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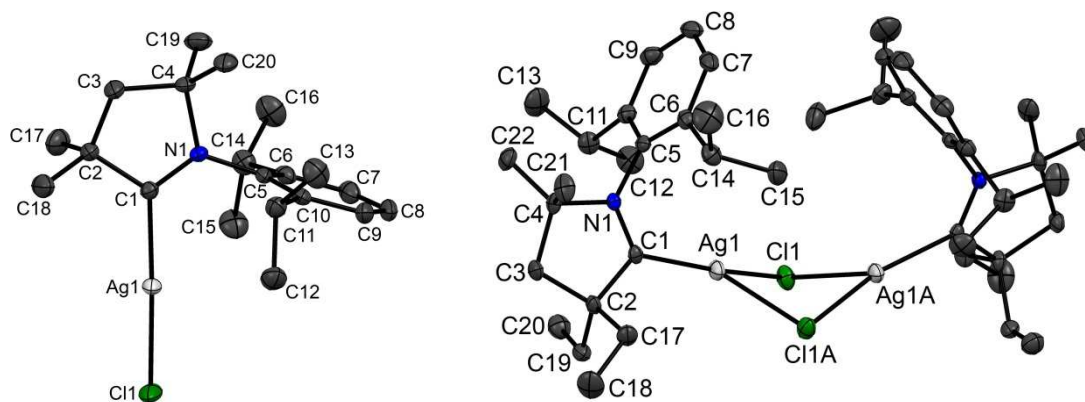
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Silver complexes with cyclic(alkyl)(amino) carbene ligands can be mononuclear or binuclear in the solid state. Complexes with sterically hindered CAAC ligands show blue photoluminescence.

Synthesis, Structures and Photoluminescence Properties of Silver Complexes of Cyclic (Alkyl)(Amino)Carbenes

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Dedicated to Professor John Gladysz on the occasion of his 65th birthday.

Abstract

Silver complexes of cyclic (alkyl)(amino)carbenes (CAACs), $(^R\text{L})_n\text{AgX}$ ($n = 1$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $n = 2$, $\text{X} = \text{OTf}$; $\text{R} = \text{Me}_2, \text{Et}_2$, or adamantyl) are accessible in high yields by reacting free carbenes with silver salts. The smaller carbene ligand $^{\text{Me}_2}\text{L}$ leads to the formation of a mixture of neutral $(^{\text{Me}_2}\text{L})\text{AgCl}$ and cationic $[(^{\text{Me}_2}\text{L})_2\text{Ag}]^+$ products. The transmetallation of $(^{\text{Ad}}\text{L})\text{AgCl}$ with copper and gold halides gives the corresponding copper and gold compounds $(^{\text{Ad}}\text{L})\text{MCl}$ ($\text{M} = \text{Cu}$ and Au) in a clean and quantitative reaction. Whereas $(^{\text{Me}_2}\text{L})\text{AgCl}$ is monomeric in the solid state, $(^{\text{Et}_2}\text{L})\text{AgCl}$ crystallizes as a Cl-bridged dimer. None of the compounds show metal-metal interactions. The complexes show blue photoluminescence, which consists of a fluorescence component with a lifetime of several nanoseconds, as well as a long-lived emission in the microsecond regime.

Keywords: Silver complex; Photoluminescence; Carbene; Transmetallation; Crystal structure

1. Introduction

The organometallic chemistry of N-heterocyclic carbene (NHC) complexes can be traced back to 1915, when Chugaev reported the reaction products of K_2PtCl_4 with hydrazine and methylisocyanide, which in the 1970s were confirmed as platinum complexes of non-cyclic N-stabilized carbene ligands [1]. Later the discoveries by Wanzlick [2] and Öfele [3] and the isolation of imidazolylidene-type N-heterocyclic carbenes (NHCs) by Arduengo [4] established carbenes as one of the most versatile ligand families in organometallic chemistry [5, 6, 7, 8]. Carbene complexes of silver have found widespread applications in synthetic chemistry as carbene transfer agents [9, 10], in medicinal chemistry as antimicrobial and antitumor agents [11], in catalysis [12], and as luminescent materials for potential applications in organic light-emitting diodes (OLEDs) [13, 14].

We have recently shown that cyclic (alkyl)(amino)carbene (CAAC) complexes of copper and gold show strong photoluminescence, with solid-state quantum yields of up to 96% [15,16]. We report here the syntheses, structures, reactivity and photoluminescence behavior of silver complexes with CAAC ligands with different degrees of steric hindrance, ^{Me_2}L , ^{Et_2}L , and ^{Ad}L (Chart I).

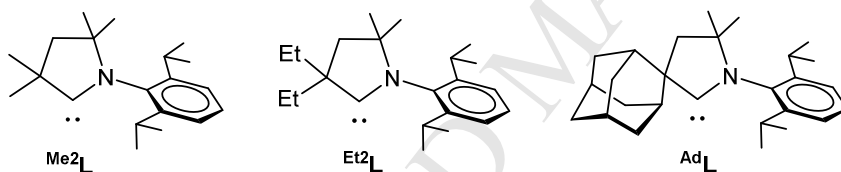
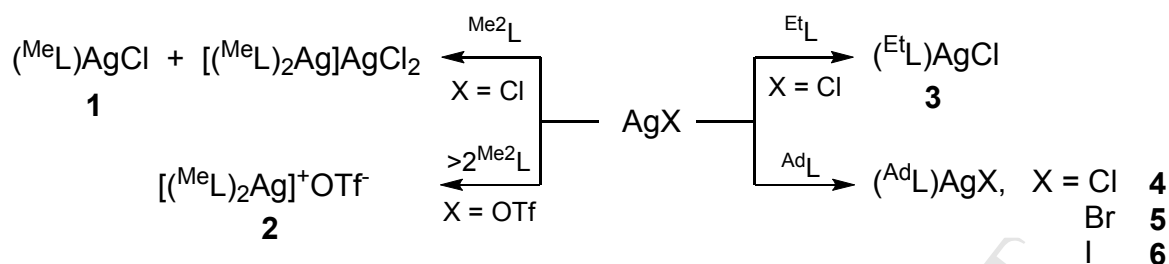


