Inorganic Chemistry
Article

Inorg. Chem. **2009**, *48*, 8613–8622 **8613**
DOI: 10.1021/ic901051f

Synthesis and Structures of Group 11 Metal Triazenide Complexes: Ligand Supported Metallophilic Interactions

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Received June 1, 2009

A homologous and homoleptic series of stable Group 11 metal triazenide complexes with the general formula $[\mathrm{M}(\mathbf{L}')]_n$ (M = Cu or Au, $n = 2$; M = Ag, $n = 3$) featuring the bulky triazenide ligand *N,N′*-bis(2,6-di-isopropylphenyl)triazene, **L′**H, have been prepared by the reaction of Li[**L′**] with the metal chlorides, CuCl, AgCl, and [(THT)AuCl], respectively, in a 1:1 stoichiometric ratio. The compounds $[\mathrm{Cu}_2(\mathbf{L}')_2]$ and $[\mathrm{Au}_2(\mathbf{L}')_2]$ crystallized as dimers with M···M separations of 2.4458(4) Å and 2.6762(4) Å, respectively. In comparison, the reaction of AgCl with Li[**L′**] results in the formation of the tri-silver complex $[\mathrm{Ag}_3(\mathbf{L}')_3]$ with Ag···Ag separations of 3.01184(17) Å, 2.95329(17) Å, and 2.92745(16) Å. Attempts to react the parent triazene system **L′**H with [Cu(Mes)] resulted in the formation of the novel tri-copper system $[\mathrm{Cu}_3(\mathbf{L}')_2(\mathrm{Mes})]$. In all cases the molecular structures of the resultant complexes have been unambiguously determined by single crystal X-ray diffraction experiments.

Introduction

Attractive interactions between formally closed shell metal centers (s^2 or d^{10}) have been the subject of considerable attention for some time,[1−3] specifically with respect to the ability to control such bonding.[4−11] Weak attractive closed shell interactions were first witnessed by Schmidbaur in gold(I) complexes exhibiting close Au···Au contacts (2.8−3.5 Å).[12,13] Although first observed in gold(I) complexes, similar interactions have now been observed in other closed shell metal systems such as Cu(I),[14−19]Ag(I),[11,20−23] Ga(I),[24] In(I),[6,25] Tl(I),[7,25−29] Pd(II),[30−33] and Pt(II)[33−36] systems, assuming the name of metallophilic interactions. These metallophilic interactions arise primarily because of weak dispersive forces but are considerably enhanced by relativistic

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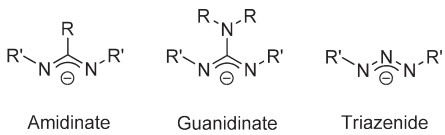
Chart 1. General Formula of the Amidinate, Guanidinate, and Triazenide Anions



effects in heavier element systems.[3,37] In fact, theoretical studies have shown that the relative strength of these interactions can increase by ~50% moving from lighter systems (Cu) to heavier (Au) because of increased relativistic effects, and are comparable in energetic terms to hydrogen bonding interactions.[37] While bridging ligands have been used successfully to promote short metal–metal contacts and control metallophilic interactions, the existence of true d^{10}–d^{10} bonding interactions in systems containing copper or silver have been both supported[38] and refuted[39] by theoretical studies. While it is recognized that ligand architecture can possibly blur the degree of metallophilic interactions, the M···M distances in such complexes are often short enough to raise the question of whether direct M···M bonding might not exist.

Anionic bridging ligands such as guanidinates, amidinates, and triazenides (Chart 1) have continued to evolve as versatile *N,N*′-donor ligands in coordination chemistry. The attractiveness of both amidinate and guanidinate ligands in this role is largely due to the large range of derivatives that are available through substitution at nitrogen.

Amidinate and guanidinate ligands have been used widely with Group 11 metals to form a range of dimeric and tetrameric complexes,[40−45] with varying coordination arrangements, and such systems have recently attracted attention as potential metal deposition precursors,[46−48] and as model systems for the study of spin delocalization super-exchange pathways.[49] In contrast, triazenide ligands $[R'NNNR']^-$, have not received the same degree of attention, despite their relative ease of preparation.[50,51] Structurally characterized examples of triazenide complexes show coordination modes typical of related amidinate[52] and guanidinate[53] systems (Chart 2), as well as alternative coordination modes including polyhapto π-aromatic interactions with aryl substituents.[54] Chart 2 shows the range of oligomeric coordination complexes that Group 11 triazenide complexes typically fall into.

Chart 2. Generic Bonding Modes and Typical Structures of Triazenide Complexes

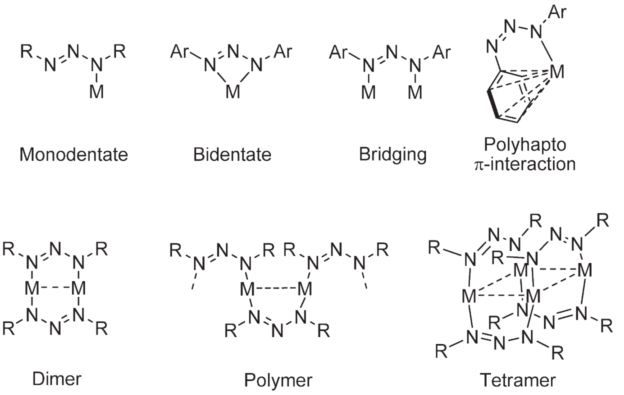
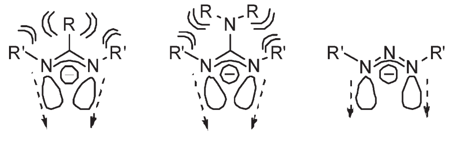


Chart 3. Effect of Sterics on *N*-Orbital Projection in Amidinate, Guanidinate, and Triazenide Ligands



In comparison to amidinate and guanidinate systems, the propensity of triazenide ligand systems to engage in bridging coordination modes[55] (Chart 2) is, in-part, attributed to the near parallel projection of the two *N*-donor atom orbitals: an effect that is more prevalent because of the lack of steric perturbation caused by substituent groups, often encountered in non-cyclic amidinate and guanidinate systems (Chart 3).[51]

While reports on the chemistry of Group 11 complexes containing amidinate and guanidinate ligands are prevalent, there is a comparative paucity of reports describing Group 11 triazenide complexes. Here we report the synthesis and structure of a homologous/homoleptic series of Group 11 metal complexes with the sterically encumbered *N,N*′-bis(2,6-di-isopropyl)triazenide ligand and have unambiguously determined the solid state structure of the resultant products, using single crystal X-ray diffraction experimentation.

Results and Discussion

The triazene system, *N,N*′-bis(2,6-di-isopropyl)triazene, **L**′H was synthesized in a simple one-pot reaction by the addition of excess *iso*-pentyl nitrite to 2,6-di-isopropylaniline in diethyl ether. Subsequent reaction of lithium *N,N*′-bis(2,6-di-isopropyl)triazide[56] generated in situ, with the cetal chlorides CuCl, AgCl, or (THT)AuCl, respectively, in a 1:1 stoichiometric ratio, followed by extraction into toluene and storage at low temperature resulted in the formation of

