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Mono- and Dinuclear Ag(I), Au(I), and Au(III) Metallamacrocycles Containing *N*-Heterocyclic Dicarbene Ligands

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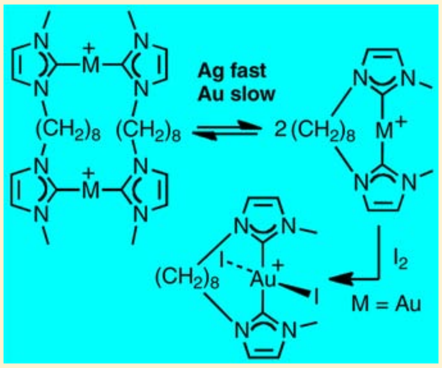
Supporting Information

ABSTRACT: Ag(I) dicarbene complexes $[Ag_m(L^n)_m]X_m$ ($L^n = Im^{Me}(CH_2)_nIm^{Me}$, Im^{Me} = *N*-methylimidazol-*N*-yl-2-ylidene; $n = 3$, X = PF_6, $m = 2$; $n = 6–8, 10$, X = $AgBr_2$, $m = 1, 2$) were prepared by reacting Ag_2O with 1 equiv of the corresponding bisimidazolium salt $[H_2L^n]A_2$ (A = PF_6, Br). The dibromoargentates react with 1 equiv of AgTfO to afford $[Ag_m(L^n)_m](TfO)_m$ ($m = 1, 2$). The room temperature transmetalation reaction of $[Ag_m(L^n)_m][AgBr_2]_m$ ($n = 3, 5, 6–8, 10$) with $[AuCl(SMe_2)]$ and AgTfO (L^n:Au:TfO = 1:1:1) affords $[Au_2(\mu\text{-}L^n)_2](TfO)_2$ ($n = 3, 5, 10$), or mixtures of $[Au(\kappa^2\text{-}L^n)]TfO$ (main product for $n = 7$) and $[Au_2(\mu\text{-}L^n)_2](TfO)_2$ (main product for $n = 6, 8$). At room temperature, the equilibrium between $[M_2(\mu\text{-}L^n)_2](TfO)_2$ and $[M(\kappa^2\text{-}L^n)]TfO$ is fast for M = Ag, but slow for M = Au, in the NMR time scale. When $n \geq 7$ and M = Ag or Au, the equilibrium is shifted toward the mononuclear complexes in the order 8 > 10 > 7, which proves that the $(CH_2)_8$ linker has the optimal length for *trans* chelation. Correspondingly, the high-temperature metalation of $[H_2L^n]Br_2$ ($n = 8, 10$) with 1 equiv of $[AuCl(SMe_2)]$ and excess of NaAcO, affords $[Au(\kappa^2\text{-}L^n)]Br$ with a small amount of $[Au_2(\mu\text{-}L^n)_2]Br_2$. If AgTfO is added to the reaction mixture, $[Au(\kappa^2\text{-}L^8)]_2[AgBr_3]$ is isolated instead of the desired triflate, which can be obtained by reacting the mixture of $[Au(\kappa^2\text{-}L^8)]Br$ and $[Au_2(\mu\text{-}L^8)_2]Br_2$ with AgTfO. $[Au(\kappa^2\text{-}L^{10})]TfO$ was isolated after thermal conversion of $[Au_2(\mu\text{-}L^{10})_2](TfO)_2$. $[Au(\kappa^2\text{-}L^8)]TfO$ reacts with I_2 to give *trans*-$[AuI_2(\kappa^2\text{-}L^8)]TfO$, which is the first Au(III) complex containing a *trans*-spanning bidentate ligand. We have determined the crystal structures of complexes $[Ag_2(\mu\text{-}L^3)_2](PF_6)_2$, $[Ag(\kappa^2\text{-}L^7)]TfO$, $[Au_2(\mu\text{-}L^3)_2](TfO)_2$, $[Au(\kappa^2\text{-}L^8)]Br$, $[Au(\kappa^2\text{-}L^8)]_2[AgBr_3]$, and *trans*-$[AuI_2(\kappa^2\text{-}L^8)]TfO$.

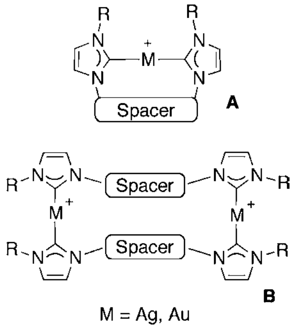


INTRODUCTION

Homoleptic NHC (NHC = *N*-heterocyclic carbene) complexes of Ag(I) or Au(I)[1−4] have attracted considerable interest because of their applications as catalysts,[5] liquid crystals,[6] metallogelators,[7] luminophores,[8−10] and potential therapeutic agents.[11] They are easy to prepare, stable in air and protic media,[12] and compatible with most of the functional groups.

Complexes with dicarbene ligands (Chart 1) have received special attention because they show promising antitumor[13,14] and antimicrobial[15] activities. In addition, some dinuclear complexes show intramolecular metallophilic interactions, which influence their emissive behavior.[8,10,16,17] The silver complexes have been used as dicarbene-transfer agents in the synthesis of Rh,[18] Pd,[19−24] and Cu[25] catalysts. Complexes of this type are generally synthesized from stable bisimidazolium salts, which can be easily obtained by reacting the corresponding imidazol and dihalo-derivative.[20,26] Ag(I) dicarbene complexes are usually obtained by reacting the bisimidazolium salt with Ag_2O[8,9,16,18−22,25,27−34] or Ag_2CO_3,[28] and those of Au(I) by carbene-transfer reactions from the corresponding Ag(I) derivatives,[9,17,27,30,35] or by reacting the bisimidazolium salt with an AuCl derivative in the presence of a base.[8−10,34,36] The reaction of the in situ generated free dicarbene with a Ag(I) or Au(I) precursor has been reported only in two cases.[37,38]

Chart 1. Mono- and Dinuclear Dicarbene Ag(I) and Au(I) Metallacycles



Complexes of Ag(I) or Au(I) with dicarbene ligands (L) generally present metallamacrocyclic structures (Chart 1) of the type $[M(\kappa^2\text{-}L)]^+$ (**A**) or $[M_2(\mu\text{-}L)_2]^{2+}$ (**B**), with the exception

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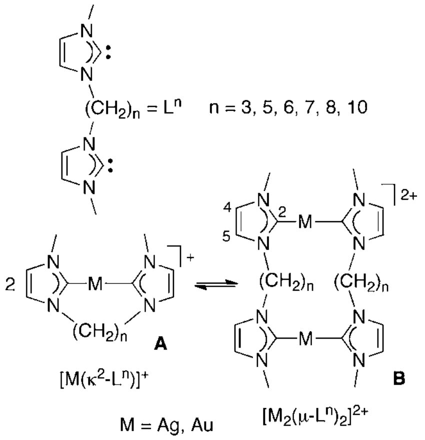
of a few polymeric compounds.[18,29] Whereas many dinuclear metallacycles have been prepared using different types of dicarbene ligands,[8−10,15,17−21,25,27,28,30−37,39] the mononuclear complexes are scarce,[13,24,38,40,41] in particular, those of Au(I).[41] Dinuclear Ag(I) or Au(I) dicarbene complexes with one- to five-membered $(CH_2)_n$ spacers have been reported,[9,10,18,19,22,25,28−32,36,39] and some of these Au(I) compounds were oxidized with halogens or $PhICl_2$ to afford Au(III)/Au(III), Au(I)/Au(III), or Au(II)/Au(II) dinuclear metallacycles.[9,42,43]

Observation of both mono- and dinuclear dicarbene metallacycles in the same reaction is very unusual,[44,45] and the exchange between them has never been studied. In the present work, we have isolated both types of metallacycles for the first time using a family of dicarbene ligands with $(CH_2)_n$ spacers of various lengths (Scheme 1). This has allowed us to relate n with the stability of each type of metallacycle and observe equilibria between them. In addition, an unprecedented Au(III) metallacycle containing a *trans*-spanning dicarbene ligand has been prepared and structurally characterized.

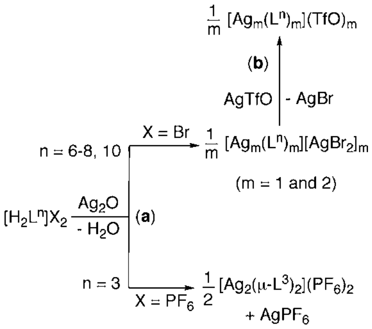
Scheme 1



RESULTS AND DISCUSSION

Synthesis of Ag(I) Dicarbene Complexes $[Ag_m(L^n)_m]X_m$ ($X = AgBr_2$, TfO, $n = 6–8, 10$, $m = 1, 2$; $X = PF_6$, $n = 3$, $m = 2$). The reaction of bisimidazolium salts $[H_2L^n]Br_2$ ($n = 6−8$, 10) with 1 equiv of Ag_2O gives Ag(I) dicarbene bromides $[Ag_m(L^n)_m][AgBr_2]_m$ (m = 1, 2) in good yields (Scheme 2, method (**a**)). Similarly, $[H_2L^3](PF_6)_2$ reacts with an excess of Ag_2O to give $[Ag_2(\mu\text{-}L^3)_2](PF_6)_2$. Triflate salts $[Ag_m(L^n)_m](TfO)_m$ ($n = 6−8$, 10; m = 1, 2) were obtained by reacting the corresponding Ag(I) dicarbene bromide with 1 equiv of AgTfO (Scheme 2, method (**b**)). We have reported recently the synthesis of $[Ag_2(\mu\text{-}L^3)_2][AgBr_2]_2$,[46] and Cavell that of $[Ag_2(\mu\text{-}L^5)_2][AgBr_2]_2$,[20] using method (**a**). Tubaro and co-workers have reported very recently the preparation of $[Ag_2(\mu\text{-}L^3)_2](PF_6)_2$ by reaction of $[H_2L^3]Br_2$, Ag_2O, and NH_4PF_6 in water.

Scheme 2



All Ag(I) carbene complexes prepared are air-stable solids which darken very slowly under the light. The dicarbene bromides are partially soluble or insoluble in common solvents except for $n = 8$ (soluble in dimethylsulfoxide (DMSO)) or 10 (soluble in DMSO and CH_2Cl_2). This low solubility could be attributed to the formation of polymeric structures through intermolecular argentophilic or Ag···Br−Ag interactions.[2,3] In contrast, the hexafluorophosphate and the triflates, except $[Ag_m(L^6)_m](TfO)_m$, are soluble in MeCN and CH_2Cl_2.

For compounds with n = 7 or 10, the C, H, and N percentages determined by combustion analysis varied for different preparations according to the formula $[Ag(L^n)][AgBr_2]_{1-x}Br_x$, x being typically around 0.1 (see Experimental Section). The NMR spectra of samples with different x values are identical. Such nonstoichiometric behavior has been reported before in Ag(I) NHC halides, and is attributed to partial coprecipitation of Ag(I) halides during the reaction.[1,47,48]

Structure of Ag(I) Dicarbene Complexes $[Ag_m(L^n)_m]X_m$ ($n = 6–8, 10$; $m = 1, 2$; $X = AgBr_2$, TfO). The nature of Ag(I) NHC halides in solution is often undetermined because of the presence of various species involved in fast equilibria at room temperature.[2] Variable temperature NMR studies have provided evidence for ligand-exchange equilibria between neutral monocarbene complexes [AgX(NHC)] and ion pairs $[Ag(NHC)_2][AgX_2]$ (X = halogen) through an associative mechanism.[48−50] However, there are no precedents for similar studies involving dicarbene complexes.

The room temperature ^1H and $^{13}C\{^1H\}$ NMR spectra of the Ag(I) dicarbene complexes in D_6-DMSO ($n = 6−8$, 10, $X = AgBr_2$; $n = 6$, X = TfO) or CD_3CN (n = 7, 8, 10, X = TfO) show only one set of signals corresponding to a symmetrically bonded dicarbene ligand. The $^{13}C\{^1H\}$ NMR spectra show a singlet between 178.9 and 180.0 ppm, which proves the Ag−(NHC) coordination.[1,2,48] The lack of C−Ag coupling and the signal shifting of the ^1H spectra on varying the concentration (Supporting Information, Figures S1 and S2) suggest a fast exchange of ligands. Compounds $[Ag_m(L^n)_m](TfO)_m$ (n = 7, 8, 10) give two sets of broad signals at room temperature in CD_2Cl_2, which sharpen on lowering the temperature. Thus, at −60 °C, their C−Ag signals appear as two pairs of doublets (Figure 1), whose $^1J_{AgC}$ values ($J_{^{107}AgC}$, 179.3−182.5 Hz; $^1J_{^{109}AgC}$, 207.1−210.4 Hz) are typical for Ag(I) bis(imidazol-2-ylidene) complexes,[1,2,48,51] and suggest the presence of the cationic complexes $[Ag(\kappa^2\text{-}L^n)]^+$ and $[Ag_2(\mu\text{-}L^n)_2]^{2+}$ in solution (Scheme 3). Similar low-temperature NMR studies in the other Ag(I) dicarbene complexes were hampered by the low solubility of $[Ag_m(L^n)_m][AgBr_2]_m$ ($n = 6−8$) and $[Ag_m(L^6)_m](TfO)_m$, or by the broadening of the NMR spectra of $[Ag_m(L^{10})_m][AgBr_2]_m$ on lowering the temperature (−60 °C, CD_2Cl_2).

The resonances of both components of $[Ag_m(L^7)_m](TfO)_m$ were assigned by means of a Diffusion Ordered Spectroscopy experiment (DOSY).[52] Thus, the signals of the slower-diffusing component were attributed to the greater macrocycle $[Ag_2(\mu\text{-}L^7)_2]^{2+}$ and the others to $[Ag(\kappa^2\text{-}L^7)]^+$ (Supporting Informa-

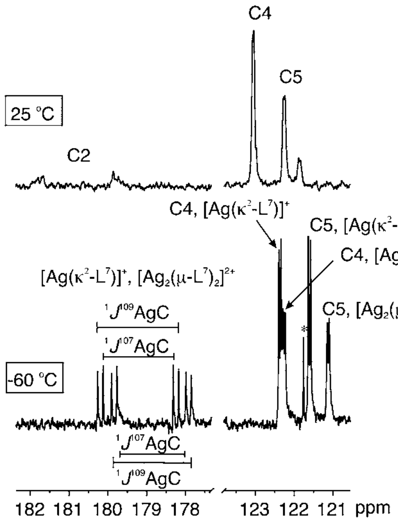
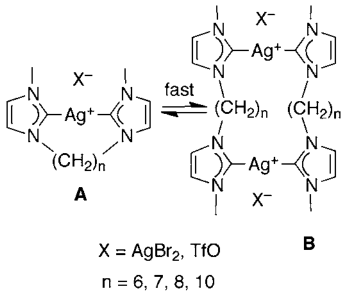


Figure 1. Resonances of the imidazole carbons in the $^{13}C\{^1H\}$ NMR spectra (CD_2Cl_2) of $[Ag(\kappa^2\text{-}L^7)]TfO$ and $[Ag_2(\mu\text{-}L^7)_2](TfO)_2$. The peak marked with an asterisk corresponds to the quadruplet of $CF_3SO_3^-$.