Chart I

2. Results and discussion

2.1. Synthesis. Mono-carbene silver(I) halide complexes with ligands ^{Me_2}L , ^{Et_2}L and ^{Ad}L were prepared in a moderate to high yields by combining solutions of the respective CAAC ligands with silver salts in THF (Scheme 1). The reaction outcome is governed by the steric requirements of the CAAC ligands. For example, the 1H NMR spectrum of the reaction with ^{Me_2}L showed a mixture of $(^{Me_2}L)AgCl$ and $[(^{Me_2}L)_2Ag]AgCl_2$ in a molar ratio of about 4:1. Flash chromatography allowed the isolation of $(^{Me_2}L)AgCl$ (**1**) in moderate yield (55%). The formation of the cationic species $[(^{Me_2}L)_2Ag]^+$ was confirmed by comparison of the 1H and ^{13}C NMR spectra with an authentic sample of $[(^{Me_2}L)_2Ag]^+OTf^-$ (**2**), which was prepared from silver triflate with two equivalents of ^{Me_2}L in 92% yield. By contrast, ^{Et_2}L and ^{Ad}L provide only the desired 1:1 silver complexes $(^{Et_2}L)AgCl$ (**3**) and $(^{Ad}L)AgX$ ($X = Cl$ (**4**); Br (**5**); I (**6**)) in high yields.



Scheme 1

Complexes **1–6** are white solids which are indefinitely stable in air for prolonged periods of time. Interestingly, the silver complexes are stable in sunlight, without showing signs of degradation or photoreduction to metallic silver. They show good solubility in polar non-protic solvents like 1,2-difluorobenzene, dichloromethane, THF, MeCN, DMF or acetone and are moderately soluble in chlorobenzene, toluene or ethanol but insoluble in hexane. The CD_2Cl_2 and CDCl_3 solutions of **1–6** proved to be stable to ligand rearrangement and formation of bis-carbene adducts $[\text{Ag}(\text{L})_2]^+$ over a period of several weeks, after which only slight decomposition could be noticed. The stability of the carbene C–Ag bond and the lack of ligand interchange in solution are demonstrated by the appearance of the ^{13}C carbene-C resonances as sharp doublets; for instance, complex **1** shows ^{13}C – ^{109}Ag and ^{13}C – ^{107}Ag coupling constants of 246 and 213 Hz, respectively. This is in sharp contrast with the behavior of imidazole-type silver NHC complexes, where the equilibrium $2(\text{L})\text{AgCl} \leftrightarrow [(\text{L})_2\text{Ag}]\text{AgCl}_2$ is commonly observed in solution at room temperature [17]. Obviously the CAAC complexes are substantially less labile. Whereas mono- and bis-CAAC complexes show very similar ^{13}C carbene-C chemical shifts (e.g. **1**, 255.7 ppm, compared to $[(\text{carbene})_2\text{Ag}]^+$ **2**, 255.9 ppm), the ^{13}C – ^{109}Ag and ^{13}C – ^{107}Ag coupling constants decrease sharply from over 200 Hz for mono-CAAC adducts to 183.5 and 159.6 Hz, respectively, for cation (**2**). Such coupling constant values fall in the range characteristic for bis-carbene cationic silver complexes [18]. The carbene-C chemical shifts of the mono-carbene complexes **1, 3–6** shift downfield with an increase in bulkiness of the CAAC ligand, from 255.7 for $(^{\text{Me}}\text{L})\text{AgCl}$ (**1**) to 262.5 ppm for $(^{\text{Ad}}\text{L})\text{AgCl}$ (**4**).

We tested $(^{\text{Ad}}\text{L})\text{AgCl}$ in transmetalation reactions with copper and gold salts (Scheme 2), which allowed the previously reported copper and gold compounds $(^{\text{Ad}}\text{L})\text{MCl}$ ($\text{M} = \text{Cu}$ and Au [19]) to be obtained in essentially quantitative yields. The attempted ligand transfer of either $^{\text{Me}}\text{L}$ or $^{\text{Ad}}\text{L}$ from neutral or cationic complexes (**1, 2**, and **4**) to $[(p\text{-cymene})\text{RuCl}_2]_2$ or $[(\text{cis-cyclooctene})\text{RhCl}]_2$ resulted in the recovery of the starting materials even after prolonged reaction times (48 h in CH_2Cl_2 at room temperature). The clean formation of $(^{\text{Ad}}\text{L})\text{AuCl}$ by ligand transfer from the corresponding

silver complex contrasts with Cazin's recent report on the formation of $[(\text{carbene})_2\text{Au}]^+$ products in similar transmetalations from $(^{\text{Cy}}\text{L})\text{CuCl}$ to gold ($^{\text{Cy}}\text{L} = \text{cyclohexyl-substituted CAAC}$) [20].



Scheme 2

2.2. Structures

Crystals of the silver halides suitable for X-ray diffraction were obtained by layering of CH_2Cl_2 solutions with hexane. Neutral compounds (**1**, **4–6**) and the cation of the bis-carbene complex (**2**) are monomeric and show an almost linear geometry for the C–Ag–X moieties, with C1–Ag1–Cl1 angles approaching 180° (Figures 1 and 2). The carbene C–Ag and Ag–Hal(1) bond lengths show negligible deviations of 0.01 \AA from various other monomeric complexes reported in the literature [18, 21]. Complexes **4** and **5** possess two independent molecules in the unit cell (see SI, Figure S1). Only weak intermolecular C–H \cdots Hal interactions were identified. There were no signs for the close metal-metal contacts in the crystal structures of monomeric complexes **1**, **2**, **4–6**.