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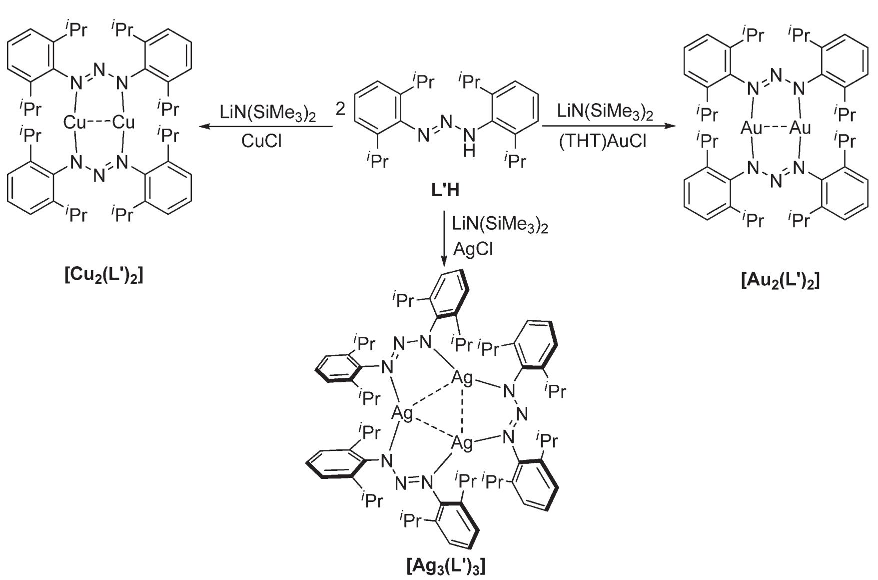
Scheme 1



air and moisture stable crystals which were isolated and characterized. The ^{1}H NMR spectroscopic data in d_2-methylene dichloride obtained for the resultant products were consistent with simple symmetrical structures in which the two 2,6-di-isopropyl groups are magnetically equivalent (for example, in the case of the copper product a single doublet resonance at $\delta = 1.20$ ppm, a single septet resonance at $\delta = 3.47$ ppm with resonances for the aromatic region ($\delta = 7.08-7.17$ ppm) are observed in the ^{1}H NMR spectrum). In the case of both the silver and gold products, NMR spectroscopy (^{1}H and ^{13}C) reveals a similar series of resonances. However, the methyl region for both complexes shows the presence of two doublets, consistent with restricted rotation about the phenyl-CHMe$_2$ bond such that the methyl groups on either side of the plane of the phenyl ring are in different magnetic environments.

Single crystal X-ray diffraction analysis of the three complexes reveals the solid state structure of the complexes to be a di-copper complex [Cu$_2$(**L**′)$_2$], a tri-silver complex [Ag$_3$(**L**′)$_3$], and the di-gold complex [Au$_2$(**L**′)$_2$], respectively. The molecular structure of the complexes [Cu$_2$(**L**′)$_2$], [Ag$_3$(**L**′)$_3$], and [Au$_2$(**L**′)$_2$] are depicted in Figures 1 ([Cu$_2$(**L**′)$_2$] and [Au$_2$(**L**′)$_2$]) and 2 ([Ag$_3$(**L**′)$_3$]), selected bond lengths and angles are shown in Table 1 ([Cu$_2$(**L**′)$_2$] and [Au$_2$(**L**′)$_2$]) and 2 ([Ag$_3$(**L**′)$_3$]). As alluded to earlier, the structures of Group 11 triazenide complexes, typically fall into three classes: dimeric, tetrameric, or polymeric systems (Chart 2, Scheme 1), the formation of which is strongly dependent upon the steric requirements of the nitrogen substituents.[57] While dimeric structures of copper-triazenide complexes have been reported previously, the dimeric gold complex [Au$_2$(**L**′)$_2$] represents a unique example of a structurally characterized gold-triazenide dimer, the only other example of a gold triazenide system having a tetrameric structure in the solid state.[58] Similarly, the structural elucidation of the tri-silver triazenide complex, [Ag$_3$(**L**′)$_3$], represents a unique addition to the structural range of Group 11 triazenide systems.

The complex [Cu$_2$(**L**′)$_2$] crystallizes in the monoclinic space group C_2/c and contains two independent halves of the di-copper complex in the asymmetric unit cell (ASU). While one-*half-molecule* is disordered with respect to the central core, which shows two orientations of the planar $\{Cu_2N_6\}$ unit rotated by 90°: the second *half-molecule* shows no disorder. The molecular structure of the non-disordered dimer [Cu$_2$(**L**′)$_2$] is shown in Figure 1a and is taken as representative of both *half-molecules* in the ASU. The silver and gold complexes [Ag$_3$(**L**′)$_3$] and [Au$_2$(**L**′)$_2$] both crystallize in the monoclinic space group $P2_1/c$. In the case of the tri-silver complex [Ag$_3$(**L**′)$_3$] one whole molecule resides within the ASU, along with one molecule of toluene of crystallization (Figure 2). In comparison, the ASU for the gold complex [Au$_2$(**L**′)$_2$] (Figure 1b) contains one-*half* of the di-gold complex, the second *half* of which is generated by symmetry. The ASU also contains one molecule of toluene of crystallization, such that there are two molecules of toluene per molecule of complex.

The copper and gold complexes [Cu$_2$(**L**′)$_2$] and [Au$_2$(**L**′)$_2$] shown in Figure 1 are *iso*typic, and share many of the gross structural features of previously structurally characterized Cu(I), Ag(I), and Au(I) di-metallic systems (Tables 4 and 5), consisting of two metal centers bridged by two triazenide ligands in an μ,η^1,η^1-fashion, with approximately linear two-coordinate geometries [N(1)−Cu(1)−N(3A): 172.63(7)° and N(1)−Au(1)−N(3A): 168.0(2)° respectively], with the deviation caused by the metal atoms moving away from each other. A consequence of the increased separation between the Au centers in [Au$_2$(**L**′)$_2$] is the increased N−N−N angle in the triazenide ligand [N(1)−N(2)−N(3): 119.5(5)°] compared to that observed in [Cu$_2$(**L**′)$_2$], [N(1)−N(2)−N(3): 115.53(15)°].

Both complexes have essentially planar bi-cyclic cores, formed by the two N$_3$-ligands and the $\{M_2\}$ unit (M = Cu or Au) (largest deviation from the least-squares plane: $\{Cu_2N_6\}$ 0.0051(12) Å; $\{Au_2N_6\}$ 0.0071(28) Å). As with related sterically demanding triazenide *N*-substituents, the 2,6-di-isopropyl rings are twisted out of the plane of the central bi-cyclic $\{M_2N_6\}$ cores, with angles between the M(1)−N(1)−N(2)−N(3)−M(1A) plane and the phenyl rings C(1)−C(6) and C(13)−C(18) approaching perpendicularity

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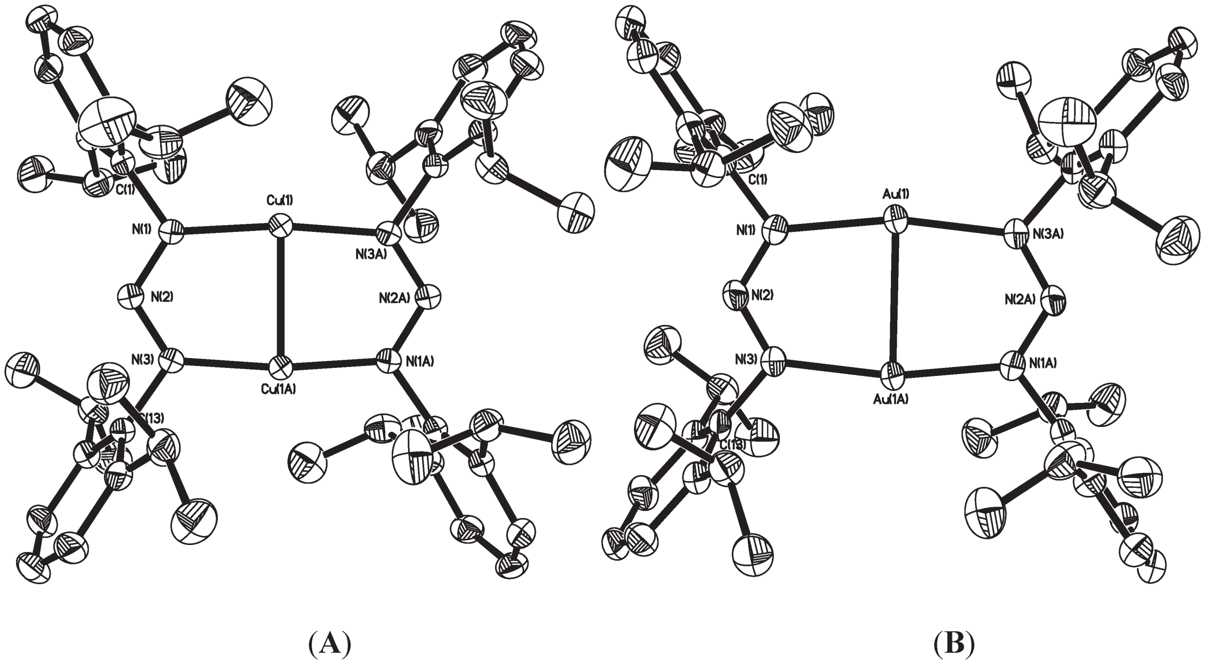

Figure 1. Diagram showing the centrosymmetric molecular structures of the complexes $[Cu_2(\mathbf{L}')_2]$ (**A**) and $[Au_2(\mathbf{L}')_2]$ (**B**): Figure 1a shows the molecular structure of one molecule of $[Cu_2(\mathbf{L}')_2]$ (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: $-x + 1/2, -y + 1/2, -z$.; Figure 1b shows the molecular structure of $[Au_2(\mathbf{L}')_2]$ (50% probability ellipsoids) Hydrogen atoms and solvent of crystallization have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: $-x, -y + 1, -z + 1$.