Scheme 3. Proposed Solution Equilibria for Ag(I) Dicarbene Complexes



tion, Figure S3).[53] The X-ray structure of the latter, which is the main component of the mixture, confirmed this assignment (see below). By extension, the signals of the mono- and dinuclear macrocycles in the NMR spectra of $[Ag_m(L^n)_m](TfO)_m$ (n = 8, 10) were assigned, and their proportion was determined (the mononuclear:dinuclear molar ratios are 5.3, 49 and 6.8, for n = 7, 8, 10, respectively; measured at 22 °C, for concentrations in the range 0.02−0.025 mol/L). Thus, $[Ag(\kappa^2\text{-}L^n)]^+$ is the major component of the mixture for n = 7, 8, and 10, in agreement with the positive change of entropy of the process $[Ag_2(\mu\text{-}L^n)_2]^{2+} \rightarrow 2\ [Ag(\kappa^2\text{-}L^n)]^+$. On decreasing the temperature to −60 °C, the mono- to dinuclear molar ratios decrease significantly (1.7, 10.1, and 1.9, respectively), which informs on the endothermic[54] nature of this process.

In agreement with the previous data, the (+)ESI-MS spectra of $[Ag_m(L^n)_m]X_m$ (X = $AgBr_2$ or TfO) intercept mainly mononuclear cations $[Ag(\kappa^2\text{-}L^n)]^+$ (n = 6−8, 10), whereas the dinuclear cations were detected with very low abundances.[55] In the (−)-ESI-MS spectra of the dibromoargentates and triflates, the anions $[AgBr_2]^-$, Br^-, and $[AgBr(CN)]^-$, or TfO^- and $[Ag(CN)_2]^-$, were detected, respectively. The unexpected formation of cyano complexes could take place by reaction of the Ag(I) complexes with the MeCN used as carrier solvent.[56]

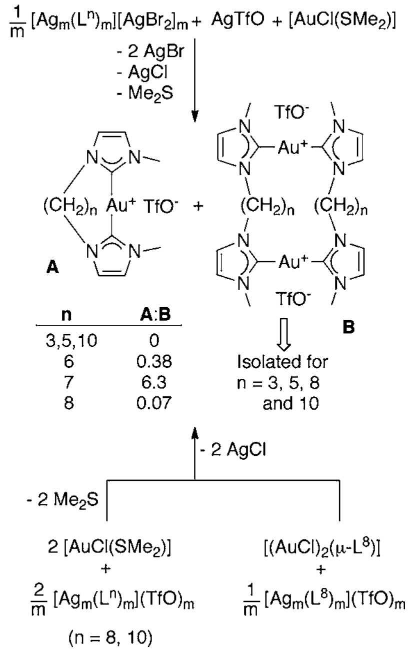
The equivalent conductivities of the dibromoargentates (59−65 Ω^{-1} cm^2 equiv^{-1}) and triflates (58−75 Ω^{-1} cm^2 equiv^{-1}) are at the lower limit of the expected range for a 1:1 electrolyte[57] (65−90 Ω^{-1} cm^2 equiv^{-1} in dimethylformamide (DMF)),[58] in agreement with their ionic nature and, likely, the formation of ion pairs in solution.

In summary, compounds $[Ag_m(L^n)_m]X_m$ (X = $AgBr_2$ or TfO; $n \geq 6$; m = 1, 2) exist in solution as a mixture of metallamacrocyclic complexes **A** and **B** (Scheme 3), which are in fast exchange at room temperature. The **A**:**B** proportion was determined for the most soluble members of the series (X = TfO and $n \geq 7$), where the equilibrium is shifted toward the mononuclear macrocycle **A**.

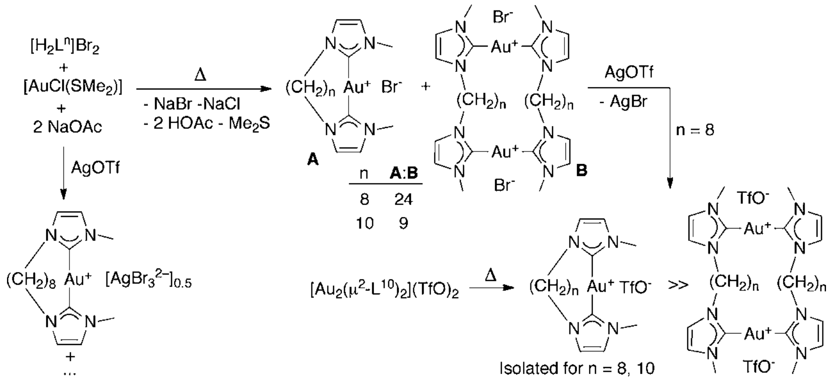
Structure of $[Ag_2(\mu\text{-}L^3)_2](PF_6)_2$. The structure of this complex is based, in solution, on the ^1H and $^{13}C\{^1H\}$ NMR spectra in CD_3CN at room temperature and −20 °C and, in the solid state, on its crystal structure (see below). This is also the proposed structure by the authors who first prepared it,[25] and the expected in agreement with its short $(CH_2)_n$ spacer. In the $^{13}C\{^1H\}$ NMR spectrum, the signal of the silver-bound carbon is not visible at room temperature, but at −20 °C it appears as a pair of doublets at 180.9 ppm ($^1J_{^{107}AgC}$ = 179, $^1J_{^{109}AgC}$ = 206 Hz).

Synthesis of Au(I) Dicarbene Complexes $[Au(\kappa^2\text{-}L^n)]X$ and $[Au_2(\mu\text{-}L^n)_2]X_2$ (X = TfO, Br, $[AgBr_3]_{0.5}$). The room temperature transmetalation reaction of $[Ag_m(L^n)_m][AgBr_2]_m$ (n = 3, 5−8, 10) with 1 equiv of $[AuCl(SMe_2)]$ and AgTfO in MeCN (Scheme 4) afforded $[Au_2(\mu\text{-}L^n)_2](TfO)_2$ (n = 3, 5, 10), or mixtures of $[Au(\kappa^2\text{-}L^n)]TfO$ (main product for n = 7) and $[Au_2(\mu\text{-}L^n)_2](TfO)_2$ (main product for n = 6, 8) complexes. As the exchange between the mono- and dinuclear gold(I) complexes is slow at room temperature (see below), we attempted to separate these mixtures by crystallization. However, only $[Au_2(\mu\text{-}L^8)_2](TfO)_2$ could be obtained pure in up to 71% yield. Complexes $[Au_2(\mu\text{-}L^n)_2](TfO)_2$ were also obtained by reaction of $[Ag_m(L^n)_m](TfO)_m$ with the equivalent amount of $[AuCl(SMe_2)]$ (for n = 8, 10) or $[(AuCl)_2(\mu\text{-}L^8)]$ (for n = 8), prepared by reacting $[Ag_m(\mu\text{-}L^8)_m][AgBr_2]_m$ with $[AuCl(SMe_2)]$.[46]

Scheme 4. Room Temperature Synthesis of Au(I) Dicarbene Complexes



Scheme 5



The high-temperature reaction of diimidazolium salts $[H_2L^n]Br_2$ (n = 1–4) with 1 equiv of $[AuCl(SMe_2)]$ and excess of NaOAc (DMF, 120 °C) had been previously used to prepare dinuclear Au(I) dicarbene complexes of the type $[Au_2(\mu\text{-}L^n)_2]Br_2$.[10] In contrast, the analogous reaction of $[H_2L^n]Br_2$ (n = 8, 10) afforded a mixture of $[Au(\kappa^2\text{-}L^n)]Br$ and small amounts (4 or 10%, respectively) of $[Au_2(\mu\text{-}L^n)_2]Br_2$ (Scheme 5). Pure $[Au(\kappa^2\text{-}L^8)]TfO$ was obtained by reacting the $[Au(\kappa^2\text{-}L^8)]Br$ + $[Au_2(\mu\text{-}L^8)_2]Br_2$ mixture with AgTfO in MeCN and recrystallizing the corresponding mixture of triflates.

In an attempt to prepare $[Au(\kappa^2\text{-}L^8)]TfO$ by a one-pot procedure, we added AgTfO to the $[H_2L^8]Br_2$ + $[AuCl(SMe_2)]$ + NaOAc reaction mixture. However, after extraction of the crude with $CHCl_3$ and precipitation with Et_2O, we isolated instead $[Au(\kappa^2\text{-}L^8)]_2[AgBr_3]$ in 39% yield (Scheme 5).

The $[Au(\kappa^2\text{-}L^{10})]Br$ + $[Au_2(\mu\text{-}L^{10})_2]Br_2$ mixture is very hygroscopic and could neither be obtained analytically pure nor be used for preparing $[Au(\kappa^2\text{-}L^{10})]TfO$ by further reaction with AgTfO. Nevertheless, $[Au(\kappa^2\text{-}L^{10})]TfO$ was isolated pure by heating an acetonitrile solution of $[Au_2(\mu\text{-}L^{10})_2](OTf)_2$ (see below) (Scheme 5).

The greater proportion of mononuclear to dinuclear complexes obtained for n = 8, 10 (Schemes 4 and 5) when the temperature increased, clearly shows that the latter are the kinetic and the former the thermodynamic products, which is the expected taking into account the entropic change of the reaction $[Au_2(\mu\text{-}L^n)_2]^{2+} \rightarrow 2\ [Au(\kappa^2\text{-}L^n)]^+$. To study this process and to extend the observation to the other complexes, solutions of complexes with n = 6–8, 10, prepared by the room temperature transmetalation method (Scheme 4), were heated at 120 °C in D_6-DMSO, and the mononuclear to dinuclear ratio was monitored by ^1H NMR (Table 1). After the equilibrium was reached, such ratio had increased for n = 6 (0.38 to 0.95), 8 (0.05 to 16), or 10 (0 to 6.3) and slightly decreased for n = 7 (from 6.3 to 4.7), reaching the maximum for n = 8, as observed in the Ag(I) analogues at room temperature (see above). This can be explained by assuming that the intracyclic C–M–C bond angle α in the mononuclear complexes with n = 8 is close to the ideal value of 180°. Therefore, decreasing the length of the chain leads to a decrease of α, destabilizing the mononuclear macrocycles with n < 8. In fact, the α angle in $[Ag(\kappa^2\text{-}L^7)]TfO$ is significantly bent (167.17(15)°, see below) while in $[Au(\kappa^2\text{-}L^8)]Br$ and $[Au(\kappa^2\text{-}L^8)]_2[AgBr_3]$ it is around 180° (176.59(10)° and 177.04(16)°, respectively). The decrease of the mononuclear:dinuclear ratio observed for n = 10 can be explained by (i) a decrease of the chelate effect with increasing chain length,[45,59] and (ii) an increase of steric repulsions.

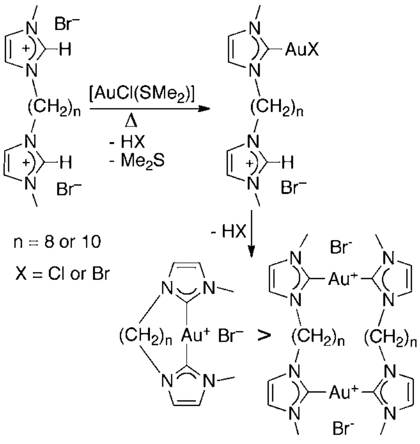
We have investigated by NMR and ESI-MS the reactions of $[Ag_m(L^8)_m]X_m$ (X = $AgBr_2$, TfO) with $[AuCl(SMe_2)]$ at short reaction times, but we did not observe any intermediate that could explain the predominant formation of the kinetic product $[Au_2(\mu\text{-}L^8)_2](TfO)_2$. However, in the high-temperature reaction of $[H_2L^8]Br_2$, $[AuCl(SMe_2)]$ and NaOAc, complexes $[AuX(L^8H)]^+$ (X = Cl, Br; Scheme 6) were detected by ^1H NMR and ESI-MS (Supporting Information, Figure S7) at short reaction times (10 min at 80 °C, in D_7-DMF). After longer reaction times, the signals of these intermediates vanished and those of $[Au(\kappa^2\text{-}L^8)]^+$ emerged. Very small amounts of the dinuclear macrocycle $[Au_2(\mu\text{-}L^8)_2]^{2+}$ were

Table 1. Variation in the Mono- to Dinuclear Ratio of Au(I) Macrocycles in D_6-DMSO Solution at 120 °C

	$[Au(\kappa^2\text{-}L^n)]TfO$: $[Au_2(\mu\text{-}L^n)_2](TfO)_2$ molar ratio[a]			
time (h)	n = 6	n = 7	n = 8	n = 10
0	0.38	6.3	0.07	0
2	0.84	4.2	2.4	0.36
8	0.95	4.5	5.2	1.7
22	0.92	4.7	16	5.7
48	0.92	4.7	16	6.3
96	0.92	4.7	16	6.3

[a] Determined by integration of the ^1H NMR spectrum at 22 °C and a total concentration of 0.04 mol/L of $Au(L^n)TfO$.

Scheme 6. Formation of Gold(I) Dicarbene Complexes from Diimidazolium Salts at High Temperature



detected. This suggests a reasonable mechanism for the formation of $[Au_m(L^n)_m]Br_m$ complexes involving $[H_2L^n]Br_2$ deprotonation by NaAcO to give the monocarbene $(L^nH)Br$ that would react with $[AuCl(SMe_2)]$ to afford $[AuCl(L^nH)]Br$ (Scheme 6). A Cl by Br replacement would give $[AuBr(L^nH)]$-Br. Dehydrohalogenation of these cationic complexes followed by intra or intermolecular cyclization would afford $[Au_m(L^n)_m]$-Br_m (m = 1, 2).

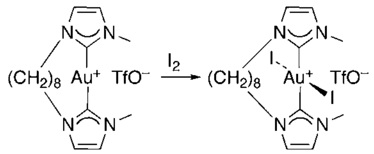
Structure of Au(I) Dicarbene Complexes. The ^1H and $^{13}C\{^1H\}$ NMR spectra of the mixtures of mono- and dinuclear Au(I) macrocycles show a slow exchange between both macrocycles, because two sets of sharp signals at room temperature in CD_3CN are observed. This contrasts with the fast exchange observed in their Ag(I) analogues. The signals of both macrocycles were assigned by means of a DOSY experiment as for their Ag(I) analogues (Supporting Information, Figure S4). The main differences between the NMR spectra of both types of complexes were found in the CH_2−N ^1H and ^{13}C nuclei, which are shielded in the dinuclear complexes with respect to the mononuclear ones. The gold-bound carbons appear in the range 184.1−185.1 ppm, which is typical for cationic Au(I) bis(NHC) complexes.[1]

In the (+)ESI-MS spectra of the Au(I) complexes, cations $[Au(\kappa^2\text{-}L^n)]^+$ and/or $[Au_2(\mu\text{-}L^n)_2]^{2+}$ were detected according to the proportions of the mono- and dinuclear complexes in the samples. Thus, the spectra of pure dinuclear macrocycles with n = 3, 5, 8, or 10, prepared by the room temperature transmetalation method (Scheme 4), show the isotopic distributions of $[Au_2(\mu\text{-}L^n)_2]^{2+}$ with high relative abundance, and the peaks of the mononuclear macrocycles $[Au(\kappa^2\text{-}L^n)]^+$ are not detected. For the mixtures of macrocycles with n = 6 or 7, both $[Au_2(\mu\text{-}L^n)_2]^{2+}$ and $[Au(\kappa^2\text{-}L^n)]^+$ are identified with comparable relative abundances (Supporting Information, Figure S6). In contrast, the spectra of the mixtures of $[Au(\kappa^2\text{-}L^n)]Br$ and $[Au_2(\mu\text{-}L^n)_2]Br_2$, prepared by the high-temperature metalation reaction (Scheme 5), and the spectra of pure $[Au(\kappa^2\text{-}L^n)]TfO$, ($n$ = 8, 10) are dominated by the signals corresponding to the mononuclear macrocycles $[Au(\kappa^2\text{-}L^n)]^+$. The detection of dinuclear cations with high relative abundance in some of the Au(I) complexes contrasts with the low abundances of the dinuclear cations in the ESI spectra of their Ag(I) congeners (see above). This difference can be attributed to the slower mononuclear/dinuclear exchange in the Au(I) complexes at room temperature.