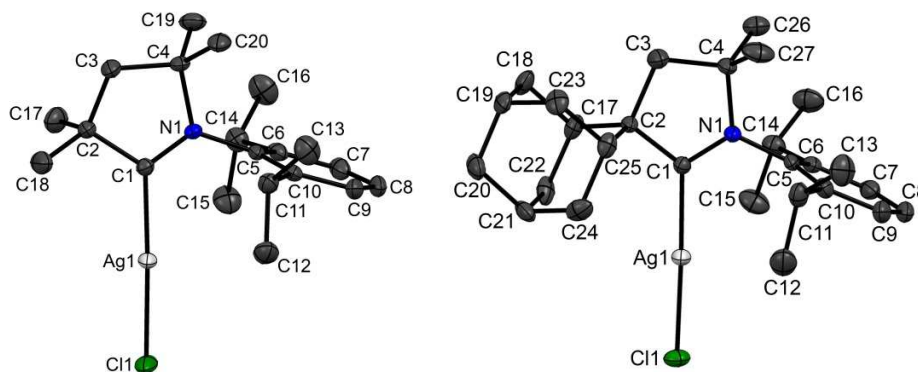


Fig. 1. Crystal structure of monomeric complexes $(^{\text{Me}2}\text{L})\text{AgCl}$ (**1**) and $(^{\text{Ad}}\text{L})\text{AgCl}$ (**4**) (independent molecule A). Ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$] with average values for two independent molecules: Ag1–C1 2.0769(18) / 2.088(2), Ag1–Cl1 2.3246(5) / 2.3168(6), C1–C2 1.514(3) / 1.522(3), C1–N1 1.295(2) / 1.303(3), C1–Ag1–Cl1 177.37(6) / 175.83(6).

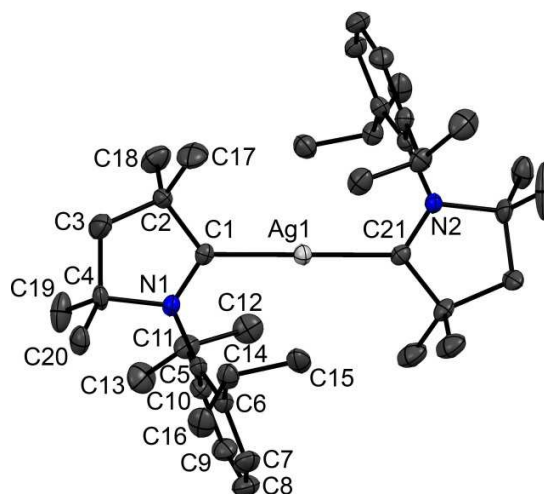


Fig. 2. The structure of cation in $[(^{\text{Me}2}\text{L})_2\text{Ag}]\text{OTf}$ (**2**). Ellipsoids are shown at 50%. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag1–C1 2.109(5), Ag1–C21 2.109(5), C1–C2 1.510(6), C1–N1 1.292(6), C1–Ag1–C21 179.7(2).

The structure of the silver chloride $(^{\text{Et}2}\text{L})\text{AgCl}$ (**3**) differs significantly. The complex forms a dimer with bridging chloride ligands (Figure 3), linked by a two-fold axis. The C1–Ag1–Cl(1) angle is $112.37(5)^\circ$. Compared to the linear complex **1**, the three-coordinate geometry of the silver atom in **3** is reflected in an elongation of the C–Ag and Ag–Cl(1) bond lengths by 0.026 and 0.1 Å, respectively. The bridging Ag–Cl1A bond length falls in the range of 2.798–2.869 Å reported for the similar dimeric structures [22]. The Ag(1)⋯Ag(1A) distance in **3** is 3.500(3) Å, rather longer than the sum of the van der Waals radii of 3.44 Å for Ag(I) [23].

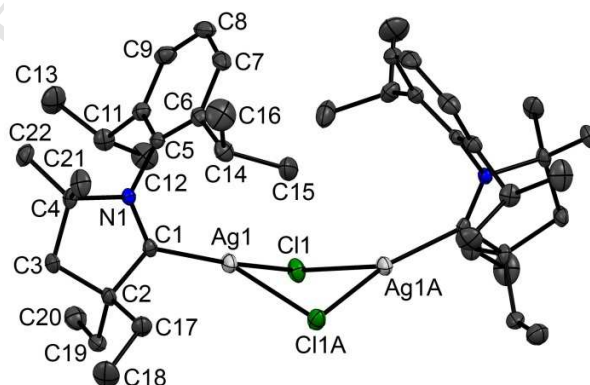


Fig. 3. Crystal structure of $[(^{\text{Et}2}\text{L})\text{AgCl}]_2$. Ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag1–C1 2.1029(19), Ag1–Cl1

2.4236(5), Ag1–C11A 2.8371(5), C1–C2 1.520(3), C1–N1 1.300(3), C1–Ag1–C11 158.93(5), C1–Ag1–C11A 112.37(5), C11–Ag1–C11A 88.368(18). Symmetry code (A): $-x + 1/2, -y + 3/2, z$.

2.3. Photophysical Properties.

We have shown recently that both the free ^{Ad}L ligands and their coinage metal complexes show pronounced photoluminescence (PL) [15]. Figure 4 shows the UV and PL spectra of ^{Me2}L and ^{Et2}L . The UV spectra of ^{Me2}L and ^{Et2}L show a π - π^* absorption at ~ 260 nm, accompanied by a low-intensity trail to about 400 nm. The free ligands are only weakly emissive at room temperature but show notable luminescence at 77K, with unstructured emissions at 452 and 435 nm for ^{Me2}L and ^{Et2}L , respectively, and lifetimes of around 12 ns.