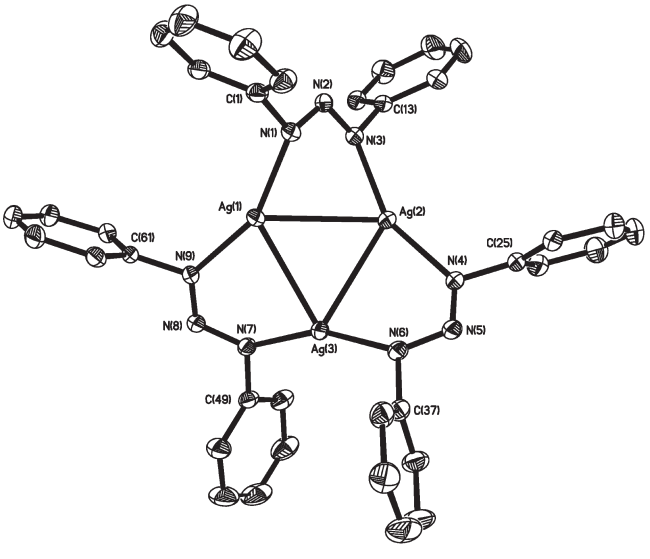

Figure 2. Diagram showing the molecular structure of the complex $[Ag_3(\mathbf{L}')_3]$ (50% probability ellipsoids). Isopropyl groups, hydrogen atoms, and solvent of crystallization have been omitted for clarity.

Table 1. Selected Geometric Data for $[Cu_2(\mathbf{L}')_2]$ and $[Au_2(\mathbf{L}')_2]$

	$[Cu_2(\mathbf{L}')_2]$, Bond Lengths (Å)		
Cu(1)−Cu(1A)	2.4458(4)	N(1)−N(2)	1.308(2)
Cu(1)−N(1)	1.8811(15)	N(2)−N(3)	1.298(2)
Cu(1)−N(3A)	1.8824(16)		
	$[Cu_2(\mathbf{L}')_2]$, Bond Angles (deg)		
N(1)−Cu(1)−N(3A)	172.63(7)	Cu(1)−Cu(1A)−N(3)	86.04(5)
N(1)−N(2)−N(3)	115.53(15)	Cu(1A)−Cu(1)−N(1)	86.58(5)
		Cu(1)−N(1)−N(2)	125.51(12)
		N(2)−N(3)−Cu(1A)	126.32(12)
	$[Au_2(\mathbf{L}')_2]$, Bond Lengths (Å)		
Au(1)−Au(1A)	2.6762(4)	N(1)−N(2)	1.308(7)
Au(1)−N(1)	2.046(5)	N(2)−N(3)	1.297(7)
Au(1)−N(3A)	2.042(5)		
	$[Au_2(\mathbf{L}')_2]$, Bond Angles (deg)		
N(1)−Au(1)−N(3A)	168.0(2)	Au(1)−Au(1A)−N(3)	84.32(14)
N(1)−N(2)−N(3)	119.5(5)	Au(1A)−Au(1)−N(1)	83.71(13)
		Au(1)−N(1)−N(2)	126.4(4)
		N(2)−N(3)−Au(1A)	126.1(4)

$[\{Cu_2N_3\}-\{C(1)-C(6)\}$: 78.85(5)°, $\{Cu_2N_3\}-\{C(13)-C(18)\}$: 78.36(5)°, $\{Au_2N_3\}-\{C(1)-C(6)\}$: 89.44(17)°, $\{Au_2N_3\}-\{C(13)-C(18)\}$: 81.37(13)°].

The Cu−N and Au−N bond distances in both $[Cu_2(\mathbf{L}')_2]$ and $[Au_2(\mathbf{L}')_2]$ are within the expected ranges for terminal M(I)−N bonds [Cu−N: 1.8811(15) Å and 1.8824(16) Å; Au−N: 2.046(5) Å and 2.042(5) Å]. Similarly the N−N bond lengths within the triazenide ligands [N(1)−N(2): 1.308(2) Å, N(2)−N(3): 1.298(2) Å in $[Cu_2(\mathbf{L}')_2]$ and N(1)−N(2): 1.308(7) Å, N(2)−N(3): 1.297(7) Å in $[Au_2(\mathbf{L}')_2]$] are also comparable to those observed in related systems. A significant point of interest in these dimeric Cu(I) and Au(I) complexes is the presence of relatively short M···M intramolecular distances. In both complexes, the metal−metal distances [Cu(1)−Cu(1A): 2.4458(4) Å and Au(1)−Au(1A): 2.6762(4) Å] are significantly shorter than the sum of the van der Waals radii[59] of Cu (1.40 Å) and Au (1.66 Å) and are directly comparable to related dimeric complexes listed in Table 4, and are also significantly shorter than M···M interactions observed in related tetrameric complexes.

The facile oxidative addition of small molecules, such as X_2, CX_4, CH_2X_2, CH_3X, $PhICl_2$ and $(PhCO_2)_2$ (X = Cl, Br, or I), to related di-gold amidinate systems has previously been shown to result in the formation of the corresponding

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Table 2. Selected Geometric Data for $[\mathrm{Ag_3}(\mathbf{L}')_3]$

Bond Lengths (Å)			
Ag(1)−Ag(2)	3.01186(17)	N(1)−N(2)	1.297(2)
Ag(2)−Ag(3)	2.95330(17)	N(2)−N(3)	1.3017(19)
Ag(1)−Ag(3)	2.92748(17)	N(4)−N(5)	1.287(2)
Ag(1)−N(1)	2.1291(14)	N(5)−N(6)	1.293(2)
Ag(1)−N(9)	2.1204(13)	N(7)−N(8)	1.2939(19)
Ag(2)−N(3)	2.1245(13)	N(8)−N(9)	1.2922(19)
Ag(2)−N(4)	2.1233(14)		
Ag(3)−N(6)	2.0907(13)		
Ag(3)−N(7)	2.0963(13)		
Bond Angles (deg)			
N(1)−Ag(1)−N(9)	154.60(5)	N(1)−Ag(1)−Ag(2)	72.45(4)
N(3)−Ag(2)−N(4)	153.69(5)	N(3)−Ag(2)−Ag(1)	72.18(4)
N(6)−Ag(3)−N(7)	157.37(5)	N(4)−Ag(2)−Ag(3)	77.35(4)
		N(6)−Ag(3)−Ag(2)	78.66(4)
Ag(3)−Ag(1)−Ag(2)	59.615(4)	N(7)−Ag(3)−Ag(1)	79.90(4)
Ag(3)−Ag(2)−Ag(1)	58.772(4)	N(9)−Ag(1)−Ag(3)	78.07(4)
Ag(1)−Ag(1)−Ag(2)	61.613(4)		
		N(1)−N(2)−N(3)	114.39(13)
		N(4)−N(5)−N(6)	116.99(13)
		N(7)−N(8)−N(9)	116.05(13)

Table 3. Selected Geometric Data for $[\mathrm{Cu_3}(\mathbf{L}')_2(\mathrm{Mes})]$

Bond Lengths (Å)			
Cu(1)−Cu(2)	2.7068(4)	Cu(1)−N(1)	1.8911(17)
Cu(2)−Cu(3)	2.4393(4)	Cu(2)−N(3)	1.8932(17)
Cu(3)−Cu(1)	2.6836(3)	Cu(1)−N(4)	1.8928(18)
Cu(2)−C(101)	1.975(2)	Cu(1)−N(6)	1.8828(19)
Cu(3)−C(101)	1.956(2)		
Bond Angles (deg)			
Cu(1)−Cu(2)−Cu(3)	62.610(10)	N(1)−Cu(1)−N(4)	156.50(7)
Cu(2)−Cu(3)−Cu(1)	63.581(10)	N(1)−N(2)−N(3)	114.91(16)
Cu(3)−Cu(1)−Cu(2)	53.808(9)	N(4)−N(5)−N(6)	114.16(17)
Cu(2)−C(101)−Cu(3)	76.71(9)	N(1)−Cu(1)−Cu(2)−N(3)	21.58(7)
		N(4)−Cu(1)−Cu(3)−N(6)	22.12(8)

Au(II) complexes, which display significantly shorter Au···Au contacts.[60,61] While analogous reactions of $[\mathrm{Au_2}(\mathbf{L}')_2]$ with halogen containing reagents have not been performed, it is noteworthy that $[\mathrm{Au_2}(\mathbf{L}')_2]$ displays increased stability in the presence of chlorinated solvents such as CD_2Cl_2 compared to the less sterically encumbered gold amidinate complex described by Fackler et al., as evidenced by the observed presence of only one species in the ^{1}H NMR spectra of $[\mathrm{Au_2}(\mathbf{L}')_2]$ in both CD_2Cl_2 and $CDCl_3$ solvents.