The crystal structures of dinuclear $[Au_2(\mu\text{-}L^3)_2](TfO)_2$ and mononuclear $[Au(\kappa^2\text{-}L^8)]X$ (X = Br and $[AgBr_3]_{0.5}$) were determined by X-ray diffraction.

Synthesis of an Au(III) Metallamacrocycle: *trans*-[AuI$_2$(κ^2-L^8)]TfO. The oxidation of $[Au(\kappa^2\text{-}L^8)]TfO$ with a solution of I_2 in MeCN at room temperature afforded the titled complex as an orange solid (Scheme 7). This complex presents a *trans* geometry (by XRD), being the first Au(III) complex containing a *trans*-spanning bidentate ligand. Their ^1H and ^{13}C NMR spectra show a symmetrical dicarbene ligand and the δ values of the imidazole signals agree with those reported in complexes of the type *trans*-$[AuI_2(NHC)_2]$.[60,61] Thus, H4, H5, C4, and C5 are deshielded and C−Au is highly shielded ($\Delta\delta$ = −41 ppm) with respect to the corresponding nuclei in the Au(I) precursor $[Au(\kappa^2\text{-}L^8)]TfO$. These shifts have been attributed to an increase in σ-donation and a greater delocalization of electronic density of the C=C bond over the gold-bound carbon, induced by the higher Lewis acidity of Au(III).[50,62] The (+)ESI-MS spectrum shows the isotopic distribution of the cationic complex.

Scheme 7



X-ray Crystal Structures. Whereas many structures of dinuclear Ag(I) or Au(I) dicarbene metallacycles have been determined, very few structures of dinuclear Au(III),[42,63] or mononuclear Ag(I) or Au(I) metallacycles[24,40,41,64] containing dicarbene ligands have been reported. We have determined the crystal structures of Ag and Au dicarbene complexes of various types: dinuclear M(I) complexes $[M_2(\mu\text{-}L^3)_2]X_2$ (M = Ag, X = PF_6; M = Au, X = TfO), mononuclear M(I) complexes $[Ag(\kappa^2\text{-}L^7)]TfO$ and $[Au(\kappa^2\text{-}L^8)]Br$, the mixed Au(I)/Ag(I) $[Au(\kappa^2\text{-}L^8)]_2[AgBr_3]$ salt, and the mononuclear Au(III) complex *trans*-$[AuI_2(\kappa^2\text{-}L^8)]TfO$.

All Ag(I) and Au(I) complexes show a linear coordination geometry, the C−M−C angle lying in the range 174.97−178.26°, except for $[Ag(\kappa^2\text{-}L^7)]TfO$ (167.17(15)°, see discussion above). The M−C bond distances do not deviate significantly from the mean values found in comparable bis(imidazol-*N*-yl-2-ylidene) complexes of Ag(I) (2.09 Å) or Au(I) (2.02 Å).[65]

The cation of $[Ag_2(\mu\text{-}L^3)_2](PF_6)_2$ (Figure 2) presents a dinuclear macrocyclic structure with a pseudochair conformation (Figure 2). The molecule is centrosymmetric, and the C−Ag−C axes are nearly parallel. The imidazole rings coordinated to the same silver cation are nearly coplanar and parallel to those coordinated to the other silver cation. Intramolecular argentophilic contacts (Ag−Ag: 3.1888(9) Å), and intra- and intermolecular π−π stacking interactions of the imidazole rings were observed. The geometrical parameters of the π−π interactions are given in the Supporting Information. The anions are rotationally disordered over two positions. The structure of the cation resembles that of $[Au_2(\mu\text{-}L^3)_2](PF_6)_2$, which was reported by Tubaro and co-workers;[10] however, the gold complex is in a pseudoboat conformation and the arrangement of cations and anions is different.

Complex $[Au_2(\mu\text{-}L^3)_2](TfO)_2$ also presents an intramolecular aurophilic interaction (Figure 3). The metal−metal distance (3.0322(4) Å) is shorter than those found in $[M_2(\mu\text{-}L^3)_2](PF_6)_2$ (Ag−Ag: 3.1888(9) Å; Au−Au:[10] 3.2722(5) Å). In addition, whereas in $[M_2(\mu\text{-}L^3)_2](PF_6)_2$ the metallamacrocycles adopt a pseudochair or boat conformation, the C−M−C axis being in mutually parallel disposition, $[Au_2(\mu\text{-}L^3)_2](TfO)_2$ presents a helical conformation where the C−Au−C axes are nearly perpendicular to each other (the C−Au−Au−C torsion angles lie in the range 84.9−96.8°). Therefore, the complex cation is chiral, and both enantiomers are placed alternatively along the c axis, connected by intermolecular π−π stacking interactions between the imidazole rings. A similar helical structure has been reported for complex $[Ag_2(\mu\text{-}Im'(CH_2)_3Im')_2](TsO)_2$, (Im′ = *N*-(2-hydroxy-2-methyl-1-propy)imidazol-*N*-yl-2-ylidene).[31] Several short contacts between triflate oxygens and methyl and imidazole hydrogens of the surrounding cations were found. Geometrical parameters of the π−π and C−H···O interactions are included in the Supporting Information.

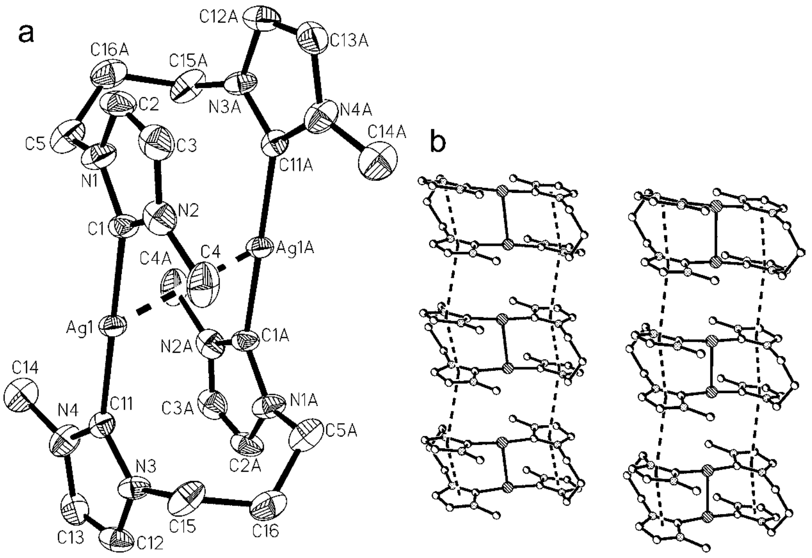


Figure 2. Crystal structure of $[Ag_2(\mu\text{-}L^3)_2](PF_6)_2$: (a) Molecular structure and (b) stacking of the complex cations showing the $\pi-\pi$ interactions. H atoms and anions have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag(1)−C(1) 2.077(6), Ag(1)−C(11) 2.090(6), Ag(1)−Ag(1A) 3.1888(9); C(1)−Ag(1)−C(11) 175.0(2), C(1)−Ag(1)−Ag(1A) 69.95(16), C(11)−Ag(1)−Ag(1A) 112.51(15).

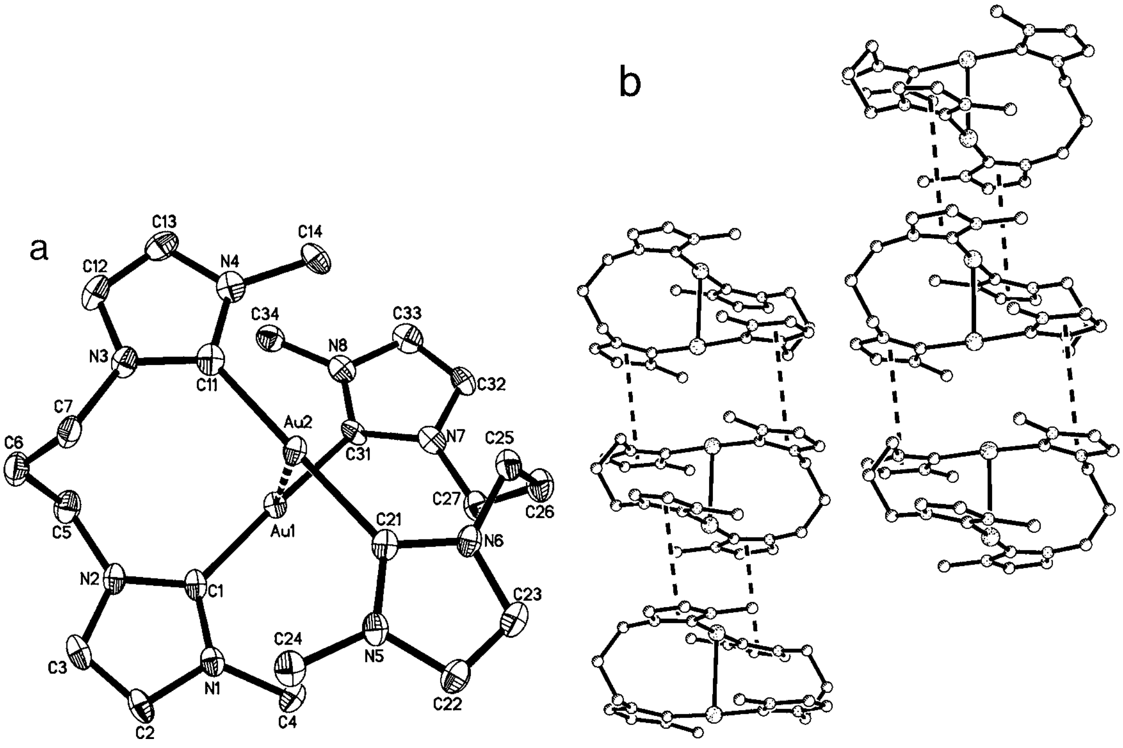


Figure 3. Crystal structure of $[Au_2(\mu\text{-}L^3)_2](TfO)_2$. (a) Molecular structure and (b) stacking of complex cations showing the $\pi-\pi$ interactions. Hydrogen atoms and anions have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Au(1)−C(1) 2.007(6), Au(1)−C(31) 2.011(6), Au(1)−Au(2) 3.0322(4), Au(2)−C(11) 2.017(6), Au(2)−C(21) 2.024(6); C(1)−Au(1)−C(31) 177.6(3), C(1)−Au(1)−Au(2) 85.72(17), C(31)−Au(1)−Au(2) 94.81(17), C(11)−Au(2)−C(21) 176.5(2), C(11)−Au(2)−Au(1) 84.63(17), C(21)−Au(2)−Au(1) 92.30(16).

In the crystal structure of $[Ag(\kappa^2\text{-}L^7)]TfO$, the macrocyclic complex has a symmetry plane (Figure 4) which passes through the silver atom and the central methylene carbon atom. As a result of the shortness of the heptamethylene chain, the coordination geometry is significantly bent (C−Ag−C: 167.16°; see discussion above), and the imidazole rings are mutually tilted. The distance between the metal and one of the central methylene hydrogens of the same molecule is smaller than the sum of the van der Waals radii[66] of Ag and H (Ag···H: 2.702 Å; $r_W(Ag) + r_W(H) = 2.92$ Å). As the Ag···H−C angle is far from 180° (128.2°), and the methylene ^1H NMR signals appear in the normal range, this close approach is attributed to the shortness of the $(CH_2)_7$ chain. Short contacts between the methylene or imidazole hydrogens and the vicinal triflate oxygens were found (See Supporting Information).

The structure of $[Au(\kappa^2\text{-}L^8)]_2[AgBr_3]$ consists of macrocyclic $[Au(\kappa^2\text{-}L^8)]^+$ cations and nearly trigonal tribromoargentate(I) dianions (Figure 5). The structural data of this dianion are

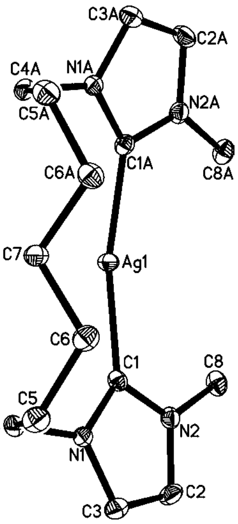


Figure 4. Molecular structure of the cation of $[Ag(\kappa^2\text{-}L^7)]TfO$. Hydrogen atoms and anions have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag(1)−C(1) 2.093(3); C(1)−Ag(1)−C(1) 167.17(15).

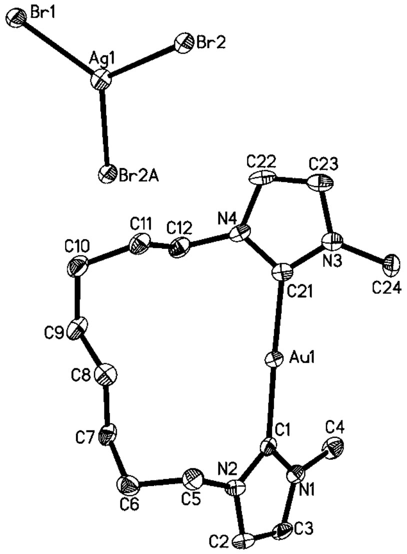


Figure 5. Molecular structure of $[Au(\kappa^2\text{-}L^8)]_2AgBr_3$. Hydrogen atoms and the second molecule of $[Au(\kappa^2\text{-}L^8)]^+$ have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag(1)−Br(1) 2.5850(8), Ag(1)−Br(2) 2.5894(5), Au(1)−C(21) 2.025(4), Au(1)−C(1) 2.027(4); Br(1)−Ag(1)−Br(2) 120.431(13), Br(2)−Ag(1)−Br(2)#1 119.14(3), C(21)−Au(1)−C(1) 177.04(16).