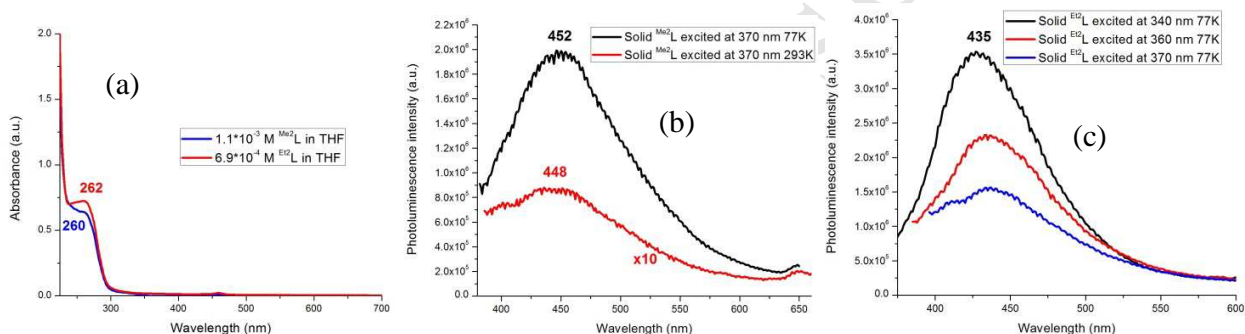


Fig. 4. UV-vis spectrum of free carbenes ^{Me2}L and ^{Et2}L in THF solution (a). Emission spectra of ^{Me2}L (b) and ^{Et2}L (c) in the solid state at 77 and 293K ($\lambda_{exc} = 370$ nm).

On complexation of the carbenes to AgCl, the low-energy absorption band near 300 nm is red-shifted in the sequence $(^{Me2}L)AgCl \leq (^{Et2}L)AgCl < (^{Ad}L)AgCl$ (Figure 5 and S2, Table 1).

Comparison of the UV-Vis spectrum of free carbenes with those of the silver halide complexes shows that this band is affected by the silver and halide atoms. In analogy to the spectra of $(^{Ad}L)MX$ (M = Cu or Au; X = Cl, Br, I) [15], this low energy band is assigned to $(\sigma + X)-\pi^*$ charge transfer [24] from the metal-halide bond to the LUMO, which has metal-carbene π^* character [15, 16]. Within the series $(^{Ad}L)AgX$ (X = Cl, Br, I) the UV absorption is essentially insensitive to the nature of X. The UV/vis spectrum of the bis(carbene) compound $[(^{Me2}L)_2Ag]OTf$ (**2**) shows a broad π - π^* band at 285 nm (Figure S2, ESI).

In contrast to the strong luminescence of copper CAAC complexes, the ^{Me2}L silver complexes **1** and **2** are non-emissive. On excitation at 340 – 360 nm, the ^{Et2}L and ^{Ad}L complexes **3–6** display featureless blue emissions, ranging from 390 to 600 nm, with λ_{max} around 430 – 440 nm (Figure 5), a blue-shift of about 20 nm compared to the analogous $(^{Ad}L)CuX$ complexes [15]. The emission

wavelengths are slightly halide-dependent and increase by *ca.* 5 nm in the sequence X = Cl > Br > I (Table 1). In THF solution complexes **3–6** are very poorly emissive. All samples showed significant photodegradation (formation of brown material) if excited with light below 310 nm.

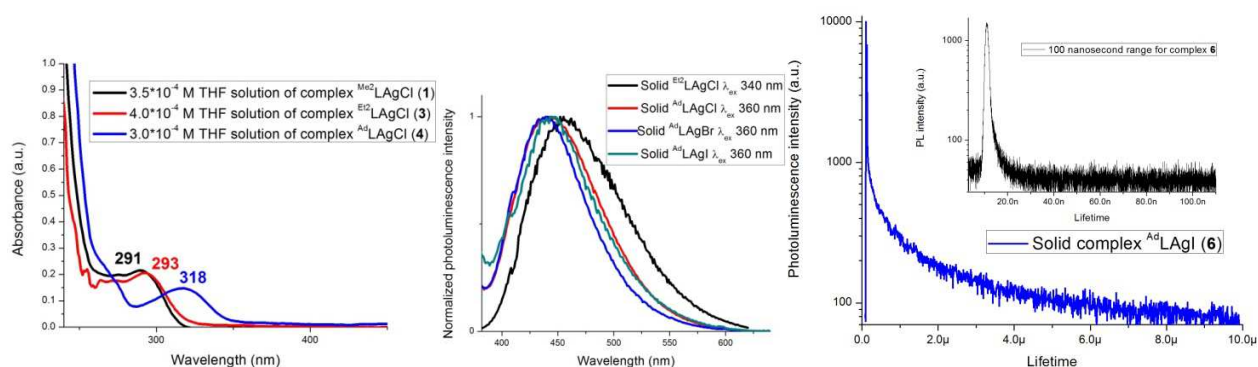


Fig. 5. Left: UV-vis spectra for THF solutions of Me_2LAgCl , $[\text{Et}_2\text{LAgCl}]_2$ and AdLAgCl . Middle: Photoluminescence spectra of Et_2LAgCl and AdLAgX (X = Cl, Br, I) in the solid state. Right: Emission kinetics of $(\text{AdL})\text{AgI}$ (**6**) on two time axes excited at 370 nm.