Surprisingly, and in direct contrast to the formation of the *iso*typic complexes $[\mathrm{Cu_2}(\mathbf{L}')_2]$ and $[\mathrm{Au_2}(\mathbf{L}')_2]$, the reaction of AgCl with Li[**L**′] in a 1:1 stoichiometric ratio, results in the formation of the tri-silver complex $[\mathrm{Ag_3}(\mathbf{L}')_3]$, crystals of which were grown from a cooled toluene solution. The molecular structure of $[\mathrm{Ag_3}(\mathbf{L}')_3]$ is shown in Figure 2 and selected bond lengths and angles in Table 2.

Table 4. Cu···Cu and Au···Au Distances in Some Bridged Di-Nuclear Cu(I) and Au(I) Complexes

Complex	$d_{(\mathrm{M}\cdots\mathrm{M})}$ (Å)	ref
	Copper	
$[\mathrm{Cu_2}(\mu\text{-Ph-NNN-Ph})_2]$	2.4405(10)	94
$[\mathrm{Cu_2}(\mu\text{-}\mathrm{C_6H_3}(^i\mathrm{Pr})_2\text{-NNN-}\mathrm{C_6H_3}(^i\mathrm{Pr})_2)_2]$	2.4458(4)	this work
$[\mathrm{Cu_2}\{\mu\text{-}o\text{-}\mathrm{C_6H_4}(\mathrm{CO_2Me})\text{-NNN-}o\text{-}\mathrm{C_6H_4}\text{-}(\mathrm{CO_2Me})\}_2]$	2.4289(12)	95
$[\mathrm{Cu_2}\{\mu\text{-}\mathrm{C_6H_3Me_2}\text{-NC(Ph)N-}\mathrm{C_6H_3Me_2}\}_2]$	2.4571(2)	49
$[\mathrm{Cu_2}(\mu\text{-}^i\mathrm{Pr}\text{-NC(Me)N-}^i\mathrm{Pr})_2]$	2.414(1)	48
$[\mathrm{Cu_2}(\mu\text{-}^s\mathrm{Bu}\text{-NC(Me)N-}^s\mathrm{Bu})_2]$	2.4031(6)	47
$[\mathrm{Cu_2}(\mu\text{-}^i\mathrm{Pr}\text{-NC(NMe}_2\text{)N-}^i\mathrm{Pr})_2]$	2.4233(10)	46
$[\mathrm{Cu_2}(\mu\text{-}^i\mathrm{Pr}\text{-NC(NH}^i\mathrm{Pr})\text{N-}^i\mathrm{Pr})_2]$	2.4289(11)	46
$[\mathrm{Cu_2}(\mu\text{-}\mathrm{Me_3Si}\text{-NC(Ph)N-}\mathrm{SiMe_3})_2]$	2.4227(12)	43
$[\mathrm{Cu_4}\{\mu\text{-}\mathrm{FC_6H_4}\text{−NNN-}\mathrm{C_6H_4F}\}_4]$	2.607(6), 2.738(6)	96
$[\mathrm{Cu_4}\{\mu\text{-}\mathrm{CF_3C_6H_4}\text{−NNN-}\mathrm{C_6H_4CF_3}\}_4]$	2.578(11)	97
$[\mathrm{Cu_4}\{\mu\text{-Ph-NC(Ph)N-Ph}\}_4]$	2.5674(6), 2.6419(7)	49
	Gold	
$[\mathrm{Au_2}(\mu\text{-}\mathrm{C_6H_3}(^i\mathrm{Pr})_2\text{-NNN-}\mathrm{C_6H_3}(^i\mathrm{Pr})_2)_2]$	2.6762(4)	this work
$[\mathrm{Au_2}(\mu\text{-}\mathrm{Me_3Si}\text{-NC(Ph)N-}\mathrm{SiMe_3})_2]$	2.6456(6)	41
$[\mathrm{Au_2}(\mu\text{-}\mathrm{C_6H_3Me_2}\text{-NC(H)N−}\mathrm{C_6H_3Me_2})_2]$	2.711(2)	60
$[\mathrm{Au_4}(\mu\text{-Ph-NNN-Ph})_4]$	2.848(1), 2.856(1), 2.855(1), 2.842(1)	58
$[\mathrm{Au_4}(\mu\text{-Nap-NC(H)N-Nap})_4]$	3.0139(11), 2.9920(9), 2.9944(10), 2.9721(11)	98
$[\mathrm{Au_4}(\mu\text{-}\mathrm{MeC_6H_4}\text{−NC(H)N-}\mathrm{C_6H_4Me})_4]$	2.968(2), 3.103(2)	44
$[\mathrm{Au_4}(\mu\text{-}\mathrm{Cl_2C_6H_3}\text{−NC(H)N-}\mathrm{C_6H_2Cl_2})_4]$	2.8662(14), 2.9699(14)	44
$[\mathrm{Au_4}(\mu\text{-}\mathrm{MeOC_6H_4}\text{−NC(H)N-}\mathrm{C_6H_4OMe})_4]$	2.9016(8), 3.0057(9), 2.9265(9), 2.9447(10)	44
$[\mathrm{Au_4}(\mu\text{-Ph-NC(Me)N-Ph})_4]$	2.9996(12), 2.9796(13), 2.9078(12), 2.8970(12)	40
$[\mathrm{Au_4}(\mu\text{-Ph-NC(Ph)N-Ph})_4]$	2.982(2), 2.970(18), 2.9252(18), 2.955(2)	40

The complex is formed from a central $\{\mathrm{Ag_3}\}$ triangle of approximately equilateral geometry [Ag(1)−Ag(2): 3.01186(17) Å, Ag(2)−Ag(3): 2.95330(17) Å, Ag(3)−Ag(1): 2.92748(17) Å]. A comparison of the Ag···Ag distances in $[\mathrm{Ag_3}(\mathbf{L}')_3]$ with related systems in Table 5 shows the distances to be comparable to those observed in related tri-metallic systems,[48] but appreciably longer than the M···M interactions observed in both $[\mathrm{Cu_2}(\mathbf{L}')_2]$ and $[\mathrm{Au_2}(\mathbf{L}')_2]$. As noted earlier, it is not unusual for short metal−metal distances to be observed in complexes with bridging ligands. For this reason the presence of true metallophilic interactions is often dubious. What is clear is that purely on the basis of atomic size differences (van der Waals radii: Cu = 1.40 Å, Au = 1.66 Å, and Ag = 1.72 Å)[59] it might have been expected that M···M distances differ by 0.64 Å (Cu···Cu vs Ag···Ag), 0.12 Å (Au···Au vs Ag···Ag), and 0.52 Å (Cu···Cu vs Au···Au), respectively. However, it may be noted that from a comparison of the M−M distances, only the Au−Au distance is notably shorter in proportion to the size of the atoms, though longer than the Cu−Cu distance (by 0.23 Å) and shorter than the Ag−Ag distance (0.29 Å) in

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Table 5. Ag···Ag Distances in Some Bridged Di- and Tri-Nuclear Ag(I) Complexes