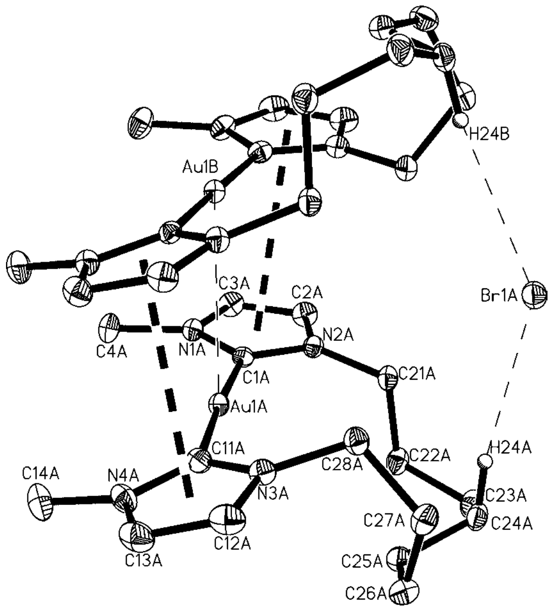


Figure 6. Crystal structure of the salt $[Au(\kappa^2\text{-}L^8)]Br$. Structure of the dimer showing the aurophilic, $\pi-\pi$, and C−H···Br interactions. All H atoms have been omitted for clarity except those involved in the HC−H···Br interactions. Selected bond lengths (Å) and angles (deg): Au(1)−C(1) 2.020(2), Au(1)−C(11) 2.027(2), Au(1)−Au(1) 3.4295 (3); C(1)−Au(1)−C(11) 176.59(10).

similar to those reported for the only examples we are aware of ($[M(\text{crown ether})_3]_3[AgBr_3]Br$; M = K, Rb).[67] No short metal···metal contacts were found. Some hydrogen atoms of the dicarbene ligand and the nearby bromine atoms are separated by distances shorter than the sum of the van der Waals radii of H and Br,[66] suggesting the existence of unconventional C−H···Br bonds (Br···H: 2.72−2.90 Å; C−H···Br angles: 142.5−178.0°; $r_w(H) + r_w(Br) = 3.05$ Å; see Supporting Information for more details).

The structure of $[Au(\kappa^2\text{-}L^8)]Br$ (Figure 6) contains $[Au(\kappa^2\text{-}L^8)]^+$ macrocycles and bromide anions. The macrocycles are grouped in dimers by means of a weak aurophilic contact (Au···Au: 3.4295(3) Å) and $\pi-\pi$ interactions between their imidazole rings. The macrocyle conformation resembles closely that of $[Au(\kappa^2\text{-}L^8)]_2[AgBr_3]$, suggesting that it is imposed by the octamethylene chain. Although the imidazole rings bonded to the same gold cation are mutually tilted, the rings of the two molecules of a dimer are in a parallel displaced disposition favorable for the $\pi-\pi$ interactions. In addition, the Br^- anions form short contacts with two or four ligand hydrogens alternatively (Supporting Information, Figure S15). These C−H···Br, $\pi-\pi$, and aurophilic interactions define parallel layers of cations and anions oriented perpendicularly to the *c* axis. Geometrical parameters of the $\pi-\pi$ and C−H···Br interactions are given in the Supporting Information.

In the crystal structure of $[AuI_2(\kappa^2\text{-}L^8)]TfO$, only one independent molecule of the cationic complex and one TfO^- anion were found in the asymmetric unit (Figure 7). As expected for a Au(III) complex, the coordination geometry around the metal is pseudo-square-planar. The Au−C and Au−I distances are similar to those found in reported Au(III) dihalo bis(NHC) complexes,[42,54,61,68] and the C−Au−C and I−Au−I angles lie close to 180°. The macrocyclic ligand is perpendicularly disposed with respect to the I−Au−I axis to minimize steric repulsions (the angle between the ligand average plane and the axis is 85.9°). Intermolecular I···I contacts give rise to I−Au−I···I−Au−I zigzag chains along the *b* axis. The I···I distances are shorter than twice the van der Waals radius of I (I···I: 3.680 Å; $2r_w(I)$: 3.96 Å[66]). Similar contacts have been reported for Au(III) iodo complexes, with I···I distances lying in the range 3.64−3.79 Å.[69] In addition, unconventional hydrogen bonds between the triflate oxygen and fluorine atoms and hydrogen atoms of the dicarbene ligand were found (see Supporting Information).

CONCLUSION

We have prepared the first family of metal dicarbene complexes which exist as mononuclear $[M(\kappa^2\text{-}L^n)]^+$ and dinuclear $[M_2(\mu\text{-}L^n)_2]^{2+}$ species in equilibrium. Ag(I) complexes with $n = 6-8$,

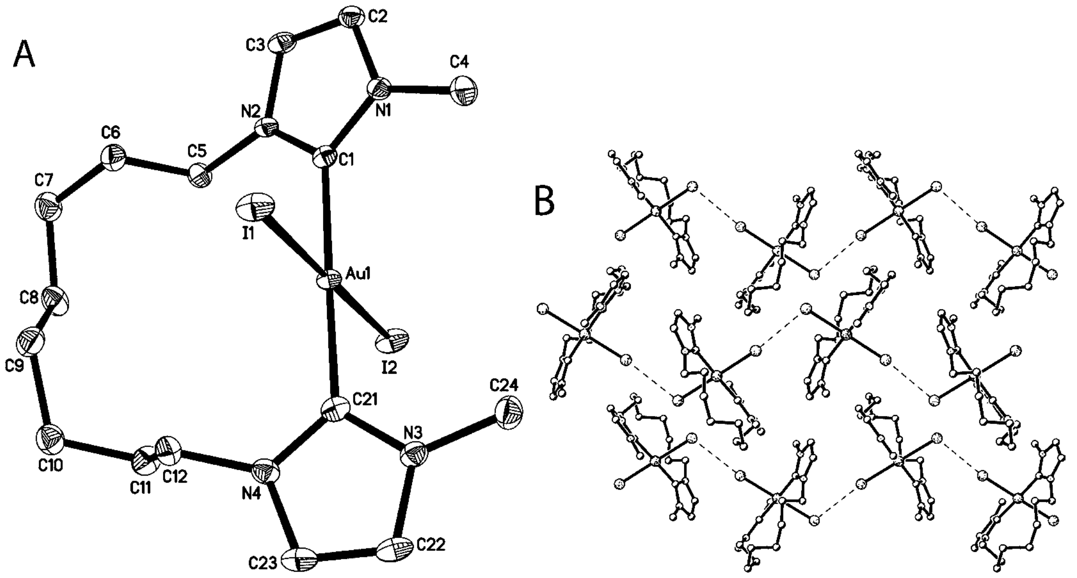


Figure 7. Crystal structure of $[AuI_2(\kappa^2\text{-}L^8)]TfO$. (A) Molecular structure of the cation (Hydrogen atoms and anions have been omitted for clarity). (B) View of the chains formed by I···I–Au–I···I interactions. Selected bond lengths (Å) and angles (deg): Au(1)–C(21) 2.038(3), Au(1)–C(1) 2.038(3), Au(1)–I(1) 2.6145(2), Au(1)–I(2) 2.6173(2); C(21)–Au(1)–C(1) 178.27(10), C(21)–Au(1)–I(1) 91.34(7), C(1)–Au(1)–I(1) 87.59(7), C(21)–Au(1)–I(2) 88.92(7), C(1)–Au(1)–I(2) 92.15(7), I(1)–Au(1)–I(2) 179.688(7).

10 have been obtained as $[AgBr_2]^-$ or TfO^- salts. Au(I) complexes, obtained by room temperature transmetalation from the Ag(I) complexes to $[AuCl(SMe_2)]$, consist of $[Au_2(\mu\text{-}L^n)_2](TfO)_2$ (n = 3, 5, 10) or mixtures of $[Au(\kappa^2\text{-}L^n)]TfO$ (main product for n = 7) and $[Au_2(\mu\text{-}L^n)_2](TfO)_2$ (main product for n = 6, 8). In contrast, high-temperature metalation of bisimidazolium salts afforded mainly mononuclear complexes (n = 8, 10). At room temperature, the exchange process $[M_2(\mu\text{-}L^n)_2](TfO)_2 \leftrightarrows 2\ [M(\kappa^2\text{-}L^n)]TfO$ is fast for M = Ag but slow for M = Au in the NMR time scale. The equilibrium is shifted toward the mononuclear complexes for $n \geq 7$, for n in the order of $7 < 10 < 8$, which proves that the $(CH_2)_8$ linker has the optimal length for *trans* chelation. When $[Au(\kappa^2\text{-}L^8)]TfO$ is oxidized with I_2 the metallamacrocyclic structure was not altered, giving an unprecedented Au(III) complex containing a *trans*-spanning dicarbene ligand.

■ EXPERIMENTAL SECTION

General Considerations. HPLC-grade solvents were used as received unless otherwise stated. When necessary, CH_2Cl_2 was previously distilled over calcium hydride and stored under nitrogen. C, H, N, and S analyses were carried out with Carlo Erba 1108 and LECO CHS-932 microanalyzers. NMR spectra were measured on Bruker Avance 200, 300, and 400 instruments. The references for NMR spectra were as follows: ^1H (residual $CDHCl_2$ (5.32 ppm), CHD_2CN (1.95 ppm), D_5-DMSO (2.50 ppm)), $^{13}C\{^1H\}$ (CD_2Cl_2 (53.8 ppm), CD_3CN (1.32 ppm), D_6-DMSO (39.5 ppm)), ^{19}F (external $CFCl_3$ (0 ppm)), and ^{31}P (external H_3PO_4 (0 ppm)). The temperature values in NMR experiments were not corrected. Abbreviations used: br (broad), s (singlet), d (doublet), t (triplet), quint (quintet), sept (septet), m (multiplet). Assignments of ^1H and $^{13}C\{^1H\}$ NMR spectra are based on COSY, DOSY, HMQC, and HMBC experiments, when necessary. ESI-MS spectra were measured on an Agilent 6620 Accurate Mass TOF LC/MS spectrometer, using MeCN as carrier solvent. Compounds insoluble in MeCN were dissolved in DMSO and diluted with MeCN. Melting points were determined on a Reichert apparatus in an air atmosphere. Equivalent conductivities were measured in DMF ($c = 5 \times 10^{-4}$ M), at 298 K and calculated using the minimum equivalent weight, that is, that corresponding to a salt of the type $[Ag(L^n)]X$. Scheme 1 shows the atom numbering used in NMR assignments.

$[H_2L^n]Br_2$ (n = 6–8, 10). These salts were prepared using a modified literature method.[20] A tetrahydrofuran (THF) solution of 1-(methy)-1*H*-imidazole (ImH) and the corresponding $Br(CH_2)_nBr$ (2:1 molar ratio, respectively) was stirred at 100 °C overnight in a Carius tube. The precipitated salts were filtered, washed with Et_2O and dried under vacuum. The NMR data of $[H_2L^{10}]Br_2$ agree with those previously reported.[70]

$[L^6H_2]Br_2{\cdot}H_2O$. Prepared from $Br(CH_2)_6Br$ (1.5 g, 6.3 mmol) and ImH (1.0 g, 12.6 mmol). White solid. Yield: 2.5 g, 6.1 mmol, 97%. Mp: 150 °C. Anal. Calcd for $C_{14}H_{24}Br_2N_4{\cdot}(H_2O)$: C, 39.45; H, 6.15; N, 13.15. Found: C, 39.71; H, 6.27; N, 13.40. The amount of water was estimated from the elemental analyses and corroborated by integration of the ^1H NMR spectrum. ^1H NMR (400.9 MHz, D_6-DMSO): δ 9.31 (br t, 2H, H2, Im), 7.85 (dd, $^3J_{HH} = {}^4J_{HH}$ = 1.6 Hz, 2H, H5, Im), 7.75 (dd, $^3J_{HH} = {}^4J_{HH}$ = 1.6 Hz, 2H, H4, Im), 4.19 (t, $^3J_{HH}$ = 7.2 Hz, 4H, α–CH_2), 3.87 (s, 6H, Me), 3.36 (s, 2H, H_2O), 1.78 (quint, $^3J_{HH}$ = 6.8 Hz, 4H, β–CH_2), 1.26 (m, 4H, γ–CH_2). $^{13}C\{^1H\}$ NMR (100.8 MHz, D_6-DMSO): δ 136.5 (C2), 123.5 (C4), 122.2 (C5), 48.5 (α–CH_2), 35.8 (Me), 29.1 (β–CH_2), 24.8 (γ–CH_2).

$[H_2L^7]Br_2$. Prepared from $Br(CH_2)_7Br$ (1.6 g, 6.1 mmol) and ImH (1.0 g, 12.2 mmol). The supernatant solution was removed to leave a pale-orange oil, which was washed with Et_2O (3 × 5 mL) and dried under vacuum. Yield: 2.3 g, 5.4 mmol, 89%. It was not possible to obtain good elemental analyses of the salt because it is a viscous oil. Exact m/z calcd. for $[H_2L^7]^{2+}$: 131.1073, found: 131.1074, Δ = 0.76 ppm. ^1H NMR (400.9 MHz, D_6-DMSO): δ 9.30 (br t, $^3J_{HH}$ = 7.2 Hz, 2H, H2, Im), 7.83 (dd, $^3J_{HH} = {}^4J_{HH}$ = 1.6 Hz, 2H, H5 or H4, Im), 7.74 (dd, $^3J_{HH} = {}^4J_{HH}$ = 1.6 Hz, 2H, H4 or H5, Im), 4.18 (t, $^3J_{HH}$ = 7.2 Hz, 4H, α–CH_2), 3.87 (s, 6H, Me), 1.77 (quint, $^3J_{HH}$ = 7.2 Hz, 4H, β–CH_2), 1.30 (m, 2H, δ–CH_2), 1.22 (m, 4H, γ–CH_2). $^{13}C\{^1H\}$ NMR (75.5 MHz, D_6-DMSO): δ 136.5 (C2), 123.5 (C4), 122.2 (C5), 48.6 (α–CH_2), 35.7 (Me), 29.2 (β–CH_2), 27.6 (δ–CH_2), 25.1 (γ–CH_2). (+)ESI-MS (MeCN) m/z: 261 ($[L^7H]^+$), 179 ($[L^7\text{-}(C_3H_2N_2Me)]^+$), 131 ($[L^7H_2]^{2+}$), 118.

$[H_2L^8]Br_2$. Prepared from $Br(CH_2)_8Br$ (1.5 g, 5.4 mmol) and ImH (0.9 g, 10.8 mmol). White solid. Yield: 2.2 g, 5.0 mmol, 93%. Mp: 127 °C. Anal. Calcd for $C_{16}H_{28}Br_2N_4$: C, 44.05; H, 6.47; N, 12.84. Found: C, 43.77; H, 6.47; N, 12.53. ^1H NMR (400.9 MHz, D_6-DMSO): δ 9.33 (br t, 2H, H2, Im), 7.86 (dd, $^3J_{HH} = {}^4J_{HH}$ = 1.2 Hz, 2H, H5, Im), 7.77 (dd, $^3J_{HH} = {}^4J_{HH}$ = 1.2 Hz, 2H, H4, Im), 4.18 (t, $^3J_{HH}$ = 7.2 Hz, 4H, α−CH$_2$), 3.87 (s, 6H, Me), 1.77 (quint, $^3J_{HH}$ = 7.2 Hz, 4H, β−CH$_2$), 1.23 (m, 8H, γ− and δ−CH$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, D$_6$-DMSO): δ 136.5 (C2), 123.5 (C4), 122.3 (C5), 48.6 (α−CH$_2$), 35.8 (Me), 29.3 (β−CH$_2$), 28.1 (δ−CH$_2$), 25.3 (γ−CH$_2$).