Table 1. Photophysical properties of silver complexes (298 K)

Complex	Absorption/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$) in deaerated THF	Solid state				
		$\lambda_{\text{em}} (\lambda_{\text{ex}})$ (nm)	τ^d (ns)	Φ^b	k_r (10^3 s^{-1}) ^c	k_{nr} (10^4 s^{-1}) ^d
$(\text{Me}_2\text{L})\text{AgCl}$ 1	291 (752)	— ^e	—	—	—	—
$[(\text{Me}_2\text{L})_2\text{Ag}]\text{OTf}$ 2	236 (3752), 285 (830) ^f	— ^e	—	—	—	—
$[(\text{Et}_2\text{L})\text{AgCl}]_2$ 3	293 (832)	454 (290–400)	3.7±0.1 ns 18.9±0.1 μs	0.05	2.7	5.1
$(\text{AdL})\text{AgCl}$ 4	318 (583)	432 (270–380)	2.7±0.1 ns 15.0±0.6 μs	0.045	3.1	6.1
$(\text{AdL})\text{AgBr}$ 5	317 (420)	437 (280–380)	4.0±0.1 ns 8.1±0.1 μs	0.05	6.3	12
$(\text{AdL})\text{AgI}$ 6	273 (1760), 315 (384)	443 (280–380)	3.3±0.1 ns 6.7±0.1 μs	0.005	0.8	15

^a Excited state lifetime, measured at λ_{max} ; ^b Quantum yields determined by using an integrated sphere; ^c radiative rate constant $k_r = \Phi/\tau$; ^d Nonradiative constant $k_{\text{nr}} = (1 - \Phi)/\tau$; ^e Poorly emissive; ^f deaerated CH_2Cl_2 solution

The emission spectra show biexponential decay, with components in both the nanosecond and microsecond region (Figure 5, Table 1). Careful comparison of photophysical properties for complexes **3–6** with those of free carbenes $^{\text{Me}2}\text{L}$, $^{\text{Et}2}\text{L}$ and $^{\text{Ad}}\text{L}$, as well as the observed photostability of (CAAC)AgX complexes, allows us to rule out the formation of free carbene as the source of fluorescence. By comparison, the emissions of the analogous ($^{\text{Ad}}\text{L}$)CuX complexes showed a strong prompt fluorescence on a sub-nanosecond time scale [25]. Further studies will be aimed at elucidating the nature of the fast and slow emission pathways in silver complexes in comparison to copper.

3. Conclusion

The reaction between free cyclic(alkyl)(amino)carbenes ($^{\text{Me}2}\text{L}$, $^{\text{Et}2}\text{L}$ and $^{\text{Ad}}\text{L}$) and silver salts represents a simple preparative protocol for the synthesis of neutral ($^{\text{R}}\text{L}$)AgCl and cationic [$^{\text{R}}\text{L}$] $_2$ Ag $^+$ silver complexes. The sterically least-demanding CAAC carbene ($^{\text{Me}2}\text{L}$) leads to a mixture of the neutral ($^{\text{Me}2}\text{L}$)AgCl and cationic [$^{\text{Me}2}\text{L}$] $_2$ Ag $^+$ products, which are easily separated. The silver complex ($^{\text{Ad}}\text{L}$)AgCl proved to be suitable as a transmetallation agent, to give the analogous copper and gold compounds in quantitative yield. On the other hand, the carbene transfer to other transition metals such as rhodium or ruthenium proved unsuccessful. Silver CAAC complexes are resistant to air, moisture, light and ligand rearrangement, as in (L)AgCl \leftrightarrow [(L) $_2$ Ag]AgCl $_2$. Depending on the steric requirements of the carbene ligands, mononuclear and binuclear structures may exist in the solid state; however, none of the complexes show close metal-metal interactions. While the $^{\text{Me}2}\text{L}$ silver complexes proved to be non-emissive, the $^{\text{Et}2}\text{L}$ and $^{\text{Ad}}\text{L}$ compounds exhibit photoluminescence which is blue-shifted by about 20 nm compared to the analogous copper complexes.

4. Experimental

General considerations

Unless stated otherwise all reactions were carried out in air. Solvents were distilled and dried as required. The carbene ligands $^{\text{Me}2}\text{L}$, $^{\text{Et}2}\text{L}$, ($^{\text{Ad}}\text{L}$), were obtained according to literature procedures [26]. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded using a Bruker Avance DPX-300 MHz NMR

spectrometer. ^1H NMR spectra (300.13 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (75.47 MHz) were referenced to CD_2Cl_2 at δ 5.32 (^{13}C , δ 53.84) and CDCl_3 at δ 7.26 (δ ^{13}C 77.16) ppm. ^{19}F NMR spectra (282.4 MHz) were referenced externally to CFCl_3 and internally to C_6F_6 (δ_{F} -164.9). UV-visible absorption spectra were recorded using a Perkin-Elmer Lambda 35 UV/vis spectrometer. Photoluminescence measurements were recorded on a Perkin Elmer LS55 Fluorescence Spectrometer with a solids mount attachment where appropriate. Time resolved fluorescence data were collected on a time-correlated single photon counting (TCSPC) Fluorolog Horiba Jobin Yvon spectrofluorimeter using Horiba Jobin Yvon DataStation v2.4 software. A NanoLED of 370 nm was used as excitation source, with an instrument response function width of 2 ns. The collected data were analysed using a Horiba Jobin Yvon DAS6 v6.3 software.