Complex	$d_{(\mathrm{M\cdots M})}$ (Å)	ref
$[\mathrm{Ag_2}(\mu\text{-Ph-NNN-Ph})_2]$	2.669(1)	99
$[\mathrm{Ag_2}\{\mu\text{-MeOC}_6\mathrm{H}_4\text{−NNN-C}_6\mathrm{H}_4\mathrm{OMe}\}_2]$	2.680(2)	100
$[\mathrm{Ag_2}\{\mu\text{-EtOC}_6\mathrm{H}_4\text{−NC(H)N-C}_6\mathrm{H}_4\mathrm{OEt}\}_2$	2.7533(4)	45
$[\mathrm{Ag_2}(\mu\text{-}^i\mathrm{Pr}\text{-NC(Me)N-}^i\mathrm{Pr})_2]$	2.6447(5)	48
$[\mathrm{Ag_2}(\mu\text{-Me}_3\mathrm{Si}\text{-NC(Ph)N-SiMe}_3)_2]$	2.6548(9)	41
$[\mathrm{Ag_3}(\mu\text{-C}_6\mathrm{H}_3(^i\mathrm{Pr})_2\text{-NNN-C}_6\mathrm{H}_3(^i\mathrm{Pr})_2)_3]$	3.01184(7), 2.92745(16), 2.95329(17)	this work
$[\mathrm{Ag_3}(\mu\text{-}^i\mathrm{Pr}\text{-NC(Me)N-}^i\mathrm{Pr})_3]$	2.8599(4), 2.8954(5), 3.2002(4)	48
$[\mathrm{Ag_4}\{\mu\text{-FC}_6\mathrm{H}_4\text{−NNN-C}_6\mathrm{H}_4\mathrm{F}\}_4]$	2.8064(4), 2.8337(4)	96
$[\mathrm{Ag_4}\{\mu\text{-MeOC}_6\mathrm{H}_4\text{−NNN-C}_6\mathrm{H}_4\mathrm{OMe}\}_4]$	2.7633(16), 2.7849(12), 2.8174(15), 2.7951(11)	101
$[\mathrm{Ag_4}(\mu\text{-N}_2\mathrm{C}_3\mathrm{H}_6\mathrm{NC}_3\mathrm{H}_6)_4]$	2.8614(6)	42
$[\mathrm{Ag}\{\mu\text{-F}_3\mathrm{CC}_6\mathrm{H}_4\text{−NNN-C}_6\mathrm{H}_4\mathrm{CF}_3\}]_\infty$	2.835(2)	97

an absolute sense. This observation is consistent with strong d^{10}−d^{10} interactions in Au−Au systems (cf. Cu−Cu and Ag−Ag).[1,3,12,13,37]

As with the bi-metallic systems described earlier the triazenide ligands in $[\mathrm{Ag_3}(\mathbf{L}')_3]$ bridge the M···M edges in an μ,η^1,η^1-fashion such that each silver atom is bound to nitrogen atoms of two different triazenide ligands, with Ag−N bond lengths (see Table 2) lying within expected values . The N−Ag−N angles about each silver atom [N(1)−Ag(1)−N(9): 154.60(5)°, N(3)−Ag(2)−N(4): 153.69(5)°, N(6)−Ag(3)−N(7): 157.37(5)°] describe a distorted linear two-coordinate geometry, such that the silver atoms deviate from linearity by moving toward each other (cf. $[\mathrm{Cu_2}(\mathbf{L}')_2]$ and $[\mathrm{Au_2}(\mathbf{L}')_2]$). As a result of this distortion away from linearity, the triazenide ligands experience significant twisting of the $\{\mathrm{N_3}\}$ backbone, while maintaining a bridging coordination mode. Figure 3 shows the relative arrangements of the three triazenide ligands about the central $\{\mathrm{Ag_3}\}$ core, and clearly shows two distinct types of triazenide coordination. The triazenide ligand {N(1)−N(2)−N(3)} bridging the Ag(1)−Ag(2) edge (Figure 3a) shows a significant distortion away from coplanarity with the $\{\mathrm{Ag_3}\}$ core, as indicated by the angle between the two planes [38.18(7)°] or the dihedral angle [N(1)−Ag(1)−Ag(2)−N(3): 38.82(6)°] (Figure 3b), the origins of which we assume to be the result of a desire to form close Ag−Ag contacts versus the steric demands of the bulky 2,6-di-isopropyl substituents. The remaining two triazenide ligands that bridge the Ag(1)−Ag(3) and Ag(2)−Ag(3) edges display a significantly less-distorted coordination geometry [N(4)−Ag(2)−Ag(3)−N(6): 20.23(6)°; N(7)−Ag(3)−Ag(1)−N(9): 15.52(6)°], with a mutually *trans*-orientation about the two edges of the $\{\mathrm{Ag_3}\}$ core.

The energetic consequences of steric bulk, and the role that this plays in molecular design and control, are well established.[51,54,57] While the propensity for Group 11 metal triazenide and related systems to form a range of oligomeric complexes (Chart 1) is well known, lower order oligomers are typically formed by more sterically demanding ligand-sets, with the formation of trimeric systems, such as $[\mathrm{Ag_3}(\mathbf{L}')_3]$, typically limited to complexes in which the directionality of the donor orbitals of the ligand systems preclude the formation of dimeric (and higher) oligomers, for example, Group 11 metal pyrazolate complexes $[\mathrm{M_3}(\mu\text{-R}_2\text{-pz})_3]$ ($\mathrm{R_2}$-pz = $\mathrm{R_2}$-3,5-$\mathrm{N_2C_3}$).[62−66] However, it is noteworthy that the only other structurally characterized neutral tri-metallic silver system, containing a related ligand, is the amidinate complex $[\mathrm{Ag_3}(^i\mathrm{Pr}\text{-NC(Me)N-}^i\mathrm{Pr})_3]$ reported by Gordon et al.[48] which exists in dynamic equilibrium in solution with its dimeric congener, $[\mathrm{Ag_3}(^i\mathrm{Pr}\text{-NC(Me)N-}^i\mathrm{Pr})_3]$, an observation that is not made in the case of $[\mathrm{Ag_3}(\mathbf{L}')_3]$. Other tri-metallic silver complexes have been described in the literature, but these are typically cationic species supported by constrained tripodal ligand systems[67−70] or strong σ-donor polydentate ligands such as phosphines or N-heterocyclic carbenes.[71−76] Despite the identical steric demands of the ligand system in the three homoleptic complexes $[\mathrm{Cu_2}(\mathbf{L}')_2]$, $[\mathrm{Ag_3}(\mathbf{L}')_3]$, and $[\mathrm{Au_2}(\mathbf{L}')_2]$, silver appears to have different bonding requirements, the reasons for which are not fully understood.[77] Reports concerning the synthesis and structure of complete homologous/homoleptic Cu, Ag, and Au complexes are rare,[78−82] but even with the paucity of data, it is correct to say that in the instances where evidence exists, there are important differences between copper, silver, and gold, and these observable differences in coordination geometry may in-part be a result of a significant variation in size within the Group 11 metals,[77]