[H$_2$L^{10}]Br$_2$. Prepared from Br(CH$_2$)$_{10}$Br (1.9 g, 6.2 mmol) and ImH (1.0 g, 12.5 mmol). White solid. Yield: 2.8 g, 6.0 mmol, 97%. Mp: 145 °C. Anal. Calcd for $C_{18}H_{32}Br_2N_4\cdot(H_2O)_{0.3}$: C, 46.03; H, 7.00; N, 11.93. Found: C, 46.19; H, 7.38; N, 11.73. The amount of water was estimated from the elemental analyses and corroborated by integration of the ^{1}H NMR spectrum. ^{1}H NMR (300.1 MHz, D$_6$-DMSO): δ 9.30 (br t, 2H, H2, Im), 7.84 (dd, $^3J_{HH}$ = $^4J_{HH}$ = 1.8 Hz, 2H, H5, Im), 7.76 (dd, $^3J_{HH}$ = $^4J_{HH}$ = 1.8 Hz, 2H, H4, Im), 4.17 (t, $^3J_{HH}$ = 7.2 Hz, 4H, α−CH$_2$), 3.87 (s, 6H, Me), 3.34 (s, 0.6H, H$_2$O), 1.77 (quint, $^3J_{HH}$ = 7.2 Hz, 4H, β−CH$_2$), 1.23 (m, 12H, γ−, δ− and ε−CH$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, D$_6$-DMSO): δ 136.5 (C2), 123.5 (C4), 122.2 (C5), 48.7 (α−CH$_2$), 35.7 (Me), 29.4 (β−CH$_2$), 28.7 (ε−CH$_2$), 28.3 (δ−CH$_2$), 25.3 (γ−CH$_2$).

[H$_2$L^3](PF$_6$)$_2$. To a solution of [H$_2$L^3]Br$_2$ (371 mg, 1.0 mmol)[46] in MeOH (20 mL), NH$_4$PF$_6$ (331 mg, 2.0 mmol) was added. A white precipitate was formed immediately. The solid was filtered, washed with H$_2$O (2 × 5 mL) and MeOH (2 × 5 mL) and dried under vacuum. Yield: 402 mg, 0.81 mmol, 81%. Mp: 142−143 °C. Anal. Calcd for $C_{11}H_{18}F_{12}N_4P$: C, 26.63; H, 3.66; N, 11.29. Found: C, 26.47; H, 3.61; N, 11.16. ^{1}H NMR (400.9 MHz, D$_6$-DMSO): δ 9.07 (br t, 2H, H2, Im), 7.73 (AB system, $^3J_{HH}$ = 2.3 Hz, $^4J_{HH}$ = 1.9 Hz, 4H, H5 and H4, Im), 4.20 (t, $^3J_{HH}$ = 7.2 Hz, 4H, α−CH$_2$), 3.85 (s, 6H, Me), 2.36 (quint, $^3J_{HH}$ = 6.8 Hz, 2H, β−CH$_2$). ^{13}C{^{1}H} NMR (50.3 MHz, D$_6$-DMSO): δ 136.8 (C2), 123.8 (C4), 122.2 (C5), 45.7 (α−CH$_2$), 35.8 (Me), 29.4 (β−CH$_2$). ^{19}F NMR (282.4 MHz, D$_6$-DMSO): δ −69.0 (d, $^1J_{FP}$ = 711.6 Hz). ^{31}P{^{1}H} NMR (162.3 MHz, D$_6$-DMSO): δ −142.8 (sept, $^1J_{FP}$ = 711.4 Hz).

Synthesis of [Ag$_m$(L^n)$_m$][AgBr$_2$]$_m$ (*n* = 3, 5, 6−8, 10). They have been prepared by reaction of the bisimidazolium salts [H$_2$L^n]Br$_2$ with an equimolar amount of Ag$_2$O in MeCN (*n* = 3, 5, 6, 7) or CHCl$_3$ (*n* = 8, 10). The resulting suspension was stirred overnight at room temperature in the dark. The compounds were isolated by filtration, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. Compounds [Ag$_2$(μ-L^3)$_2$][AgBr$_2$]$_2$ and [Au$_2$(μ-L^5)$_2$][AgBr$_2$]$_2$ have been previously reported.[20,46]

[Ag$_m$(L^6)$_m$][AgBr$_2$]$_m$. Prepared from [H$_2$L^6]Br$_2$·H$_2$O (332 mg, 0.78 mmol) and Ag$_2$O (181 mg, 0.78 mmol). Yield: 432 mg, 0.69 mmol, 89%. Mp: 117−118 °C. Anal. Calcd for $C_{14}H_{22}Ag_2Br_2N_4$: C, 27.04; H, 3.57; N, 9.01. Found: C, 26.71; H, 3.56; N, 8.78. ^{1}H NMR (400.9 MHz, D$_6$-DMSO): δ 7.47 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H5, Im), 7.42 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H4, Im), 4.10 (t, $^3J_{HH}$ = 6.4 Hz, 4H, α−CH$_2$), 3.82 (s, 6H, Me), 1.75 (quint, $^3J_{HH}$ = 6.4 Hz, 4H, β−CH$_2$), 1.35 (m, 4H, γ−CH$_2$). ^{13}C{^{1}H} RMN (50.3 MHz, D$_6$-DMSO): δ 180.0 (s, C2), 122.9 (s, C4), 121.7 (s, C5), 49.7 (α−CH$_2$), 38.0 (Me), 30.6 (β−CH$_2$), 24.3 (γ−CH$_2$). (+)ESI-MS (MeCN, DMSO) *m*/*z*: 787.1 ([Ag$_2$(L^6)$_2$Br]$^+$), 435.0 ([AgBr(L^6)H]$^+$), 353.1 ([Ag(L^6)]$^+$); (−)ESI-MS (MeCN, DMSO) *m*/*z*: 266.7 ([AgBr$_2$]$^-$), 213.8 ([AgBrCN]$^-$), 78.9 (Br$^-$). Exact *m*/*z* calcd. for ([Ag(L^6)]$^+$): 353.0890, found: 353.0898, Δ = 2.3 ppm. Λ_E (Ω^{-1} cm^2 mol^{-1}) = 58.8.

[Ag$_m$(L^7)$_m$][AgBr$_2$]$_m$. Prepared from [H$_2$L^7]Br$_2$ (257 mg, 0.61 mmol) and Ag$_2$O (141 mg, 0.61 mmol). The reaction mixture was filtered, and the gray precipitate was stirred with CHCl$_3$ (30 mL). The suspension was filtered through Celite, and the filtrate was concentrated up to about 2 mL. Addition of Et$_2$O (30 mL) precipitated a white solid, which was filtered, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. Yield: 256 mg, 0.40 mmol, 66%. Mp: 111−112 °C Anal. Calcd for $C_{15}H_{24}Ag_{1.9}Br_{1.9}N_4$ (see Discussion): C, 29.19; H, 3.92; N, 9.08. Found: C, 29.19; H, 3.82; N, 9.03. ^{1}H NMR (400.9 MHz, D$_6$-DMSO): δ 7.47 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H5, Im), 7.42 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H4, Im), 4.15 (t, $^3J_{HH}$ = 6.8 Hz, 4H, α−CH$_2$), 3.82 (s, 6H, Me), 1.73 (m, 4H, β−CH$_2$), 1.50−1.42 (m, 2H, δ−CH$_2$), 1.25 (m, 4H, γ−CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, D$_6$-DMSO): δ 179.7 (s, C2), 123.0 (s, C4), 121.9 (s, C5), 49.3 (α−CH$_2$), 38.1 (Me), 30.5 (β−CH$_2$), 26.5 (δ−CH$_2$), 24.7 (γ−CH$_2$). (+)ESI-MS (MeCN, DMSO) *m*/*z*: 815.1 ([Ag$_2$(L^7)$_2$Br]$^+$), 449.0 ([AgBr(L^7)H]$^+$), 367.1 ([Ag(L^7)]$^+$); (−)ESI-MS (MeCN, DMSO) *m*/*z*: 266.7 ([AgBr$_2$]$^-$), 213.8 ([AgBrCN]$^-$), 78.9 (Br$^-$). Exact *m*/*z* calcd. for ([Ag(L^7)]$^+$): 367.1046, found: 367.1049, Δ = 0.8 ppm. Λ_E (Ω^{-1} cm^2 mol^{-1}) = 64.7.

[Ag$_m$(L^8)$_m$][AgBr$_2$]$_m$. To a solution of [H$_2$L^8]Br$_2$ (351 mg, 0.80 mmol) in CHCl$_3$ (40 mL), Ag$_2$O (185 mg, 0.80 mmol) was added. The resulting suspension was stirred overnight at room temperature in the dark and filtered through Celite. The filtrate was concentrated under vacuum up to about 1 mL. Addition of Et$_2$O (30 mL) gave a white precipitate, which was filtered, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. Yield: 424 mg, 0.65 mmol, 82%. Mp: 124−125 °C Anal. Calcd for $C_{16}H_{26}Ag_2Br_2N_4$: C, 29.57; H, 4.03; N, 8.62. Found: C, 29.57; H, 3.84; N, 8.53. ^{1}H NMR (400.9 MHz, D$_6$-DMSO): δ 7.51 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H5, Im), 7.55 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H4, Im), 4.12 (t, $^3J_{HH}$ = 7.2 Hz, 4H, α−CH$_2$), 3.82 (s, 6H, Me), 1.79 (m, 4H, β−CH$_2$), 1.39 (m, 4H, δ−CH$_2$), 1.28 (m, 4H, γ−CH$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, D$_6$-DMSO): δ 179.8 (s, C2), 123.1 (s, C4), 121.5 (s, C5), 49.3 (α−CH$_2$), 38.0 (Me), 29.5 (β−CH$_2$), 26.2 (γ−CH$_2$), 24.2 (δ−CH$_2$). (+)ESI-MS (MeCN, DMSO) *m*/*z*: 843.2 ([Ag$_2$(L^8)$_2$Br]$^+$), 799.2 ([Ag$_2$(L^8)$_2$Cl]$^+$), 463.0 ([AgBr(L^8)H]$^+$), 381.1 ([Ag(L^8)]$^+$); (−)ESI-MS (MeCN, DMSO) *m*/*z*: 266.7 ([AgBr$_2$]$^-$), 213.8 ([AgBrCN]$^-$), 78.9 (Br$^-$). Λ_E (Ω^{-1} cm^2 mol^{-1}) = 62.9.

[Ag$_m$(L^{10})$_m$][AgBr$_2$]$_m$. Prepared from [H$_2$L^{10}]Br$_2$ (776 mg, 1.67 mmol) and Ag$_2$O (387 mg, 1.67 mmol) by the same method as for [Ag$_m$(L^8)$_m$][AgBr$_2$]$_m$. Yield: 800 mg, 1.18 mmol, 71%. Mp: 118−119 °C. Anal. Calcd for $C_{18}H_{30}Ag_{1.9}Br_{1.9}$ (see discussion): C, 32.80; H, 4.59; N, 8.50. Found: C, 32.84; H, 4.21; N, 8.43. ^{1}H NMR (400.9 MHz, D$_6$-DMSO): δ 7.49 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H5, Im), 7.44 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H4, Im), 4.10 (t, $^3J_{HH}$ = 7.2 Hz, 4H, α−CH$_2$), 3.81 (s, 6H, Me), 1.76 (quint, $^3J_{HH}$ = 7.2 Hz, 4H, β−CH$_2$), 1.31−1.22 (m, 12H, γ−, δ− and ε−CH$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, D$_6$-DMSO): δ 179.3 (s, C2), 123.0 (s, C4), 121.6 (s, C5), 50.5 (α−CH$_2$), 38.1 (Me), 30.4 (β−CH$_2$), 27.8 (δ− or ε−CH$_2$), 27.2 (ε− or δ−CH$_2$), 25.2 (γ−CH$_2$). (+)ESI-MS (MeCN, DMSO) *m*/*z*: 933.3 ([Ag$_2$(L^{10})$_2$Cl(Me$_2$SO)]$^+$), 901.2 ([Ag$_2$(L^{10})$_2$Br]$^+$), 882.3 ([Ag$_2$(L^{10})$_2$Cl(HCN)]$^+$), 855.3 ([Ag$_2$(L^{10})$_2$Cl]$^+$), 409.2 ([Ag(L^{10})]$^+$); (−)ESI-MS (MeCN, DMSO) *m*/*z*: 266.7 ([AgBr$_2$]$^-$), 213.8 ([AgBrCN]$^-$), 78.9 (Br$^-$). Exact *m*/*z* calcd. for ([Ag(L^{10})]$^+$): 409.1516, found: 409.1509, Δ = 1.7 ppm. Λ_E (Ω^{-1} cm^2 mol^{-1}) = 57.9.

[Ag$_2$(μ-L^3)$_2$](PF$_6$)$_2$. Ag$_2$O (129 mg, 0.56 mmol) was added to a solution of [H$_2$L^3](PF$_6$)$_2$ (139 mg, 0.28 mmol) in MeCN (15 mL). The mixture was stirred for 2 days at room temperature in the dark and filtered through Celite. The filtrate was concentrated under vacuum up to about 1 mL. Addition of Et$_2$O (30 mL) gave a white precipitate, which was filtered, washed with Et$_2$O (3 × 5 mL) and dried under vacuum. Yield: 70 mg, 0.077 mmol, 55%. Mp: 139−140 °C. Anal. Calcd for $C_{22}H_{32}Ag_2F_{12}N_8P_2$: C, 28.90; H, 3.53; N, 12.26. Found: C, 29.02; H, 3.92; N, 12.00. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ 7.32 (d, $^3J_{HH}$ = 2.0 Hz, 4H, H5, Im), 7.28 (d, $^3J_{HH}$ = 2.0 Hz, 4H, H4, Im), 4.12 (m, 8H, α−CH$_2$), 3.53 (s, 12H, Me), 2.52 (m, 4H, β−CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CD$_3$CN, −20 °C): δ 180.9 (two d, $^1J_{^{107}Ag^{13}C}$ = 178.6 Hz, $^1J_{^{107}Ag^{13}C}$ = 205.9 Hz, C2), 124.7 (C4), 121.6 (C5), 47.7 (α−CH$_2$), 38.3 (Me), 30.0 (β−CH$_2$). ^{19}F NMR (282.4 MHz, CD$_3$CN): δ −71.6 (d, $^1J_{FP}$ = 706.4). ^{31}P{^{1}H} NMR (121.5 MHz, CD$_3$CN): δ −143.2 (sept, $^3J_{PF}$ = 706.5 Hz). Λ_E (Ω^{-1} cm^2 mol^{-1}) = 67.4.

