bimy. Compounds **3** and **4**, however, could not be obtained under PTC/OH$^-$ conditions, because the reduction of Au(I) to Au metal occurred during the workup. *trans*-Pd(Et$_2$-Bimy)$_2$ Cl$_2$ (**5**) was also obtained in high yield by the reaction of Pd(NCMe)$_2$Cl$_2$ with **1** in a 1:1 molar ratio in CH$_2$Cl$_2$. Freshly prepared **5** adopts a *trans* configuration which shows a set of N−CH$_2$ proton signals at δ 4.96 ppm in the ^{1}H NMR spectrum. Upon prolonged standing (2 days) of **5** in CHCl$_3$ at room temperature, the *trans* form converts to a *cis* isomer, which shows two N−CH$_2$ proton signals at δ 4.85 and 5.31 ppm in the ^{1}H NMR spectrum. The two signals are due to the diastereotopic protons on the N atom.

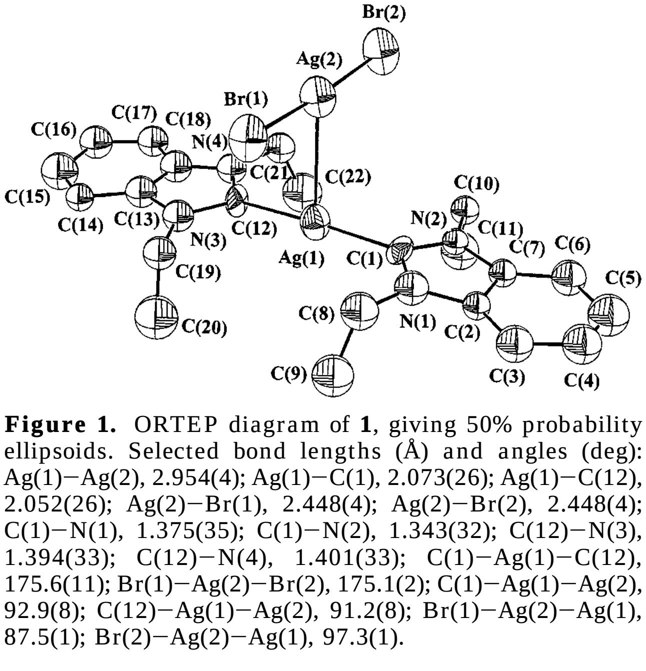


Figure 1. ORTEP diagram of **1**, giving 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Ag(1)−Ag(2), 2.954(4); Ag(1)−C(1), 2.073(26); Ag(1)−C(12), 2.052(26); Ag(2)−Br(1), 2.448(4); Ag(2)−Br(2), 2.448(4); C(1)−N(1), 1.375(35); C(1)−N(2), 1.343(32); C(12)−N(3), 1.394(33); C(12)−N(4), 1.401(33); C(1)−Ag(1)−C(12), 175.6(11); Br(1)−Ag(2)−Br(2), 175.1(2); C(1)−Ag(1)−Ag(2), 92.9(8); C(12)−Ag(1)−Ag(2), 91.2(8); Br(1)−Ag(2)−Ag(1), 87.5(1); Br(2)−Ag(2)−Ag(1), 97.3(1).

The molecular structure of **1** (Figure 1) in the solid state was determined by the X-ray diffraction technique. Selected bond distances and bond angles are given in the figure caption. Compound **1** consists of a linear [Ag(Et$_2$-Bimy)$_2$]$^+$ cation and a linear [AgBr$_2$]$^-$ anion. These two ions associate through an Ag^{I}−Ag^{I} interaction, and these two linear ions are staggered in an angle of 84.62°. The interplanar angle between the Bimy(C(12)) ring and the C(12)−Ag(1)−Ag(2) plane is 82.74°, and that between Bimy(C(1)) ring and the C(1)−Ag(1)−Ag(2) plane is 87.20°. The cationic Ag−C bond distances (Ag(1)−C(1) = 2.073 Å and Ag(1)−C(12) = 2.052 Å) are comparable to those found in the [Ag(Mes$_2$-Imy)$_2$]$^+$ carbene complex (2.067 and 2.078 Å)[8] but shorter than those found in [Ag(CO)$_2$]$^+$ (2.14 Å)[11a] and Ag$_2$(dmb)$_2$X$_2$ (dmb = 1,8-diisocyano-*p*-menthane; 2.10−2.19 Å).[11b] Considering each Bimy in the cation as a plane, these two Bimy planes have a dihedral angle of 10.27°. The geometry of C(1)−Ag(1)−C(12) is close to linear (175.6°) and is comparable to that of [Ag(Mes$_2$−Imy)$_2$]$^+$ (176.3°). The Ag(1)−Ag(2) separation of 2.954 Å is considerably smaller than the van der Waals contact distance of 3.44 Å and is at the lower range of the ligand-unsupported Ag−Ag bond lengths (range 2.80−3.30 Å).[12] This distance is even shorter than that of known[13] ligand-supported Ag^{I}−Ag^{I} interactions possibly because of the