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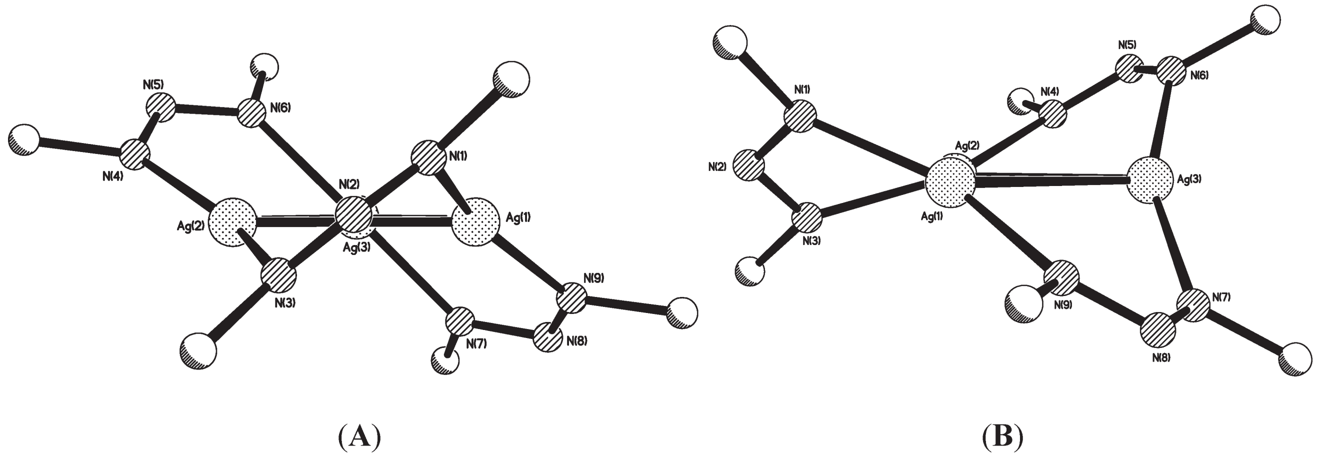
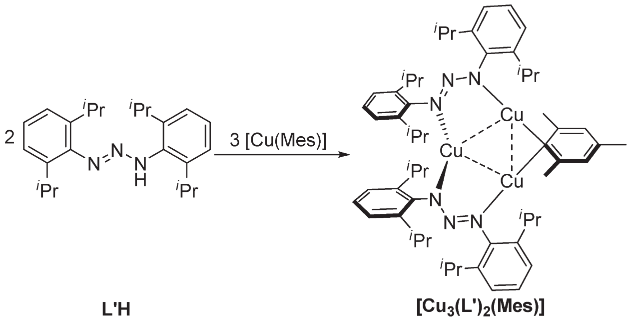


Figure 3. Diagrams showing the core of the complex $[Ag_3(\mathbf{L}')_3]$: (A) a view along the approximate N(2)−Ag(3) vector, illustrating the distribution and orientation of the triazenide ligands about the $\{Ag_3\}$ core; (B) a view along the approximate Ag(1)−Ag(2) vector, illustrating the twisting of the triazenide ligands. Selected angles: N(1)−Ag(1)−Ag(2)−N(3): 38.82(6)°, N(7)−Ag(3)−Ag(1)−N(9): 15.52(6)°, N(4)−Ag(2)−Ag(3)−N(6): 20.23(6)°, N(4)−Ag(2)−Ag(1)−N(9): 70.63(7)°, N(3)−Ag(2)−Ag(1)−N(9): 125.27(6)°, N(1)−Ag(1)−Ag(2)−N(4): 125.28(7)°, N(9)−Ag(1)−Ag(3)−N(6): 156.15(6)°, N(4)−Ag(2)−Ag(3)−N(7): 148.93(6)°.

Scheme 2



with computational and experimental data showing the size order within the group to be Cu < Au < Ag.[83−86]

During the course of our studies, the potential utility of [Cu(Mes)][79] as a precursor for metal triazenide complex formation was investigated. Previous studies by others have demonstrated that reaction of triazenes with metal alkyl and amide complexes such as BuLi, $MgBu_2$, $ZnEt_2$, or $[M\{N(SiMe_3)_2\}_n]$ (M = Li or K, *n* = 1; M = Ca, Sr, or Ba, *n* = 2) result in the formation of the corresponding metal triazenide complexes[51,54,56,87] A stoichiometric reaction between [CuMes] (Mes = 2,4,6-trimethylphenyl) and the triazene system **L**′H in toluene at room temperature as shown in Scheme 2, resulted in the formation of a complex determined to be different from the expected di-copper system $[Cu_2(\mathbf{L}')_2]$.

Concentration of the reaction mixture followed by standing at −28 °C, gave colorless crystals, which were isolated in a 60% yield with respect to **L**′H. ^{1}H NMR studies clearly show the presence of triazenide ligand within the ^{1}H NMR spectrum: with broad doublet resonances at δ = 0.97 ppm (12H) and δ = 1.20 ppm (36H) in a 1:3 ratio for the isopropyl CH_3 groups. Single resonances at δ = 2.12 ppm (3H),

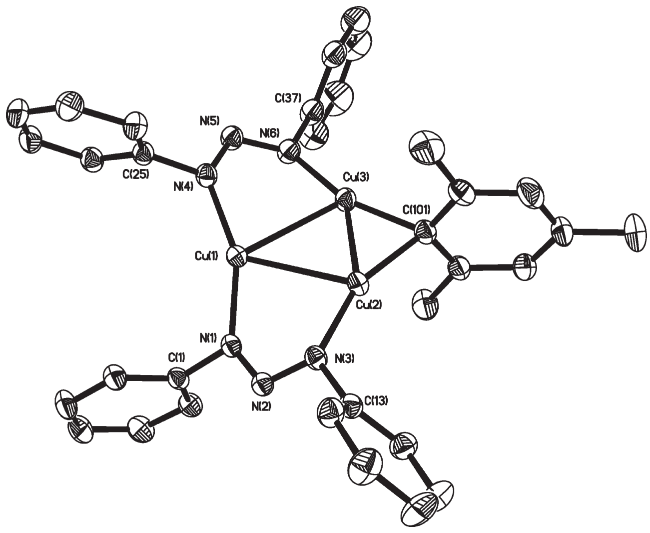


Figure 4. Diagram showing the molecular structures of the complex $[Cu_3(\mathbf{L}')_2(Mes)]$ (50% probability ellipsoids). Isopropyl groups, hydrogen atoms, and solvent of crystallization have been omitted for clarity.

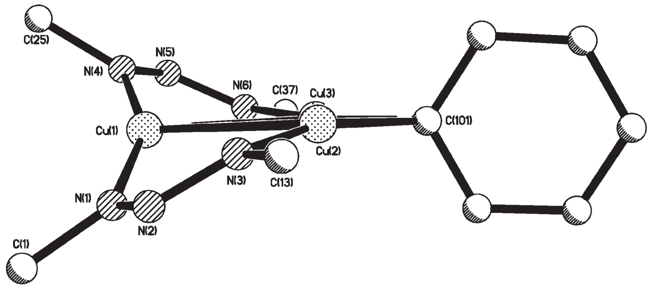


Figure 5. Diagram showing the core of $[Cu_3(\mathbf{L}')_2(Mes)]$: a view along the approximate Cu(2)−Cu(3) vector, illustrating twisting of the triazenide ligands. Selected angles: N(1)−Cu(1)−Cu(2)−N(3): 21.58(1)°, N(4)−Cu(1)−Cu(3)−N(6): 22.12(8)°, N(3)−Cu(2)−Cu(3)−N(6): 24.64(15)°, N(1)−Cu(1)−Cu(3)−N(6): 150.28(9)°, N(4)−Cu(1)−Cu(2)−N(3): 153.63(9)°.

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Table 6. Crystallographic Data for the Complexes $[Cu_2(\mathbf{L}')_2]$, $[Ag_3(\mathbf{L}')_3]\cdot$Tol, $[Au_2(\mathbf{L}')_2]\cdot$2Tol, $[Cu_3(\mathbf{L}')_2(Mes)]\cdot$2Tol, and $[Cu_3(\mathbf{L}')_2(Mes)]$