[Ag$_m$(L^6)$_m$](TfO)$_m$. To a suspension of [Ag$_m$(L^6)$_m$][AgBr$_2$]$_m$ (112 mg, 0.18 mmol) in MeCN (15 mL), AgTfO (46 mg, 0.18 mmol) was added. The mixture was stirred 10 min at room temperature and filtered through Celite. Addition of Et$_2$O (40 mL) gave a white precipitate which was filtered, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. Yield: 66 mg, 0.13 mmol, 73% (overall based on Ag). Because of the fast exchange in DMSO and the poor solubility of the compound in low melting point solvents solvents, the mononuclear:dinuclear ratio could not be determined. Anal. Calcd for $C_{15}H_{22}AgF_3N_4O_3S$: C, 35.80; H, 4.41; N, 11.13; S: 6.37. Found: C, 35.79; H, 4.56; N, 11.01; S: 6.43. ^{1}H NMR (400.9 MHz, D$_6$-DMSO): δ 7.50 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H5 or H4, Im), 7.45 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H4 or H5, Im), 4.11 (t, $^3J_{HH}$ = 6.4 Hz, 4H, α−CH$_2$), 3.83 (s, 6H, Me), 1.75 (m, 4H, β−CH$_2$), 1.34 (m, 4H, γ−CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, D$_6$-DMSO): δ 179.8 (br s, C2), 123.0 (br s, C4), 121.9

(br s, C5), 120.7 (q, $^{1}J_{FC}$ = 322.2 Hz, CF$_3$), 50.4 (br s, α−CH$_2$), 38.0 (Me), 31.0 (br s, β−CH$_2$), 26.5 (br s, γ−CH$_2$). ^{19}F NMR (188.30 MHz, D$_6$-DMSO): δ −77.3 (s). (+)ESI-MS (MeCN) *m*/*z*: 857.1 ([Ag$_2$(L^6)$_2$(TfO)]$^+$), 353.1 ([Ag(L^6)]$^+$; (−)ESI-MS (MeCN) *m*/*z*: 149 (TfO$^-$). Λ$_E$ (Ω^{-1} cm^2 mol^{-1}) = 58.2.

[Ag$_m$(L^7)$_m$](TfO)$_m$. It was prepared in the same way as for [Ag$_m$(L^6)$_m$](TfO)$_m$, starting from [Ag$_m$(L^7)$_m$][AgBr$_2$]$_m$ (163 mg, 0.26 mmol) and AgTfO (66 mg, 0.26 mmol). Yield: 112 mg, 0.22 mmol, 84% (overall based on Ag). The [Ag(κ^2-L^7)]TfO: [Ag$_2$(μ-L^7)$_2$](TfO)$_2$ ratio (M:M$_2$) is 5.3, as determined from the ^{1}H NMR spectrum in CD$_2$Cl$_2$, at 22 °C, and a total concentration (based on Ag(L^7)TfO) of 0.025 mol/L. Anal. Calcd for $C_{16}H_{24}AgF_3N_4O_3S$: C, 37.15; H, 4.68; N, 10.83; S: 6.20. Found: C, 37.01; H, 4.24; N, 10.69; S: 6.28. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ 7.19 (d, $^{3}J_{HH}$ = 2.0 Hz, 2H, H5 or H4, Im), 7.18 (d, $^{3}J_{HH}$ = 2.0 Hz, 2H, H4 or H5, Im), 4.18 (t, $^{3}J_{HH}$ = 6.4 Hz, 4H, α−CH$_2$), 3.86 (s, 6H, Me), 1.73 (quint, $^{3}J_{HH}$ = 6.4 Hz, 4H, β−CH$_2$), 1.56 (br s, 2H, δ−CH$_2$), 1.36 (br s, 4H, γ−CH$_2$). ^{1}H NMR (400.9 MHz, CD$_2$Cl$_2$): δ 7.13−7.09 (m, 12H, H5 and H4, Im, M and M$_2$), 4.18 (t, $^{3}J_{HH}$ = 6.2 Hz, 4H, α−CH$_2$, M), 4.11 (t, $^{3}J_{HH}$ = 7.0 Hz, 8H, α−CH$_2$, M$_2$), 3.90 (s, 6H, Me, M), 3.86 (s, 12H, Me, M$_2$), 1.85 (m, 12H, β−CH$_2$, M and M$_2$), 1.64 (m, 2H, δ−CH$_2$, M), 1.48−1.41 (m, 4H, γ−CH$_2$, M), 1.34 (m, 12H, γ− and δ−CH$_2$, M$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CD$_3$CN): δ 123.8 (br s, C4 or C5), 122.8 (br s, C5 or C4), 50.4 (br s, α−CH$_2$), 39.1 (Me), 30.4 (br s, CH$_2$), 26.3 (br s, CH$_2$). The signals for C2 and one CH$_2$ were not observed. ^{13}C{^{1}H} NMR (100.8 MHz, CD$_2$Cl$_2$, −60 °C): δ 179.2 (two d, $^{1}J_{^{107}Ag^{13}C}$ = 182.5 Hz, $^{1}J_{^{109}Ag^{13}C}$ = 210.4 Hz, C2, M or M$_2$), 178.9 (two d, $^{1}J_{^{107}Ag^{13}C}$ = 179.3 Hz, $^{1}J_{^{109}Ag^{13}C}$ = 207.1 Hz, C2, M$_2$ or M), 122.4 (d, $^{3}J_{Ag^{13}C}$ = 5.3 Hz, C4, M), 122.3 (d, $^{3}J_{Ag^{13}C}$ = 5.0 Hz, C4, M$_2$), 121.6 (d, $^{3}J_{Ag^{13}C}$ = 5.8 Hz, C5, M), 121.1 (d, $^{3}J_{Ag^{13}C}$ = 5.0 Hz, C5, M$_2$), 120.2 (q, $^{1}J_{FC}$ = 320.2 Hz, CF$_3$), 51.5 (α−CH$_2$, M$_2$), 47.7 (α−CH$_2$, M), 38.5 (d, $^{3}J_{Ag^{13}C}$ = 2.6 Hz, Me, M), 38.5 (d, $^{3}J_{Ag^{13}C}$ = 3.5 Hz, Me, M$_2$), 31.8 (β−CH$_2$, M$_2$), 29.7 (β−CH$_2$, M), 29.2 (δ−CH$_2$, M$_2$), 26.5 (γ−CH$_2$, M$_2$), 24.3 (δ−CH$_2$, M), 22.9 (γ−CH$_2$, M). C4 and C5 give one doublet instead of the expected pair of doublets because the values of $^{3}J_{^{107}Ag^{13}C}$ and $^{3}J_{^{109}Ag^{13}C}$ are very similar. The observed $^{3}J_{Ag^{13}C}$ value corresponds approximately to the mean of $^{3}J_{^{107}Ag^{13}C}$ and $^{3}J_{^{109}Ag^{13}C}$. ^{19}F NMR (188.3 MHz, CD$_3$CN): δ −78.0 (s). (+)ESI-MS (MeCN) *m*/*z*: 885.2 ([Ag$_2$(L^7)$_2$(TfO)]$^+$), 367.1 ([Ag(L^7)]$^+$); (−)ESI-MS (MeCN) *m*/*z*: 158.9 ([Ag(CN$_2$)]$^-$), 149 (TfO$^-$). Λ$_E$ (Ω^{-1} cm^2 mol^{-1}) = 69.2.

[Ag$_m$(L^8)$_m$](TfO)$_m$. It was prepared in the same way as for [Ag$_m$(L^6)$_m$](TfO)$_m$, starting from [Ag$_m$(L^8)$_m$][AgBr$_2$]$_m$ (128 mg, 0.20 mmol) and AgTfO (51 mg, 0.20 mmol). Yield: 92 mg, 0.17 mmol, 87% (overall based on Ag). The [Ag(κ^2-L^8)]TfO: [Ag$_2$(μ-L^8)$_2$](TfO)$_2$ ratio (M:M$_2$) is 49, as determined from the ^{13}C{^{1}H} NMR spectrum in CD$_2$Cl$_2$, at 22 °C, and a total concentration (based on Ag(L^8)TfO) of 0.020 mol/L. Anal. Calcd for $C_{17}H_{26}AgF_3N_4O_3S$: C, 38.43; H, 4.93; N, 10.54; S, 6.03. Found: C, 38.40; H, 4.60; N, 10.39; S, 5.98. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ 7.20 (d, $^{3}J_{HH}$ = 1.6 Hz, 2H, H5, Im), 7.18 (d, $^{3}J_{HH}$ = 1.6 Hz, 2H, H4, Im), 4.16 (t, $^{3}J_{HH}$ = 7.2 Hz, 4H, α−CH$_2$), 3.83 (s, 6H, Me), 1.89−1.82 (m, 4H, β−CH$_2$), 1.47−1.45 (m, 4H, γ−CH$_2$), 1.36−1.33 (m, 4H, δ−CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CD$_3$CN): δ 124.0 (br s, C4), 122.0 (br s, C5), 50.1 (br s, α−CH$_2$), 39.0 (Me), 30.1 (br s, β−CH$_2$), 26.6 (br s, γ−CH$_2$), 24.6 (br s, δ−CH$_2$). The signal of C2 was not observed. ^{13}C{^{1}H} NMR (100.8 MHz, CD$_2$Cl$_2$, −60 °C): δ 179.2 (two d, $^{1}J_{^{107}Ag^{13}C}$ = 180.4 Hz, $^{1}J_{^{109}Ag^{13}C}$ = 208.4 Hz, C2, M), 122.6 (d, $^{3}J_{Ag^{13}C}$ = 5.4 Hz, C4, M), 122.3 (d, $^{3}J_{Ag^{13}C}$ = 4.6 Hz, C4, M$_2$), 121.0 (d, $^{3}J_{Ag^{13}C}$ = 5.1 Hz, C5, M$_2$), 120.5 (d, $^{3}J_{Ag^{13}C}$ = 5.5 Hz, C5, M), 120.2 (q, $^{1}J_{FC}$ = 320.4 Hz, CF$_3$), 51.7 (α−CH$_2$, M$_2$), 48.5 (α−CH$_2$, M), 38.5 (Me, M), 38.5 (Me, M$_2$), 31.6 (β−CH$_2$, M$_2$), 29.4 (δ−CH$_2$, M$_2$), 28.7 (β−CH$_2$, M), 26.8 (γ−CH$_2$, M$_2$), 24.9 (δ−CH$_2$, M), 23.0 (γ−CH$_2$, M). The signal of C2 of M$_2$ was not observed because the concentration of M$_2$ was too low. ^{19}F NMR (282.4 MHz, CD$_3$CN): δ −78.1 (s). (+)ESI-MS (MeCN) *m*/*z*: 913.2 ([Ag$_2$(L^8)$_2$(TfO)]$^+$), 381 ([Ag(L^8)]$^+$); (−)ESI-MS (MeCN) *m*/*z*: 158.9 ([Ag(CN$_2$)]$^-$), 149 (TfO$^-$). Λ$_E$ (Ω^{-1} cm^2 mol^{-1}) = 75.1.

[Ag$_m$(L^{10})$_m$](TfO)$_m$. It was prepared in the same way as for [Ag$_m$(L^6)$_m$](TfO)$_m$, starting from [Ag$_m$(L^{10})$_m$][AgBr$_2$]$_m$ (175 mg, 0.26 mmol) and AgTfO (67 mg, 0.26 mmol). Yield: 99 mg, 0.18 mmol, 68% (based on Ag). The [Ag(κ^2-L^{10})]TfO: [Ag$_2$(μ-L^{10})$_2$](TfO)$_2$ ratio (M:M$_2$) is 6.8, as determined from the ^{1}H NMR spectrum in CD$_2$Cl$_2$, at 22 °C, and a total concentration (based on Ag(L^{10})TfO) of 0.020 mol/L. Anal. Calcd for $C_{19}H_{30}AgF_3N_4O_3S$: C, 40.80; H, 5.41; N, 10.02; S, 5.73. Found: C, 40.74; H, 5.15; N, 9.89; S, 5.70. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ 7.21 (d, $^{3}J_{HH}$ = 2.0 Hz, 2H, H5, Im), 7.16 (d, $^{3}J_{HH}$ = 2.0 Hz, 2H, H4, Im), 4.15 (t, $^{3}J_{HH}$ = 7.2 Hz, 4H, α−CH$_2$), 3.84 (s, 6H, Me), 1.82 (quint, $^{3}J_{HH}$ = 7.2 Hz, 4H, β−CH$_2$), 1.32−1.28 (m, 12H, γ−, δ− and ε−CH$_2$). ^{1}H NMR (400.9 MHz, CD$_2$Cl$_2$, −40 °C): δ 7.10−7.08 (m, 12H, H5 and H4, Im, M and M$_2$), 4.08 (t, $^{3}J_{HH}$ = 7.2 Hz, 4H, α−CH$_2$, M), 4.04 (t, $^{3}J_{HH}$ = 6.8 Hz, 8H, α−CH$_2$, M$_2$), 3.82 (s, 6H, Me, M), 3.81 (s, 12H, Me, M$_2$), 1.78−1.73 (m, 12H, β−CH$_2$, M and M$_2$), 1.32−1.18 (m, 36H, δ−, γ− and ε−CH$_2$, M and M$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CD$_3$CN): δ 181.5 (br s, C2), 123.9 (br s, C4), 122.2 (q, $^{1}J_{FC}$ = 320.9 Hz, CF$_3$SO$_3$$^-$), 122.2 (br s, C5), 52.0 (br, α−CH$_2$), 39.1 (Me), 30.7 (br s, CH$_2$), 27.3 (br s, CH$_2$), 25.3 (br s, CH$_2$); two CH$_2$ signals are overlapped. ^{13}C{^{1}H} NMR (100.8 MHz, CD$_2$Cl$_2$, −60 °C): δ 179.2 (two d, $^{1}J_{^{107}Ag^{13}C}$ = 182.5 Hz, $^{1}J_{^{109}Ag^{13}C}$ = 210.4 Hz, C2, M or M$_2$), 178.9 (two d, $^{1}J_{^{107}Ag^{13}C}$ = 179.3, Hz, $^{1}J_{^{109}Ag^{13}C}$ = 207.1 Hz, C2, M$_2$ or M), 122.6 (d, $^{3}J_{Ag^{13}C}$ = 5.4 Hz, C4, M), 122.3 (d, $^{3}J_{Ag^{13}C}$ = 4.9 Hz, C4, M$_2$), 121.1 (d, $^{3}J_{Ag^{13}C}$ = 5.2 Hz, C5, M$_2$), 120.4 (d, $^{3}J_{Ag^{13}C}$ = 5.6 Hz, C5, M), 120.2 (q, $^{1}J_{FC}$ = 320.3 Hz, CF$_3$SO$_3$$^-$), 51.7 (α−CH$_2$, M$_2$), 50.5 (α−CH$_2$, M), 38.5 (d, $^{3}J_{Ag^{13}C}$ = 2.6 Hz, Me, M), 38.5 (d, $^{3}J_{Ag^{13}C}$ = 2.1 Hz, Me, M$_2$), 31.7 (CH$_2$, M$_2$), 29.9 (CH$_2$, M$_2$), 29.5 (β−CH$_2$, M), 29.3 (CH$_2$, M$_2$), 26.8 (CH$_2$, M$_2$), 25.9 (δ−CH$_2$, M), 25.3 (ε−CH$_2$, M), 23.6 (γ−CH$_2$, M). ^{19}F{^{1}H} NMR (282.4 MHz, CD$_3$CN): δ −78.1 (s). ESI-MS (MeCN) *m*/*z*: 969.3 ([Ag$_2$(L^{10})$_2$(TfO)]$^+$), 409.2 ([Ag(L^{10})]$^+$); (−)ESI-MS (MeCN) *m*/*z*: 158.9 ([Ag(CN$_2$)]$^-$), 149 (TfO$^-$). Λ$_E$ (Ω^{-1} cm^2 mol^{-1}) = 60.4.