Synthesis of $(^{\text{Me}2}\text{L})\text{AgCl}$ (1)

An oven-dried 100-mL Schlenk flask was equipped with a stirring bar and charged with $(^{\text{Me}2}\text{L})$ (0.63 g, 2.2 mmol) and AgCl (0.314 g, 2.2 mmol) under an argon atmosphere. Anhydrous THF (20 mL) was added, and the resulting suspension was stirred overnight in the absence of light. The solvent was removed; the residue was washed with hexane, dissolved in CH_2Cl_2 and filtered through short pad of silica (1.0 cm). The colourless filtrate was concentrated to give a white solid (0.9 g), which according to NMR spectroscopy is a mixture of $(^{\text{Me}2}\text{L})\text{AgCl}$ and $[(^{\text{Me}2}\text{L})\text{Ag}]\text{AgCl}_2$ in a 4:1 molar ratio. The mixture was separated by column chromatography on a silica gel (5×2 cm). The neutral complex $(^{\text{Me}2}\text{L})\text{AgCl}$ was eluted first with THF (white solid, 0.52 g, 55 % yield), while the ionic product was eluted with CH_2Cl_2 (white solid, 0.13 g, 14 % yield). ^1H NMR (300 MHz, CDCl_3) for $(^{\text{Me}2}\text{L})\text{AgCl}$: δ 7.40 (t, $J = 7.6$ Hz, 1H, CH-aromatic), 7.24 (d, $J = 7.6$ Hz, 2H, CH-aromatic), 2.75 (sept, $J = 6.7$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.05 (s, 2H, CH_2), 1.43 (s, 6H, 2CH_3), 1.35 (s, 6H, 2CH_3), 1.29 (d, $J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$) overlapped with 1.27 (d, $J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 255.7 (dd, $J_{\text{C-109Ag}} = 245.9$ Hz, $J_{\text{C-107Ag}} = 213.0$ Hz, $\text{C}_{\text{carbene}}$), 145.0 (*o*-C), 134.3 (d, $J_{\text{C-Ag}} = 2.9$ Hz, C_{ipso}), 130.0 (*p*-CH), 125.0 (*m*-CH), 83.3 (d, $J_{\text{C-Ag}} = 12.7$ Hz, C_q), 54.7 (d, $J_{\text{C-Ag}} = 11.3$ Hz, C_q), 49.1 (d, $J_{\text{C-Ag}} = 4.8$ Hz, CH_2), 29.4 (CH_3), 29.1 (CH_3), 28.4 (CH_3), 27.5 (CH), 22.6 (CH_3) ppm. Anal. Calcd. for $\text{C}_{20}\text{H}_{31}\text{NAgCl}$ (427.12): C, 56.02; H, 7.29; N, 3.27. Found: C, 56.36; H, 7.47; N, 3.20.

Synthesis of $[(^{\text{Me}2}\text{L})_2\text{Ag}]\text{OTf}$ (2)

An oven-dried 100-mL Schlenk flask was equipped with a stirring bar and charged with $^{\text{Me}2}\text{L}$ (0.445 g, 1.6 mmol) and AgOTf (0.2 g, 0.78 mmol) under an argon atmosphere. Anhydrous THF (20 mL)

was added, and the resulting suspension was stirred overnight. After removal of the solvent, the residue was washed with hexane and filtered through a short pad of silica (1.0 cm) with CH_2Cl_2 . The colourless filtrate was concentrated and hexane was added to precipitate the silver complex. Solvents were decanted and the residue dried in vacuum. Yield: 0.6 g (0.72 mmol, 92 %). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.41 (t, $J = 7.4$ Hz, 1H, CH-aromatic), 7.23 (d, $J = 7.4$ Hz, 2H, CH-aromatic), 2.63 (sept, $J = 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.00 (s, 2H, CH_2), 1.31 (s, 6H, 2 CH_3), 1.25 (d, $J = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.17 (s, 6H, 2 CH_3), 0.9 (d, $J = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ 255.9 (dd, $J_{\text{C-109Ag}} = 183.5$ Hz, $J_{\text{C-107Ag}} = 159.6$ Hz, C carbene), 144.6 (*o*-C), 134.3 (C_{ipso}), 130.0 (*p*-CH), 125.0 (*m*-CH), 83.6 (d, $J_{\text{C-Ag}} = 9.5$ Hz, C_q), 54.7 (d, $J_{\text{C-Ag}} = 9.0$ Hz, C_q), 48.6 (d, $J_{\text{C-Ag}} = 3.5$ Hz, CH_2), 28.9 (CH_3), 28.8 (CH_3), 28.0 (CH_3), 27.0 (CH), 22.2 (CH_3) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2): δ -78.91 ppm. Anal. Calcd. for $\text{C}_{41}\text{H}_{62}\text{N}_2\text{AgF}_3\text{O}_3\text{S}$ (826.35): C, 59.48; H, 7.55; N, 3.38. Found: C, 59.31; H, 7.63; N, 3.46.

Synthesis of (Et^2L)AgCl (3).

An oven-dried 100-mL Schlenk flask was equipped with a stirring bar and charged with (Et^2L) (0.25 g, 0.8 mmol) and AgCl (0.115 g, 0.8 mmol) under argon atmosphere. Anhydrous THF (20 mL) was added, and the resulting suspension was stirred overnight. The solvent was removed; the residue was washed with hexane and filtered through short pad of silica (1.0 cm) with CH_2Cl_2 . The colourless filtrate was concentrated and hexane was added to precipitate the silver complex, solvents were decanted and the residue dried in vacuum. Yield: 0.311 g (0.68 mmol, 85 %). ^1H NMR (300 MHz, CDCl_3): δ 7.39 (t, $J = 7.3$ Hz, 1H, CH-aromatic), 7.24 (d, $J = 7.3$ Hz, 2H, CH-aromatic), 2.80 (sept, $J = 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.00 (s, 2H, CH_2), 1.95–1.68 (m, $J = 7.4$ Hz, 4H, CH_2CH_3), 1.37 (s, 6H, 2 CH_3), 1.29 (d, $J = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$) overlapped with 1.26 (d, $J = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$) 1.03 (t, $J = 7.4$ Hz, 6H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 256.4 (dd, $J_{\text{C-109Ag}} = 246$ Hz, $J_{\text{C-107Ag}} = 214$ Hz, C carbene), 145.0 (*o*-C), 134.9 (d, $J_{\text{C-Ag}} = 3.7$ Hz, C_{ipso}), 130.0 (*p*-CH), 125.0 (*m*-CH), 82.8 (d, $J_{\text{C-Ag}} = 13.5$ Hz, C_q), 62.9 (d, $J_{\text{C-Ag}} = 10.6$ Hz, C_q), 41.3 (d, $J_{\text{C-Ag}} = 4.9$ Hz, CH_2), 31.0 (CH_2), 29.5 (CH_3), 29.2 (CH_3), 27.5 (CH), 22.5 (CH_3), 9.5 (CH_3) ppm. Anal. Calcd. for $\text{C}_{22}\text{H}_{35}\text{NAgCl}$ (456.85): C, 57.84; H, 7.72; N, 3.07. Found: C, 57.65; H, 7.51; N, 3.11.