	$[Cu_2(\mathbf{L}')_2]$	$[Ag_3(\mathbf{L}')_3]\cdot$Tol	$[Au_2(\mathbf{L}')_2]\cdot$2Tol	$[Cu_3(\mathbf{L}')_2(Mes)]\cdot$2Tol	$[Cu_3(\mathbf{L}')_2(Mes)]$
empirical formula	$C_{48}H_{69}Cu_2N_6$	$C_{72}H_{102}Ag_3N_9\cdot C_7H_8$	$C_{48}H_{68}Au_2N_6\cdot 2(C_7H_8)$	$C_{57}H_{79}Cu_3N_6\cdot 2(C_7H_8)$	$C_{57}H_{79}Cu_3N_6$
formula weight	857.17	1509.37	1307.29	1223.15	1038.88
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	46.4390(4)	19.77800(10)	12.9430(2)	11.5430(2)	11.9480(3)
b (Å)	10.43100(10)	19.97300(10)	10.0730(2)	15.3140(2)	15.3420(4)
c (Å)	21.2250(2)	19.96700(10)	22.5260(5)	20.2000(3)	15.5620(4)
α (deg)				71.6040(10)	93.0140(10)
β (deg)	115.4740(10)	99.5770(10)	102.6100(10)	81.2990(10)	99.3270(10)
γ (deg)				83.8170(10)	92.364(2)
V	9281.93(15)	7777.55(7)	2865.98(10)	3342.43(9)	2807.42(12)
Z	8	4	2	2	2
ρ_{calc} mg/m^{-3}	1.227	1.289	1.515	1.215	1.229
μ(Mo Kα), mm^{-1}	0.954	0.794	5.156	0.989	1.166
F(000)	3656	3152	1312	1300	1100
crystal size, mm	0.1 × 0.25 × 0.40	0.1 × 0.13 × 0.22	0.1 × 0.17 × 0.2	0.2 × 0.2 × 0.4	0.13 × 0.25 × 0.25
θ range (deg)	3.62 to 27.49	8.17 to 30.50	8.17 to 27.48	8.53 to 27.56	8.52 to 27.56
reflections collected	77888	144388	44149	53645	53616
independent reflections [R(int)]	10630 (0.0492)	23190 (0.0634)	6356 (0.1134)	14779 (0.0528)	12403 (0.0692)
reflections observed [$I > 2\sigma(I)$]	8674	19033	5154	10989	8645
max.,min transmission	0.9106 and 0.7014	0.9248 and 0.8447	0.6266 and 0.4253	0.8267 and 0.6930	0.8680 and 0.7593
goodness-of-fit	1.071	1.071	1.153	1.023	1.021
final $R1$ (wR_2) [$I > 2\sigma(I)$]	0.0360 (0.0830)	0.0300 (0.0665)	0.0504 (0.1220)	0.0404 (0.0872)	0.0453 (0.0960)
final $R1$ (wR_2) (all data)	0.0509 (0.0899)	0.0431 (0.0737)	0.0668 (0.1398)	0.0690 (0.0993)	0.0821 (0.1128)
largest diff. peak and hole, e Å^{-3}	0.355 and −0.877	0.936 and −0.666	4.751 and −4.512	0.784 and −0.500	0.961 and −0.540

$\delta = 2.71$ ppm (6H) and a multiplet at $\delta = 3.13-3.38$ ppm (8H) can also be observed along with a series of resonances in the aromatic region, which is consistent with a system containing triazenide and mesityl ligands in a 2:1 ratio. These observations are consistent with the potential formation of a system of the general formula $[Cu_3(\mathbf{L}')_2(Mes)]$ which experiences molecular fluxionality at room temperature. Elemental analysis further supports this assertion. Attempts to resolve the ^{1}H NMR spectrum at low temperature were unsuccessful, and failed to *freeze-out* fluxional processes in solution. Similarly, a full assignment of the ^{13}C NMR spectra was also not possible because of poor resolution of resonances. Attempts were made to resolve the spectrum by modifying relaxation delay parameters, extended data collections, and variable temperature experimentation, but to little avail.

The results of a single crystal X-ray diffraction experiment demonstrate the product formed from the reaction to be the unanticipated tri-copper system $[Cu_3(\mathbf{L}')_2(Mes)]$, Figure 4. Selected bond lengths and angles are shown in Table 3. The complex, $[Cu_3(\mathbf{L}')_2(Mes)]$ crystallizes in the triclinic space group $P\bar{1}$ and is fashioned from a central tri-copper unit reminiscent of $[Ag_3(\mathbf{L}')_3]$, of approximately isoscelean geometry [Cu(1)−Cu(2): 2.7068(4) Å, Cu(1)−Cu(3): 2.6836(3) Å, Cu(2)−Cu(3): 2.4393(4) Å]. Two triazenide ligands bridge the Cu−Cu edges with distances that are significantly longer than that observed in $[Cu_2(\mathbf{L}')_2]$ [cf. Cu(1)−Cu(1A): 2.4458(4) Å]. As with $[Cu_2(\mathbf{L}')_2]$, the Cu−N distances are in the range expected for comparable copper-amidinate and -triazenide complexes, [Cu(1)−N(1) 1.8911(17) Å; Cu(1)−N(4) 1.8928(18) Å; Cu(2)−N(3) 1.8932(17) Å; Cu(2)−N(6) 1.8828(12) Å].

The bridging triazenide ligands form two twisted five-membered $\{Cu_2N_3\}$ rings (Figure 5), and as with the structurally related tri-silver complex, it is believed that the triazenide ligands are twisted in such a way as to relieve the steric interaction between the 2,6-di-isopropyl substituents on N(1) and N(4). A comparison between the torsion angles shown in Figure 5 for $[Cu_3(\mathbf{L}')_2(Mes)]$ and those of $[Ag_3(\mathbf{L}')_3]$ (Figure 3), indicate significantly less distortion within the tri-copper complex $[Cu_3(\mathbf{L}')_2(Mes)]$. The mesityl group, which bridges the shortest Cu−Cu edge, possesses Cu−C distances [Cu(2)−C(101): 1.975(2) Å, Cu(3)−C(101): 1.956(2) Å] which are also comparable to those found in both [Cu(Mes)][79] and the tri-copper system $[Cu_3(O_2CPh)_2(Mes)]$,[88,89] and is orientated such that the planes defined by the tri-copper unit and the mesityl ring are approximately perpendicular [86.32(7)°], reflecting the three-center two-electron (3c-2e) bonding between Cu(1), Cu(3) and the mesityl group (the range for Cu−Cu distances bridged by 3c-3e bonds has previously been shown to be 2.37−2.53 Å[88]). The ASU also contains two molecules of toluene of crystallization.

The synthesis of tri-copper based cluster systems such as $[Cu_3(\mathbf{L}')_2(Mes)]$ is currently of interest because of their role in enzymatic systems,[90,91] for example, ascorbate oxidase, ceruplasmin, and laccase, since tri-nuclear copper clusters at the active site of these enzymes have been implicated in the reduction of O_2 to H_2O. The complex $[Cu_3(\mathbf{L}')_2(Mes)]$ represents a well-defined tri-nuclear copper system which is presently under investigation in our laboratory with respect to its ability to activate small molecules such as O_2, CO, and CO_2.

Successive attempts to produce the di-copper complex $[Cu_2(\mathbf{L}')_2]$ by reacting [Cu(Mes)] with $\mathbf{L}'$H in different solvents (hexane or tetrahydrofuran) resulted in further isolation of the tri-copper system $[Cu_3(\mathbf{L}')_2(Mes)]$, suggesting that the product is in some way kinetically or thermodynamically stabilized. Attempts to induce complete reaction with

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additional heating of reaction mixtures at reflux temperatures in both tetrahydrofuran and toluene resulted in the thermal degradation of the product, such that only intractable material was isolated. During the course of our investigations, crystals of the tri-copper complex $[\mathrm{Cu_3}(\mathbf{L}')_2(\mathrm{Mes})]$, which were free of toluene of crystallization, were isolated, and the molecular structure determined by single crystal X-ray diffraction, details of which are included in Table 6 for completeness.

Conclusions

Reported here in are the structures of several novel Group 11 M(I) complexes containing metal−metal interactions supported by sterically demanding triazenide ligands. In contrast to the reactions of the metal chlorides CuCl, AgCl, and (THT)AuCl with lithium triazenide Li-$[\mathbf{L}']$, which provide a series of homoleptic complexes, $[\mathrm{M}(\mathbf{L}')]_n$ (M = Cu or Au, $n = 2$; M = Ag, $n = 3$), which have been structurally characterized. Reaction of [Cu(Mes)] with the triazene system $\mathbf{L}'$H results in the serendipitous formation of a novel Cu(I) tri-metallic system, $[\mathrm{Cu_3}(\mathbf{L}')_2(\mathrm{Mes})]$. The precise reasons for this difference in reactivity are not fully understood, but it is possible to speculate that there is a fine balance between any energetic gain in the disruption of 3c-2e bonding present in [Cu(Mes)] versus loss of mesitylene and formation of Cu−N bonds. Such energetic considerations are not relevant in the case of salt metathesis reactions.