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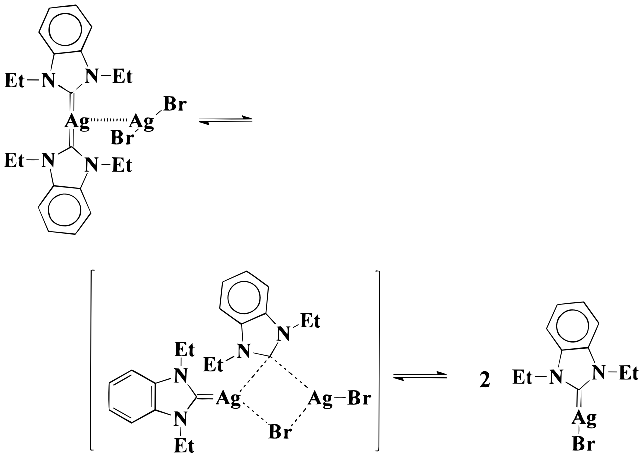
formation of ion pairs. From the literature, two-coordinated $[AgX_2]^-$ species have been shown to exist in solution;[14] however, the solid structures of the majority of such halogenoargentates are polymer anions.[15] Only two solid compounds containing discrete $[AgX_2]^-$ ions have been characterized structurally, one of which contains $[AgBr_2]^-$.[16] The Ag−Br bond distances of 2.448 Å in **1** are comparable to that of the known $[AgBr_2]^-$ (2.450 Å). The Br−Ag−Br angle of 175.1° deviates only slightly from that of the two-coordinated linear species.

Mass spectrometry can provide fundamental data on the structure of compounds in the gas phase.[17] The maximal peak intensity for **1**, observed from fast atom bombardment (FAB) mass spectrometry, is *m/z* 546 (M − Bim$^+$), indicating the existence of an Ag^I-Ag^I interaction in the gas phase in **1**. Molar conductivities of **1**, measured in ca. $10^{-3}-10^{-4}$ M solutions in acetonitrile, have an average value of 74 Ω^{-1} mol^{-1} cm^2, which is lower than that expected for 1:1 electrolytes in CH_3CN (120−160 Ω^{-1} mol^{-1} cm^2),[18] suggesting that about half of the cations and anions are associated in CH_3CN (argentophilicity). For comparison, the molar conductivity of **2**, measured in ca. $10^{-3}-10^{-4}$ M solutions in CH_3CN, has a value of 146 Ω^{-1} mol^{-1} cm^2. Attempts to evaluate the thermodynamic data of the ionic association by electronic absorption spectroscopy were unsuccessful. We only observed intraligand transitions from 248 to 283 nm in CH_3CN, and we could not observe any absorption band due to the formation of ion pairs. The lability of the Ag−carbene bond in solution was demonstrated by ^{13}C NMR spectroscopic studies. Compound **1** in $CDCl_3$ or DMSO-d_6 shows only a sharp signal (no $^{13}C-^{107,109}Ag$ coupling) for the carbene carbon. In contrast, **2** has $^{13}C-^{107}Ag$ and $^{13}C-^{109}Ag$ coupling constants of 180 and 204 Hz, respectively, compared to the values of 188 and 209 Hz observed by Arduengo et al. The lack of C−Ag coupling in **1** but not in **2** is interpreted in terms of the fluxional behavior of **1** shown in Scheme 2. In the solid state, the cation and anion in **1** are paired through a Ag−Ag bond and conductivity measurement also suggests that about half of **1** is ion-paired in solution; the transfer of a carbene and bromide between the cation and anion in an ion pair through a carbene and bromide bridge to form two neutral Ag(Et-Bimy)Br species is likely.

Scheme 2



This work provides a convenient method for the preparation of Ag^I−carbene complexes, which serve as good carbene transfer agents and could be regenerated. The fluxional behavior observed in **1** suggests that the silver(I)−carbene bond is labile and is relevant to the carbene transfer reactions observed in this work. There is also evidence that ligand-unsupported Ag^I-Ag^I interactions do exist in both the solid and solution. Further utilization of this type of Ag^I−carbene complexes is under investigation.

Experimental Section

The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-F300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts, δ, are reported relative to the internal standard TMS for both ^1H and ^{13}C NMR. Absorption spectra were obtained by a Shimadzu UV-2101 PC spectrophotometer. Microanalyses were performed by the Taiwan Instrumentation Center.