Synthesis of (Ad^dL)AgCl (4).

The compound was prepared as described for (Et^2L)AgCl from Ad^dL (0.603 g, 1.6 mmol) and AgCl (0.228 g, 1.6 mmol) as a white solid. Yield: 0.781 g (1.5 mmol, 94 %). ^1H NMR (300 MHz, CDCl_3): δ 7.41 (t, $J = 7.5$ Hz, 1H, aryl), 7.25 (d, $J = 7.5$ Hz, 2H, aryl), 3.43 (d, $J = 12.6$ Hz, 2H, CH_2), 2.77

(sept, $J = 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.24-1.77 (m, 14H, adamantyl CH and CH_2), 1.36 (s, 6H, CMe_2), 1.32 (d, $J = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.30 (d, $J = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ 262.5 (dd, $J_{\text{C-109Ag}} = 245$ Hz, $J_{\text{C-107Ag}} = 212$ Hz, C carbene), 145.4 (*o*-C), 136.5 (*ipso*-C), 130.1 (*p*-CH), 125.4 (*m*-CH), 79.9 (d, $J_{\text{C-Ag}} = 12.3$ Hz, C_q), 64.8 (d, $J_{\text{C-Ag}} = 12.5$ Hz, C_q), 48.1 (d, $J_{\text{C-Ag}} = 6.0$ Hz, CH_2), 39.0 (CH_2), 37.5 (CH), 35.7 (d, $J_{\text{C-Ag}} = 1.8$ Hz, CH_2), 34.7 (CH_2), 29.7 (CH), 29.3, 28.3, 27.6, 27.2, 22.9 (CH_3) ppm. Anal. Calcd. for $\text{C}_{27}\text{H}_{39}\text{NAgCl}$ (520.93): C, 62.25; H, 7.55; N, 2.69. Found: C, 62.09; H, 7.36; N, 2.77.

Synthesis of ($^{\text{Ad}}\text{L}$)AgBr (5).

The compound was prepared as described for ($^{\text{Et}2}\text{L}$)AgCl from $^{\text{Ad}}\text{L}$ (0.368 g, 0.98 mmol) and AgBr (0.183 g, 0.98 mmol) as a white solid. Yield: 0.373 g (0.65 mmol, 66 %). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.47 (t, $J = 7.6$ Hz, 1H, aryl), 7.31 (d, $J = 7.6$ Hz, 2H, aryl), 3.39 (d, $J = 11.9$ Hz, 2H, CH_2), 2.80 (sept, $J = 6.6$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.26-1.78 (m, 14H, adamantyl CH and CH_2), 1.36 (s, 6H, CMe_2), 1.30 (d, $J = 6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ 263.5 (dd, $J_{\text{C-109Ag}} = 241$ Hz, $J_{\text{C-107Ag}} = 209$ Hz, C carbene), 145.3 (*o*-C), 136.3 (d, $J_{\text{C-Ag}} = 2.7$ Hz, *ipso*-C), 130.1 (*p*-CH), 125.3 (*m*-CH), 79.8 (d, $J_{\text{C-Ag}} = 12.9$ Hz, C_q), 64.8 (d, $J_{\text{C-Ag}} = 11.1$ Hz, C_q), 48.0 (d, $J_{\text{C-Ag}} = 6.0$ Hz, CH_2), 38.9 (CH_2), 37.5 (CH), 35.7 (d, $J_{\text{C-Ag}} = 2.1$ Hz, CH_2), 34.6 (CH_2), 29.6 (CH), 29.2, 28.2, 27.5, 27.3, 22.9 (CH_3) ppm. Anal. Calcd. for $\text{C}_{27}\text{H}_{39}\text{NAgBr}$ (565.39): C, 57.36; H, 6.95; N, 2.48. Found: C, 57.11; H, 6.73; N, 2.55.

Synthesis of ($^{\text{Ad}}\text{L}$)AgI (6).

The compound was prepared as described for ($^{\text{Et}2}\text{L}$)AgCl from $^{\text{Ad}}\text{L}$ (0.368 g, 0.98 mmol) and AgI (0.23 g, 0.98 mmol) as a white solid. Yield: 0.464 g (0.76 mmol, 77 %). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.47 (t, $J = 7.9$ Hz, 1H, aryl), 7.31 (d, $J = 7.9$ Hz, 2H, aryl), 3.40 (d, $J = 12.1$ Hz, 2H, CH_2), 2.81 (sept, $J = 7.0$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.26-1.78 (m, 14H, adamantyl CH and CH_2), 1.37 (s, 6H, CMe_2), 1.31 (d, $J = 7.0$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$) overlapped with 1.30 (d, $J = 7.0$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ 265.3 (dd, $J_{\text{C-109Ag}} = 231$ Hz, $J_{\text{C-107Ag}} = 200$ Hz, C carbene), 145.4 (*o*-C), 136.3 (d, $J_{\text{C-Ag}} = 2.3$ Hz, *ipso*-C), 130.0 (*p*-CH), 125.3 (*m*-CH), 79.9 (d, $J_{\text{C-Ag}} = 11.5$ Hz, C_q), 64.9 (d, $J_{\text{C-Ag}} = 11.7$ Hz, C_q), 48.1 (d, $J_{\text{C-Ag}} = 5.5$ Hz, CH_2), 38.9 (CH_2), 37.5 (CH), 35.7 (d, $J_{\text{C-Ag}} = 2.3$ Hz, CH_2), 34.6 (CH_2), 29.7 (CH), 29.2, 28.2, 27.6, 27.4, 23.0 (CH_3) ppm. Anal. Calcd. for $\text{C}_{27}\text{H}_{39}\text{NAgI}$ (611.12): C, 52.96; H, 6.42; N, 2.29. Found: C, 52.73; H, 6.15; N, 2.21.