[Au$_2$(μ-L^3)$_2$](TfO)$_2$. [AuCl(SMe$_2$)] (70 mg, 0.24 mmol) and AgTfO (61 mg, 0.24 mmol) were added to a suspension of [Ag$_2$(μ-L^3)$_2$][AgBr$_2$]$_2$ (137 mg, 0.12 mmol) in MeCN (10 mL). The mixture was stirred for 15 h at room temperature in the dark and filtered through Celite. The filtrate was concentrated under vacuum up to about 1 mL. Addition of Et$_2$O (30 mL) gave a white precipitate which was filtered, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. Yield: 87 mg, 0.079 mmol, 66%. Mp: 210 °C dec. Anal. Calcd for $C_{24}H_{32}Au_2F_6N_8O_6S_2$: C, 26.19; H, 2.93; N, 10.18; S, 5.83. Found: C, 26.10; H, 3.08; N, 10.18; S, 6.14. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ 7.33 (d, $^{3}J_{HH}$ = 2.0 Hz, 4H, H5), 7.26 (d, $^{3}J_{HH}$ = 2.0 Hz, 4H, H4), 4.23 (m, 8H, α−CH$_2$), 3.55 (s, 12H, Me), 2.55 (m, 4H, β−CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CD$_3$CN): δ 184.1 (C2), 125.0 (C4), 121.9 (C5), 48.0 (α−CH$_2$), 38.0 (Me), 30.0 (β−CH$_2$). ^{19}F NMR (282.4 MHz, CD$_3$CN): δ −78.0 (s). (+)ESI-MS (MeCN) *m*/*z*: 951.2 ([Au$_2$(L^3)$_2$(TfO)]$^+$), 401.1 ([Au$_2$(L^3)$_2$]$^{2+}$).

[Au$_2$(μ-L^5)$_2$](TfO)$_2$. It was prepared in the same way as for [Au$_2$(μ-L^3)$_2$](TfO)$_2$, starting from [Ag$_2$(μ-L^5)$_2$][AgBr$_2$]$_2$ (110 mg, 0.090 mmol), [AuCl(SMe$_2$)] (54 mg, 0.18 mmol), and AgTfO (47 mg, 0.18 mmol). Yield: 90 mg, 0.078 mmol, 86%. Mp: 255 °C dec Anal. Calcd for $C_{28}H_{40}Au_2F_6N_8O_6S_2$: C, 29.07; H, 3.49; N, 9.69; S, 5.54. Found: C, 28.72; H, 3.41; N, 9.51; S, 5.92. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ 7.24 (d, $^{3}J_{HH}$ = 2.0 Hz, 4H, H5 or H4), 7.23 (d, $^{3}J_{HH}$ = 2.0 Hz, 4H, H4 or H5), 4.23 (t, $^{3}J_{HH}$ = 6.8 Hz, 8H, α−CH$_2$), 3.55 (s, 12H, Me), 1.86 (quint, $^{3}J_{HH}$ = 6.8 Hz, 8H, β−CH$_2$), 1.38−1.30 (m, 4H, γ−CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CD$_3$CN): δ 184.8 (C2), 124.4 (C4 or C5), 122.4 (C5 or C4), 51.6 (α−CH$_2$), 38.1 (Me), 31.0 (β−CH$_2$), 24.5 (γ−CH$_2$). ^{19}F NMR (188.3 MHz, CD$_3$CN): δ −78.0 (s). (+)ESI-MS (MeCN) *m*/*z*: 1007.2 ([Au$_2$(L^5)$_2$(TfO)]$^+$), 429.1 ([Au$_2$(L^5)$_2$]$^{2+}$).

[Au$_m$(L^6)$_m$](TfO)$_m$. [AuCl(SMe$_2$)] (79 mg, 0.27 mmol) and AgTfO (69 mg, 0.27 mmol) were added to a suspension of [Ag$_m$(L^6)$_m$][AgBr$_2$]$_m$ (167 mg, 0.27 mmol) in MeCN (10 mL). The mixture was stirred for 1 h at room temperature in the dark and filtered through Celite. Addition of Et$_2$O (50 mL) gave a white precipitate, which was filtered, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. Yield: 119 mg, 74% (based on Au). The isolated solid is a mixture of [Au(κ^2-L^6)]TfO (M, 37%) and [Au$_2$(μ-L^6)$_2$](TfO)$_2$ (M$_2$, 63%). Anal. Calcd for $C_{15}H_{22}AuF_3N_4O_3S$: C, 30.41; H, 3.74; N, 9.46; S, 5.41. Found: C, 30.36; H, 3.41; N, 9.26; S, 5.32. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ

7.22 (d, $^3J_{HH}$ = 2.0 Hz, 2H, H5, M), 7.20 (d, $^3J_{HH}$ = 2.0 Hz, 2H, H4, M), 7.20 (d, $^3J_{HH}$ = 2.0 Hz, 4H, H5, M$_2$), 7.17 (d, $^3J_{HH}$ = 2.0 Hz, 4H, H4, M$_2$), 4.22 (t, $^3J_{HH}$ = 5.6 Hz, 4H, α−CH$_2$, M), 4.17 (t, $^3J_{HH}$ = 7.2 Hz, 8H, α−CH$_2$, M$_2$), 3.85 (s, 12H, Me, M$_2$), 3.82 (s, 6H, Me, M), 1.84 (m, 12H, β−CH$_2$, M and M$_2$), 1.69 (m, 4H, γ−CH$_2$, M), 1.33 (m, 8H, γ−CH$_2$, M$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CD$_3$CN): δ 184.9 (C2, M and M$_2$), 124.0 (C4, M$_2$), 123.8 (C4, M), 122.8 (C5, M), 122.6 (C5, M$_2$), 51.9 (α−CH$_2$, M$_2$), 48.9 (α−CH$_2$, M), 38.4 (Me, M$_2$), 38.3 (Me, M), 32.3 (β−CH$_2$, M$_2$), 31.1 (β−CH$_2$, M), 27.2 (γ−CH$_2$, M$_2$), 23.1 (γ−CH$_2$, M). ^{19}F NMR (100.8 MHz, CD$_3$CN): δ −78.1 (s). (+)ESI-MS (MeCN) *m/z:* 1035.3 [Au$_2$(L^6)$_2$(TfO)]$^+$), 443.2 ([Au(L^6)]$^+$ + [Au$_2$(L^6)$_2$]$^{2+}$), 124.1 ([H$_2$L^6]$^{2+}$).

[Au$_m$(L^7)$_m$](TfO)$_m$. It was prepared in the same way as for [Au$_m$(L^6)$_m$](TfO)$_m$, starting from [Ag$_m$(L^7)$_m$][AgBr$_2$]$_m$ (134 mg, 0.21 mmol), [AuCl(SMe$_2$)] (62 mg, 0.21 mmol), and AgTfO (54 mg, 0.21 mmol). Yield: 85 mg, 67% (based on Au). The isolated solid is a mixture of [Au(κ^2-L^7)]TfO (M, 86%) and [Au$_2$(μ-L^7)$_2$](TfO)$_2$ (M$_2$, 14%). Anal. Calcd for C$_{16}$H$_{24}$AuF$_3$N$_4$O$_3$S: C, 31.69; H, 3.99; N, 9.24; S, 5.29. Found: C, 31.84; H, 3.61; N, 9.23; S, 4.97. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ 7.20 (d, $^3J_{HH}$ = 2.0 Hz, 6H, H5, M and M$_2$), 7.19 (m, $^3J_{HH}$ = 1.8 Hz, 6H, H4, M and M$_2$), 4.23 (t, $^3J_{HH}$ = 6.41 Hz, 4H, α−CH$_2$, M), 4.17 (t, $^3J_{HH}$ = 7.2 Hz, 8H, α−CH$_2$, M$_2$), 3.90 (s, 6H, Me, M), 3.85 (s, 12H, Me, M$_2$), 1.90−1.80 (m, 12H, β−CH$_2$, M and M$_2$), 1.68−1.60 (m, 2H, δ−CH$_2$, M), 1.53−1.47 (m, 4H, γ−CH$_2$, M), 1.41−1.26 (m, 12H, γ− and δ−CH$_2$, M$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, CD$_3$CN): δ 185.0 (C2, M$_2$), 184.9 (C2, M), 124.1 (C4, M), 124.0 (C4, M$_2$), 123 (C5, M), 122.4 (C5, M$_2$), 51.8 (α−CH$_2$, M$_2$), 49.3 (α−CH$_2$, M), 38.5 (Me, M and M$_2$), 32.2 (β−CH$_2$, M$_2$), 30.9 (β−CH$_2$, M), 29.7 (δ−CH$_2$, M$_2$), 27.2 (γ−CH$_2$, M$_2$), 25.5 (δ−CH$_2$, M), 24.3 (γ−CH$_2$, M). ^{19}F NMR (188.3 MHz, CD$_3$CN): δ −78.0 (s). (+)ESI-MS (MeCN) *m/z:* 1027.3([Au$_2$(L^7)$_2$(TfO)]$^+$), 457.2 ([Au(L^7)]$^+$ and [Au$_2$(L^7)$_2$]$^{2+}$), 130.1 ([H$_2$L^7]$^{2+}$).

[Au$_2$(μ-L^8)$_2$](TfO)$_2$. *Method A*: It was prepared in the same way as for [Au$_m$(L^6)$_m$](TfO)$_m$, starting from [Ag$_m$(L^8)$_m$][AgBr$_2$]$_m$ (166 mg, 0.26 mmol), [AuCl(SMe$_2$)] (76 mg, 0.26 mmol), and AgTfO (67 mg, 0.26 mmol). The complex was isolated pure by slow addition of Et$_2$O to the reaction solution. Yield: 115 mg, 0.09 mmol, 71%. Mp: 169−171 °C. *Method B*: To a solution of [Au$_m$(L^8)$_m$](TfO)$_m$ (75 mg, 0.14 mmol), [AuCl(SMe$_2$)] (42 mg, 0.14 mmol) was added. The mixture was stirred for 1 h at room temperature and filtered through Celite. Addition of Et$_2$O (50 mL) gave a white precipitate, which was filtered, washed with Et$_2$O (3 × 5 mL) and dried under vacuum. Yield: 35 mg, 0.028 mmol, 41%. *Method C*: To a suspension of [(AuCl)$_2$(μ-L^8)] (50 mg, 0.068 mmol) in MeCN (7 mL), AgTfO (17 mg, 0.068 mmol) and [Au$_m$(L^8)$_m$](TfO)$_m$ (36 mg, 0.068 mmol) were added. The mixture was stirred for 3 h at room temperature in the dark and filtered through Celite. Addition of Et$_2$O (50 mL) gave a white precipitate, which was filtered, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. Yield: 52 mg, 0.041 mmol, 61%. Mp: 169−171 °C. Anal. Calcd for C$_{34}$H$_{52}$Au$_2$F$_6$N$_8$O$_6$S$_2$: C, 32.91; H, 4.22; N, 9.03; S, 5.17. Found: C, 32.77; H, 4.23; N, 9.00; S, 5.06. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ 7.20 (d, $^3J_{HH}$ = 2.0 Hz, 4H, H5), 7.18 (d, $^3J_{HH}$ = 2.0 Hz, 4H, H4), 4.17 (t, $^3J_{HH}$ = 7.2 Hz, 8H, α−CH$_2$), 3.85 (s, 12H, Me), 1.83 (m, 8H, β−CH$_2$), 1.29 (m, 16H, γ− and δ−CH$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, CD$_3$CN): δ 184.9 (C2), 124.0 (C4), 122.5 (C5), 51.9 (α−CH$_2$), 38.5 (Me), 32.3 (β−CH$_2$), 30.1 (γ− or δ−CH$_2$), 27.4 (δ− or γ−CH$_2$). ^{19}F NMR (282.4 MHz, CD$_3$CN): δ −78.1 (s). (+)ESI-MS (MeCN) *m/z*: 1091.3 ([Au$_2$(L^8)$_2$(TfO)]$^+$), 471.2 ([Au$_2$(L^8)$_2$]$^{2+}$).

[Au$_2$(μ-L^{10})$_2$](TfO)$_2$. *Method A*: It was prepared in the same way as for [Au$_m$(L^6)$_m$](TfO)$_m$, starting from [AuCl(SMe$_2$)] (62 mg, 0.21 mmol), AgTfO (54 mg, 0.21 mmol), and [Ag$_m$(L^{10})$_m$][AgBr$_2$]$_m$ (143 mg, 0.21 mmol) in MeCN (10 mL). Yield: 85 mg, 0.065 mmol, 62%. *Method B*: It was prepared in the same way as [Au$_2$(μ-L^8)$_2$](TfO)$_2$ starting from [Ag$_m$(L^{10})$_m$](TfO)$_m$ (50 mg, 0.087 mmol) and [AuCl(SMe$_2$)] (27 mg, 0.092 mmol). Yield: 30 mg, 0.023 mmol, 51%. Mp: 191−192 °C. Anal. Calcd for C$_{38}$H$_{60}$Au$_2$F$_6$N$_8$O$_6$S$_2$: C, 35.19; H, 4.66; N, 8.64; S, 4.94. Found: C, 35.18; H, 4.55; N, 8.56; S, 4.79. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ 7.20 (d, $^3J_{HH}$ = 2.0 Hz, 4H, H5), 7.18 (d, $^3J_{HH}$ = 2.0 Hz, 4H, H4), 4.18 (t, $^3J_{HH}$ = 7.2 Hz, 8H, α−CH$_2$), 3.86 (s, 12H, Me), 1.85 (m, 8H, β−CH$_2$), 1.28−1.23 (m, 24H, γ−, δ− and ε−CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CD$_3$CN): δ 184.9 (C2), 124.0 (C4), 122.6 (C5), 51.9 (α−CH$_2$), 38.5 (Me), 32.4 (β−CH$_2$), 30.5 (CH$_2$), 30.2 (CH$_2$), 27.4 (CH$_2$). ^{19}F NMR (282.4 MHz, CD$_3$CN): δ −78.0 (s). (+)ESI-MS (MeCN) *m/z:* 1147.4 ([Au$_2$(L^{10})$_2$(TfO)]$^+$), 499.2 ([Au$_2$(L^{10})$_2$]$^{2+}$).