$[Ag(Et_2\text{-}Bimy)_2][AgBr_2]$ (1). Method a. Ag_2O (141 mg, 0.61 mmol) was added to a solution of 1,3-diethylbenzimidazolium bromide (310 mg, 1.22 mmol) in CH_2Cl_2 (30 mL). The suspension became clear after stirring for 2 h at room temperature. The volume of the solution was reduced to 10 mL under vacuum, and 20 mL of hexane was then added to a produce a white solid. The solid was filtered and recrystallized from CH_2Cl_2/hexane to produce a colorless crystalline product in 89% yield.

Method b. AgBr (150 mg, 1.05 mmol), NaOH (1 N, 2 mL), and the phase transfer catalyst $[Bu_4N]Br$ were added to a solution of [BimyH][Br] (267 mg, 1.05 mmol) in CH_2Cl_2 (30 mL). The suspension was stirred for 4 h at room temperature to give a clear colorless solution. After drying under vacuum, the white solid was washed with 20 mL of water and was filtered. The crude product was recrystallized from CH_2Cl_2/hexane. The yield was 94% (356 mg). Mp: 147−149 °C dec. ^1H NMR ($CDCl_3$): δ 7.43 and 7.48 (dd, $^3J = 6$ Hz, $^4J = 3$ Hz, 8H, CH), 4.48 (q, $^3J = 7$ Hz, 8H, CH_2), 1.53 (t, $^3J = 7$ Hz, 12H, CH_3). ^{13}C NMR (DMSO-d_6): δ 188.9 (C−Ag), 133.5, 124.1, and 111.5 (C_6H_4), 44.6 (CH_2), 16.0 (CH_3). Anal. Calcd for $C_{22}H_{28}N_4Ag_2Br_2$: C, 36.50; H, 3.90; N, 7.74. Found: C, 36.39; H, 3.88; N, 7.76.

$[Ag(Et_2\text{-}Bimy)_2]PF_6$ (2). Ag_2O (129 mg, 0.56 mmol) and NaOH (1 N, 3 mL) were added to a solution of $[BimyH]PF_6$ (356 mg, 1.11 mmol) in CH_2Cl_2 (50 mL), with $[Bu_4N]PF_6$ as a phase transfer catalyst. The suspension was stirred for 4 h at room temperature to produce a colorless solution and some black solid. The precipitates were filtered off, and the solution was dried under vacuum. The white residue obtained from

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solution was recrystallized from CH_2Cl_2−hexane to give a colorless crystalline product in 86% yield. Mp: 245−247 °C dec. ^{1}H NMR ($CDCl_3$): δ 7.44 and 7.55 (dd, $^3J = 6$ Hz, $^4J = 3$ Hz, 8H, CH), 4.57 (q, $^3J = 7$ Hz, 8H, CH_2), 1.63 (t, $^3J = 7$ Hz, 12H, CH_3). ^{13}C NMR (DMSO-d_6): δ 188 (C−Ag, $^1J_{^{107}\mathrm{AgC}} = 180$ Hz, $^1J_{^{109}\mathrm{AgC}} = 204$ Hz), 133.6, 124.4, and 111.7 (C_6H_4), 44.8 (CH_2), 16.2 (CH_3). Anal. Calcd for $C_{22}H_{28}N_4AgPF_6$: C, 43.94; H, 4.69; N, 9.32. Found: C, 43.65; H, 4.72; N, 9.00.

Au(Et$_2$-Bimy)Br (3). Au(SMe_2)Cl (227 mg, 0.679 mmol) was added to a solution of [Ag(Et$_2$-Bimy)$_2$][AgBr_2] (279 mg, 0.385 mmol) in CH_2Cl_2 (30 mL). The resultant solution was stirred for 2 h, during which time white precipitates formed. The precipitates were filtered off, and the remaining clear colorless solution was reduced to 5 mL under vacuum. The residue formed after the addition of 20 mL of hexane to the clear solution was filtered and dried to give Au(Et$_2$-Bimy)Br (0.347 g, 91%). Recrystallization from CH_2Cl_2/hexane yields a colorless crystalline product. Dec pt: 223−225 °C. ^{1}H NMR ($CDCl_3$): δ 7.43 and 7.48 (dd, $^3J = 6$ Hz, $^4J = 3$ Hz, 4H, CH), 4.54 (q, $^3J = 7$ Hz, 4H, CH_2), 1.56 (t, $^3J = 7$ Hz, 6H, CH_3). Anal. Calcd for $C_{11}H_{14}N_2AuBr$: C, 29.29; H, 3.13; N, 6.21. Found: C, 29.24; H, 3.12; N, 6.13.