Transmetallation with CuCl

A 50-mL round-bottom flask was equipped with a stirring bar and charged with (^{Ad}L)AgCl (0.11 g, 0.21 mmol) and CuCl (0.025 g, 0.25 mmol) under air. Dry CH₂Cl₂ (15 mL) was added, and the resulting suspension was stirred overnight. The resulted suspension was filtered through a short pad of Celite (3.0 cm). The colourless filtrate was evaporated, washed with hexane. The white residue was dried in vacuum. Yield: 0.099 g (0.208 mmol, 99 %). ¹H and ¹³C NMR spectra are identical to those previously reported [15].

Transmetallation with (Me₂S)AuCl

Prepared as described for (^{Ad}L)CuCl from (^{Ad}L)AgCl (0.10 g, 0.19 mmol) and (Me₂S)AuCl (0.056 g, 0.19 mmol) as a white solid. Yield: 0.113 g (0.186 mmol, 98 %). ¹H and ¹³C NMR spectra are identical to those previously reported [19].

X-ray crystallography

Crystals suitable for X-ray diffraction were obtained by layering CH₂Cl₂ solutions with hexanes. Compounds (^{Ad}L)AgX (X = Cl and Br) crystallize with two independent molecules in the unit cell. Compounds (^{Ad}L)AgX (X = Br and I) and [(^{Me}L)₂Ag]OTf crystallize as solvates with CH₂Cl₂ molecule. For complex (^{Ad}L)AgI·CH₂Cl₂ the CH₂Cl₂ molecule was disordered over two positions with equal occupancies linked by a center of inversion. The CH₂ group (atom C23) was disordered over two positions with equal occupancies for complex [(^{Me}L)₂Ag]OTf·CH₂Cl₂. Crystals were mounted in oil on glass fibres and fixed on the diffractometer in a cold nitrogen stream. Data were collected at 140 K using Oxford Diffraction Xcalibur-3/Sapphire3-CCD (complexes (^{Me}L)AgCl, [(^{Me}L)₂Ag]OTf) and (^{Ad}L)AgCl) and Rigaku Oxford Diffraction XtaLAB Synergy/Dualflex/HyPix diffractometers, using graphite monochromated Mo K_α radiation (λ = 0.71073 Å). Data were processed using the CrystAlisPro-CCD and –RED software [27]. The principal crystallographic data and refinement parameters are listed in Table S1. The structures were solved by direct methods and refined by the full-matrix least-squares against F² in an anisotropic (for non-hydrogen atoms) approximation. All hydrogen atom positions were refined in isotropic approximation in “riding” model with the U_{iso}(H) parameters equal to 1.2 U_{eq}(C_i), for methyl groups equal to 1.5 U_{eq}(C_{ii}), where U(C_i) and U(C_{ii}) are respectively the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded. All calculations were performed using the SHELXTL software [28].

Acknowledgement

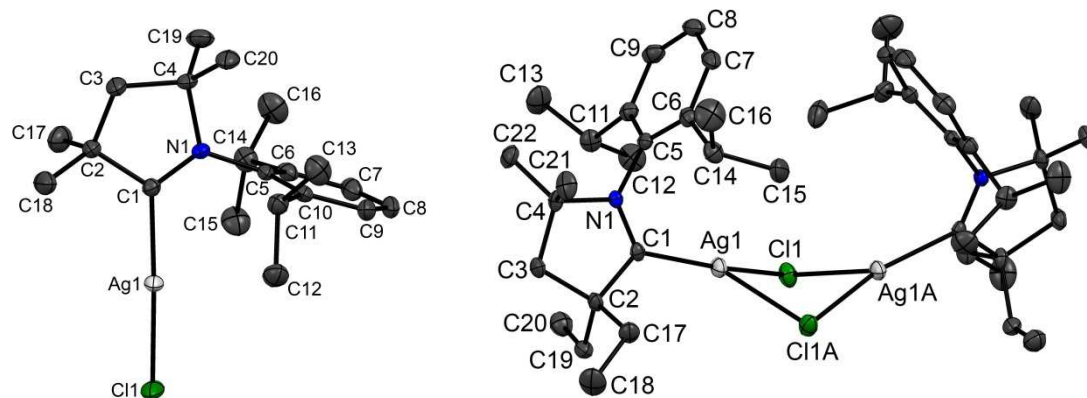
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Appendix A. Supplementary material

CCDC 1523753-1523758 contain the supplementary crystallographic data for this paper, see Table S1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jorgchem.XXXX>

Synthesis, Structures and Photoluminescence Properties of Silver Cyclic(alkyl)(amino)-carbene Complexes

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Silver complexes with cyclic(alkyl)(amino) carbene ligands can be mononuclear or binuclear in the solid state. Complexes with sterically hindered CAAC ligands show blue photoluminescence.

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Highlights

- Facile synthesis of silver complexes of cyclic (alkyl)(amino) carbene (CAAC) ligands is described.
- Surprisingly, ethyl-substituted CAAC leads to the formation of a chloride-bridged dimer.
- Remarkably for silver carbene complexes, the new compounds are stable to light and show no evidence of ligand dissociation.
- The complexes show blue photoluminescence, which is blue-shifted by 20 nm compared to copper analogues.