[Au$_m$(L^8)$_m$]Br$_m$. To a solution of [H$_2$L^8]Br$_2$ (223 mg, 0.51 mmol) in DMF (10 mL), [AuCl(SMe$_2$)] (151 mg, 0.51 mmol) and NaAcO (105 mg, 1.28 mmol) were added. The mixture was heated at 120 °C overnight and filtered through Celite. Addition of Et$_2$O (50 mL) gave a precipitate, which was recrystallized in CH$_2$Cl$_2$. The resulting white solid was washed with Et$_2$O (3 × 5 mL) and dried under vacuum. Yield: 239 mg, 75% (based on Au). The isolated solid is a mixture of [Au(κ^2-L^8)]Br (M, 96%) and [Au$_2$(μ-L^8)$_2$]Br$_2$ (M$_2$, 4%). By diffusion of Et$_2$O into a MeCN solution of the isolated solid, single crystals of [Au(κ^2-L^8)]Br were obtained. Anal. Calcd for C$_{16}$H$_{26}$AuBrN$_4$: C, 34.86; H, 4.75; N, 10.16. Found: C, 34.54; H, 4.50; N, 9.97. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ 7.24 (d, $^3J_{HH}$ = 2.0 Hz, 6H, H5, M and M$_2$), 7.22 (d, $^3J_{HH}$ = 2.0 Hz, 4H, H4, M$_2$), 7.21 (d, $^3J_{HH}$ = 2.0 Hz, 2H, H4, M), 4.23 (t, $^3J_{HH}$ = 7.2 Hz, 4H, α−CH$_2$, M), 4.18 (t, $^3J_{HH}$ = 7.2 Hz, 8H, α−CH$_2$, M$_2$), 3.86 (s, 12H, Me, M$_2$), 3.85 (s, 6H, Me, M), 1.91−1.85 (m, 12H, β−CH$_2$, M and M$_2$), 1.54−1.51 (m, 4H, δ−CH$_2$, M), 1.40−1.36 (m, 4H, γ−CH$_2$, M and 16H, δ− and γ−CH$_2$, M$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CD$_3$CN): δ 185.1 (C2), 124.2 (C4), 122.1 (C5), 49.5 (α−CH$_2$), 38.4 (Me), 29.7 (β−CH$_2$), 26.2 (δ−CH$_2$), 24.5 (γ−CH$_2$). The signals of M$_2$ were not detected in the ^{13}C{^{1}H} NMR spectrum because of its low concentration. (+)ESI-MS (MeCN) *m/z*: 471.2 ([Au(L^8)]$^+$).

[Au(κ^2-L^8)]$_2$[AgBr$_3$]. To a solution of [H$_2$L^8]Br$_2$ (266 mg, 0.61 mmol) in DMF (10 mL), [AuCl(SMe$_2$)] (180 mg, 0.61 mmol), AgTfO (157 mg, 0.61 mmol), and NaAcO (126 mg, 1.54 mmol) were added. The mixture was heated at 120 °C overnight and filtered through Celite. Addition of Et$_2$O (50 mL) gave a white precipitate, which was filtered, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. The solid was extracted with CHCl$_3$ (40 mL), and the extract was filtered and concentrated up to about 2 mL. Addition of Et$_2$O gave a white solid, which was filtered, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. Yield: 154 mg, 0.12 mmol, 39%. Anal. Calcd for C$_{32}$H$_{52}$Au$_2$AgBr$_3$N$_8$: C, 29.79; H, 4.06; N, 8.68. Found: C, 29.61; H, 4.27; N, 8.44. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ 7.22 (d, $^3J_{HH}$ = 2.0 Hz, 2H, H5), 7.19 (d, $^3J_{HH}$ = 2.0 Hz, 2H, H4), 4.24 (t, $^3J_{HH}$ = 7.6 Hz, 4H, α−CH$_2$), 3.86 (s, 6H, Me), 1.92−1.85 (m, 4H, β−CH$_2$), 1.54−1.51 (m, 4H, δ−CH$_2$), 1.40−1.36 (m, 4H, γ−CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CD$_3$CN): δ 185.1 (C2), 124.2 (C4), 122.1 (C5), 49.6 (α−CH$_2$), 38.5 (Me), 29.8 (β−CH$_2$), 26.2 (δ−CH$_2$), 24.5 (γ−CH$_2$). (+)ESI-MS (MeCN) *m/z*: 471.2 ([Au(L^8)]$^+$); (−)ESI-MS (MeCN) *m/z*: 266.7 ([AgBr$_2$]$^-$), 213.8 ([AgBrCN]$^-$), 78.9 (Br$^-$).

[Au(κ^2-L^8)]TfO. To a solution of [Au$_m$(L^8)$_m$]Br$_m$ (83 mg, 0.15 mmol, M:M$_2$ = 96:4) in MeCN (7 mL), AgTfO (33 mg, 0.15 mmol) was added. The mixture was stirred for 10 min and filtered through Celite. Addition of Et$_2$O (50 mL) gave a white precipitate, which was filtered, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. The isolated solid was a 95:5 mixture of [Au(κ^2-L^8)]TfO and [Au$_2$(μ-L^8)$_2$](TfO)$_2$. Yield: 73 mg, 0.12 mmol, 78%. The mixture was dissolved in MeCN (2 mL), and Et$_2$O (2 mL) was added, precipitating a little amount of solid, which was filtered. Addition of 20 mL of Et$_2$O to the filtrate yielded pure [Au(κ^2-L^8)]TfO. Yield: 60 mg, 0.10 mmol, 64%. Mp: 168−169 °C. Anal. Calcd for C$_{17}$H$_{26}$AuF$_3$N$_4$O$_3$S: C, 32.91; H, 4.22; N, 9.03; S, 5.17. Found: C, 32.66; H, 4.28; N, 8.86; S, 5.10. ^{1}H NMR (400.9 MHz, CD$_3$CN): δ 7.22 (d, $^3J_{HH}$ = 2.0 Hz, 2H, H5), 7.18 (d, $^3J_{HH}$ = 2.0 Hz, 2H, H4), 4.23 (t, $^3J_{HH}$ = 7.6 Hz, 4H, α−CH$_2$), 3.85 (s, 6H, Me), 1.92−1.85 (m, 4H, β−CH$_2$), 1.54−1.51 (m, 4H, δ−CH$_2$), 1.39−1.36 (m, 4H, γ−CH$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, CD$_3$CN): δ 185.0 (C2), 124.2 (C4), 122.5 (C5), 49.5 (α−CH$_2$), 38.4 (Me), 29.8 (β−CH$_2$), 27.4 (δ−CH$_2$), 26.2 (γ−CH$_2$). ^{19}F NMR (282.4 MHz, CD$_3$CN): δ −78.1 (s). (+)ESI-MS (MeCN) *m/z*: 471.2 ([Au(L^8)]$^+$).

[Au$_m$(L^{10})$_m$]Br$_m$. To a solution of [H$_2$L^{10}]Br$_2$ (197 mg, 0.42 mmol) in DMF (10 mL), [AuCl(SMe$_2$)] (125 mg, 0.42 mmol) and NaAcO (86 mg, 1.05 mmol) were added. The mixture was heated at 120 °C for one day and filtered through Celite. Addition of Et$_2$O (50 mL) gave a precipitate, which was recrystallized from CH_2Cl_2. The resulting white solid was washed with Et_2O (3 × 5 mL) and dried under vacuum. Yield: 209 mg, 76% (based on Au). The isolated solid was a mixture of $[Au(\kappa^2\text{-}L^{10})]Br$ (M, 90%) and $[Au_2(\mu\text{-}L^{10})_2]Br_2$ (M_2, 10%). This mixture is hygroscopic and becomes oily in contact with air. Because of this it was not possible to obtain a correct elemental analysis. ^1H NMR (400.9 MHz, CD_3CN): δ 7.26 (d, $^3J_{HH}$ = 2.0 Hz, 4H, H5, Im, M_2), δ 7.25 (d, $^3J_{HH}$ = 2.0 Hz, 2H, H5, Im, M), 7.23 (d, $^3J_{HH}$ = 2.0 Hz, 6H, H4, Im, M_2 and M), 4.24 (t, $^3J_{HH}$ = 7.2 Hz, 4H, α−CH_2, M), 4.19 (t, $^3J_{HH}$ = 7.2 Hz, 8H, α−CH_2, M_2), 3.86 (s, 18H, Me, M and M_2), 1.86 (quint, $^3J_{HH}$ = 7.2 Hz, 12H, β−CH_2, M and M_2), 1.43−1.39 (m, 4H, CH_2, M), 1.38−1.29 (m, 36H, CH_2, M and M_2). $^{13}C\{^1H\}$ NMR (100.1 MHz, CD_3CN): δ 184.9 (C2, M and M_2), 124.3 (C4, M), 124.0 (C4, M_2), 122.5 (C5, M_2) 122.0 (C5, M), 52.0 (α−CH_2, M_2), 51.1 (α−CH_2, M), 38.5 (Me, M_2 and M), 32.3 (β−CH_2, M_2), 30.4 (CH_2, M_2 and β−CH_2, M), 30.1 (CH_2, M_2), 27.3 (γ−CH_2, M_2 and δ−CH_2, M), 26.9 (ε−CH_2, M), 25.2 (γ−CH_2, M). (+)ESI-MS (MeCN) *m*/*z*: 499.2 ($[Au(L^{10})]^+$).

$[Au(\kappa^2\text{-}L^{10})]$TfO. A solution of $[Au_2(\mu\text{-}L^{10})_2](TfO)_2$ (44 mg, 0.034 mmol) in MeCN (5 mL) was heated for one day at 120 °C in a Carius tube. On addition of Et_2O (10 mL), a little amount of solid precipitated. The suspension was filtered, and the filtrate was concentrated under vacuum up to about 1 mL. Addition of Et_2O (30 mL) gave pure $[Au(\kappa^2\text{-}L^{10})]$OTf as a white precipitate, which was filtered, washed with Et_2O (2 × 5 mL), and dried under vacuum. Yield: 18 mg, 0.03 mmol, 21%. Mp: 129−130 °C. Anal. Calcd for $C_{19}H_{30}AuF_3N_4O_3S$: C, 35.19; H, 4.66; N, 8.64; S, 4.94. Found: C, 35.01; H, 4.72; N, 8.40; S, 4.75. ^1H NMR (400.9 MHz, CD_3CN): δ 7.22 (d, $^3J_{HH}$ = 2.0 Hz, 2H, H5), 7.20 (d, $^3J_{HH}$ = 1.6 Hz, 2H, H4), 4.23 (t, $^3J_{HH}$ = 7.2 Hz, 4H, α−CH_2), 3.86 (s, 6H, Me), 1.86 (quint, $^3J_{HH}$ = 7.2 Hz, 4H, β−CH_2), 1.43−1.38 (m, 4H, δ−CH_2), 1.38−1.32 (m, 8H, γ− and ε−CH_2). $^{13}C\{^1H\}$ NMR (100.8 MHz, CD_3CN): δ 184.8 (C2), 124.3 (C4), 122.0 (C5), 51.2 (α−CH_2), 38.4 (Me), 30.4 (β−CH_2), 27.4 (δ−CH_2), 26.9 (ε−CH_2), 25.2 (γ−CH_2). ^{19}F NMR (282.4 MHz, CD_3CN): δ −78.0 (s). (+)ESI-MS (MeCN) *m*/*z*: 499.2 ($[Au(L^{10})]^+$).

$[(AuCl)_2(\mu\text{-}L^8)]$. To a suspension of $[Ag_m(L^8)_m][AgBr_2]_m$ (132 mg, 0.20 mmol) in CH_2Cl_2 (10 mL), $[AuCl(SMe_2)]$ (120 mg, 0.41 mmol) was added. The mixture was stirred for 3 h at room temperature in the dark and filtered through Celite. The filtrate was concentrated under vacuum up to about 1 mL. Addition of Et_2O (30 mL) gave a white precipitate, which was filtered, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 80 mg, 0.11 mmol, 54%. Mp: 161−162 °C. Anal. Calcd for $C_{16}H_{26}Au_2Cl_2N_4$: C, 26.00; H, 3.55; N, 7.58. Found: C, 25.69; H, 3.37; N, 7.42. ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.03 (d, $^3J_{HH}$ = 2.0 Hz, 2H, H5), 6.98 (d, $^3J_{HH}$ = 2.0 Hz, 2H, H4), 4.16 (t, $^3J_{HH}$ = 7.2 Hz, 4H, α−CH_2), 3.84 (s, 6H, Me), 1.85 (m, 4H, β−CH_2), 1.35 (m, 8H, γ− and δ−CH_2). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 170.5 (C2), 121.8 (C4), 120.6 (C5), 51.0 (α−CH_2), 38.3 (Me), 30.7 (β−CH_2), 28.4 (δ−CH_2), 25.8 (γ−CH_2).

***trans*-$[AuI_2(\kappa^2\text{-}L^8)]$TfO.** To a solution of $[Au(\kappa^2\text{-}L^8)]$TfO (25 mg, 0.040 mmol) in MeCN (2 mL), a 0.062 M solution of I_2 in MeCN (642 μL, 0.040 mmol of I_2) was added at room temperature. A yellow solution was formed immediately. Addition of Et_2O (20 mL) gave an orange precipitate, which was filtered, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 28 mg, 0.032 mmol, 80%. Mp: 190 °C. Anal. Calcd for $C_{17}H_{26}Au_2F_3I_2N_4O_3S$: C, 23.36; H, 3.00; N, 6.41; S, 3.67. Found: C, 23.35; H, 3.12; N, 6.12; S, 4.05. ^1H NMR (300.1 MHz, CD_3CN): δ 7.45 (d, $^3J_{HH}$ = 1.8 Hz, 2H, H5), 7.40 (d, $^3J_{HH}$ = 1.8 Hz, 2H, H4), 4.18 (m, 4H, α−CH_2), 3.79 (s, 6H, Me), 1.98 (m, 4H, β−CH_2), 1.54 (m, 4H, δ−CH_2), 1.48 (m, 4H, γ−CH_2). $^{13}C\{^1H\}$ NMR (100.8 MHz, CD_3CN): δ 144.5 (C2), 127.1 (C4), 125.4 (C5), 51.1 (α−CH_2), 38.9 (Me), 29.3 (β−CH_2), 27.1 (δ−CH_2), 24.8 (γ−CH_2). ^{19}F NMR (282.4 MHz, CD_3CN): δ −78.1 (s). (+)ESI-MS (MeCN) *m*/*z*: 725.0 ($[Au(L^8)I_2]^+$), 471.2 ($[Au(L^8)]^+$).

X-ray Crystallography. Crystals of $[Ag_2(\mu\text{-}L^3)_2][PF_6]_2$, $[Au_2(\mu\text{-}L^3)_2]TfO)_2$, $[Ag(\kappa^2\text{-}L^7)]$TfO, $[Au(\kappa^2\text{-}L^8)]_2[AgBr_3]$, $[Au(\kappa^2\text{-}L^8)]Br$, and $[AuI_2(\kappa^2\text{-}L^8)]$TfO were obtained by liquid diffusion between a CH_3CN solution and Et_2O, and measured on a Bruker Smart APEX machine. Data were collected using monochromated Mo−Kα radiation in ω scan. The structures were solved by direct methods. All were refined anisotropically on F^2. The methyl groups were refined using rigid groups, and the other hydrogens were refined using a riding model. Special features: For complex $[Ag_2(\mu\text{-}L^3)_2](PF_6)_2$, the PF_6^- anion is disordered over two positions with an about 80:20 distribution; for complex $[Au_2(\mu\text{-}L^3)_2](TfO)_2$ the relatively high electron density near the Au atoms can be ascribed to absorption errors (thin-plate).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional NMR and ESI-MS spectra, geometrical description of the intermolecular interactions in the crystal structures, crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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