[Au(Et$_2$-Bimy)$_2$]PF$_6$ (4). Au(SMe_2)Cl (227 mg, 0.679 mmol) was added to a solution of [Ag(Et$_2$-Bimy)$_2$]PF_6 (231 mg, 0.385 mmol) in CH_2Cl_2 (30 mL). The resultant solution was stirred for 2 h, during which time white precipitates formed. The precipitates were filtered off, and the remaining clear colorless solution was reduced to 5 mL under vacuum. The residue formed after the addition of 20 mL of hexane to the clear solution was filtered and dried to give [Au(Et$_2$-Bimy)$_2$]PF_6 (238 mg, 89%). Recrystallization from CH_2Cl_2/hexane yields a colorless crystalline product. Dec pt: 167−169 °C. ^{1}H NMR ($CDCl_3$): δ 7.49 and 7.57 (dd, $^3J = 6$ Hz, $^4J = 3$ Hz, 8H, CH), 4.64 (q, $^3J = 7$ Hz, 8H, CH_2), 1.65 (t, $^3J = 7$ Hz, 12H, CH_3). Anal. Calcd for $C_{22}H_{28}N_4AuPF_6$: C, 38.26; H, 4.02; N, 8.22. Found: C, 38.27; H, 4.09; N, 8.11.

***trans*-Pd(Et$_2$-Bimy)$_2$Cl$_2$ (5).** Pd(CH_3CN)$_2$Cl$_2$ (158 mg, 0.610 mmol) was added to a CH_2Cl_2 (30 mL) solution of [Ag(Et$_2$-Bimy)$_2$][AgBr_2] (442 mg, 0.610 mmol). After the mixture was stirred for 30 min at room temperature, the solid AgBr was filtered off and the volume of the clear yellow solution was reduced to 5 mL. The yellow solid, formed after the addition of 20 mL of hexane, was filtered and dried under vacuum to give *trans*-Pd(Et$_2$-Bimy)$_2$Cl$_2$ (279 mg, 87%). Recrystallization from CH_2Cl_2/hexane yielded a colorless crystalline product. Dec pt: 253−255 °C.. ^{1}H NMR ($CDCl_3$): δ 7.29 and 7.43 (dd, $^3J = 6$ Hz, $^4J = 3$ Hz, 8H, CH), 4.96 (q, $^3J = 7$ Hz, 8H, CH_2), 1.81 (t, $^3J = 7$ Hz, 12H, CH_3). Anal. Calcd for $C_{22}H_{28}N_4PdCl_2$: C, 50.25; H, 5.37; N, 10.66. Found: C, 49.33; H, 5.34; N, 10.37. *cis*-Pd(Et$_2$-Bimy)$_2$Cl$_2$ was obtained by stirring a CH_2Cl_2 solution of **5** at room temperature for 2 days. ^{1}H NMR ($CDCl_3$): δ 7.37 and 7.49 (dd, $^3J = 6$ Hz, $^4J = 3$ Hz, 8H, CH), 4.85 and 5.31 (q, $^3J = 7$ Hz, 8H, CH_2), 1.47 (t, $^3J = 7$ Hz, 12H, CH_3).

Crystal Structure Determination of [Ag(Bimy)$_2$][AgBr$_2$]. A colorless cuboid crystal with dimensions 0.30 × 0.10 × 0.10 mm was used for X-ray structural analysis. Cell constants were derived from least-squares refinement of 25 reflections having $7.0 < 2\theta < 45.0°$. Intensity data were collected using ω-scan mode on a Siemens P4 diffractometer equipped with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å). A total of 5551 unique reflections was measured, of which 1263 were observed ($I > 4\sigma(I)$). An empirical absorption correction based on a series of ψ-scans was applied to the data. Three standard reflections were measured every 497 reflections and diffraction intensity decay 8.49%. The collected data were corrected for the observed decay. Lorentz and polarization corrections were applied. The structure was solved by direct methods and refined by full-matrix least-squares fitting based on F^2. Ag, Br, C(1), and C(12) atoms were refined anisotropically, and the hydrogen atoms were calculated in ideal positions with $r_{\mathrm{C-H}} = 0.95$ Å. The molecular weight is 724.0 for $Ag_2N_4C_{22}H_{28}Br_2$: orthorhombic, *Pbca*, $a = 17.324(4)$ Å, $b = 16.350(3)$ Å, $c = 18.355(2)$ Å, $V = 5199.0(16)$ Å^3, $Z = 8$, $D_{\mathrm{exptl}} = 1.850$ Mg/m^3, $\mu = 4.596$ mm^{-1}, $T = 298$ K, $R = 7.24\%$, $R_w = 7.87\%$.

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Supporting Information Available: Tables giving positional and isotropic thermal parameters, anisotropic thermal parameters, and bond lengths and angles for the structural analysis of **1** (8 pages). Ordering information is given on any current masthead page.

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