All the complexes described exhibit bridging triazenide ligand systems which can be accused of enhancing any inherent metallophilic interactions. Despite this, there is no doubt that significant M−M interactions exist in all four systems that we have described. In fact, our observations would lead us to conclude that the triazenide ligands are not solely responsible for M−M contacts in the complexes $[\mathrm{Cu_2}(\mathbf{L}')_2]$, $[\mathrm{Ag_3}(\mathbf{L}')_3]$, $[\mathrm{Au_2}(\mathbf{L}')_2]$, and $[\mathrm{Cu_3}(\mathbf{L}')_2(\mathrm{Mes})]$: empirical analysis of the experimentally determined M−M distances versus calculated van der Waals radii would suggest that the bridging nature of the triazenide ligands is actually facilitated by the presence of significant metallophilic interactions in complexes such as these.

Experimental Section

General Procedures. Elemental analyses were performed by Elemental Microanalysis Ltd., Okehampton, Devon, U.K. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz FT−NMR spectrometer, as saturated solutions in d_2-$\mathrm{CD_2Cl_2}$; chemical shifts are quoted in units of parts per million, relative to $\mathrm{Me_4Si}$ (^{1}H, ^{13}C); coupling constants are in hertz.

All reactions were carried out under an inert atmosphere using standard Schlenk techniques. Solvents were dried over activated alumina columns using an Innovative Technology solvent purification system (SPS) and degassed under an argon atmosphere. The ligand system 1,3-bis(2,6-di-isopropyl)triazene[51] and [Cu(Mes)][79] were made according to literature procedures. All other reagents were purchased from commercial sources.

Synthesis of $[\mathrm{Cu_2}(\mathbf{L}')_2]$. Copper(I) chloride (0.495 g, 5.00 mmol), 1,3-bis(2,6-di-isopropyl)triazene (1.83 g, 5.00 mmol), and lithium bis(trimethylsilyl)amide (0.837 g, 5.00 mmol) were placed in a dry Schlenk tube, under Argon, into which tetrahydrofuran (20 mL) was added. The reaction mixture was allowed to stir for 4 h, after which the volatiles were removed under reduced pressure, and the product was extracted into toluene and filtered through Celite. The resultant filtrate was concentrated, and storage of the material at −28 °C facilitated the growth of yellow crystals suitable for single crystal X-ray diffraction (2.84 g, 66%). Elemental analysis: calcd. (%): C 67.41, H 8.02, N 9.83; Found: C 67.4, H 7.95, N 9.85. ^{1}H NMR (300 Hz, $\mathrm{CD_2Cl_2}$): $\delta = 1.20$ (48H, d, $\mathrm{CH(C}H_3)_2$, $J = 6.96$ Hz), 3.47 (8H, sept, $\mathrm{C}H\mathrm{(CH_3)_2}$, $J = 6.96$ Hz), 7.08−7.17 (12H, m, C*H*), ^{13}C NMR (75.49 Hz, $\mathrm{CD_2Cl_2}$): $\delta = 24.0$, 28.72, 123.9, 127.2, 144.0 and 144.7.

Synthesis of $[\mathrm{Ag_3}(\mathbf{L}')_3]$. Silver(I) chloride (0.287 g, 2.00 mmol), 1,3-bis(2,6-di-isopropyl)triazene (0.731 g, 2.00 mmol), and lithium bis(trimethylsilyl)amide (0.335 g, 2.00 mmol) were placed in a dry Schlenk tube under Argon, into which tetrahydrofuran (20 mL) was added. The reaction mixture was allowed to stir for 16 h, after which time the solvent was removed under reduced pressure. Dry hexane (20 mL) was added to the resultant residue and left to stir for 15 min, after which time the hexane was removed under reduced pressure. The process was repeated twice to remove any residual tetrahydrofuran. The product was then extracted into hexane and filtered through Celite. The resultant filtrate was concentrated, and storage of the material at −28 °C facilitated the growth of yellow crystals suitable for single crystal X-ray diffraction (0.699 g, 74%). Elemental analysis: calcd. (%): C 61.12, H 7.27, N 8.92; Found: C 61.30, H 7.34, N 8.84. ^{1}H NMR (300 Hz, $\mathrm{CD_2Cl_2}$): $\delta = 0.85$ (36H, d, $\mathrm{CH(C}H_3)_2$, $J = 6.87$ Hz), 1.02 (36H, d, $\mathrm{CH(C}H_3)_2$, $J = 6.87$ Hz), 3.14 (12H, sept, $\mathrm{C}H\mathrm{(CH_3)_2}$, $J = 6.87$ Hz), 6.99−7.14 (18H, m, C*H*) ^{13}C NMR (75.49 Hz, $\mathrm{C_6D_6}$): $\delta = 23.2$, 24.3, 28.5, 123.9, 127.1, 143.6, and 145.6.

Synthesis of $[\mathrm{Au_2}(\mathbf{L}')_2]$. Tetrahydrothiophene gold(I) chloride (0.317 g, 1.00 mmol), 1,3-bis(2,6-di-isopropyl)triazene (0.366 g, 1.00 mmol), and lithium bis(trimethylsilyl)amide (0.167 g, 1.00 mmol) were placed in a dry Schlenk tube under Argon, into which tetrahydrofuran (15 mL) was added. The reaction mixture was allowed to stir for 16 h, after which time the solvent was removed under reduced pressure and dry hexane (15 mL) was added to the resultant residue. This was left to stir for 15 min, after which the volatiles were removed under reduced pressure. The process was repeated twice, to remove any residual tetrahydrofuran. The product was then extracted into hexane and filtered through Celite. The resultant filtrate was concentrated, and storage of the material at −28 °C facilitated the growth of pale yellow crystals suitable for single crystal X-ray diffraction (0.343 g, 61%). Elemental analysis, calcd (%): C 51.31, H 6.11, N 7.49; Found: C 51.0, H 6.19, N 7.16. ^{1}H NMR (300.22 Hz, $\mathrm{CD_2Cl_2}$): δ 1.20 (24H, d, $\mathrm{CH(C}H_3)_2$, $J = 6.82$ Hz), 1.37 (24H, d, $\mathrm{CH(C}H_3)_2$, $J = 6.82$ Hz), 3.66 (8H, sept, $\mathrm{C}H\mathrm{(CH_3)_2}$, $J = 6.82$ Hz), 7.05−7.16 (12H, m, C*H*); ^{13}C NMR (75.49 Hz, $\mathrm{CD_2Cl_2}$): $\delta = 24.2$, 24.4, 28.0, 123.9, 128.0, 143.8 and 146.0.

Synthesis of $[\mathrm{Cu_3}(\mathbf{L}')_2(\mathrm{Mes})]$. Copper(I) mesitylene (0.914 g, 5.00 mmol) and 1,3-bis(2,6-*di-iso*propylphenyl)triazene (1.83 g, 5.00 mmol) were placed in a dry Schlenk tube under Argon, into which toluene (15 mL) was added. The reaction mixture was allowed to stir for 16 h, after which time the solution was concentrated and storage of the material at −28 °C facilitated the growth of colorless crystals suitable for single crystal X-ray diffraction (0.945 g, 61%). Elemental analysis: calcd. (%): C 65.90, H 7.66, N 8.09; Found: C 65.70 H 7.49, N 8.09. ^{1}H NMR (300.22 Hz, DCM-d_2): 0.97 (12H, d, $\mathrm{CH(C}H_3)_2$, $J = 6.97$ Hz), 1.20 (36H, d, $\mathrm{CH(C}H_3)_2$, $J = 6.97$ Hz), 2.12 (3H, s, Mes-*p*-$\mathrm{C}H_3$), 2.71 (6H, s, Mes-*o*-$\mathrm{C}H_3$), 3.13−3.38 (8H, m, $\mathrm{C}H\mathrm{(CH_3)_2}$, 6.94 (2H, s, C*H*), 6.98−7.09 (12H, m, C*H*). ^{13}C NMR (75.49 Hz, DCM-d_2): 21.7, 21.9, 23.0, 23.6, 23.78, 24.2, 24.4, 28.7, 28.9, 29.2, 123.9, 124.0, 127.4, 127.5, 143.8, 144.2, 144.6, 144.9, 145.2, 155.9.

Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarized in Table 6. For all structures, data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo Kα radiation (λ = 0.71073 Å). Structure solution and refinements were performed using SHELX86[92] and SHELX97[93] software. Corrections for absorption were made in all cases. For all complexes, hydrogen atoms were included at calculated positions.

The asymmetric unit of $[Cu_2(\mathbf{L}')_2]$ consists of two independent halves of the di-copper complex. One of the two '*half-molecules*' is disordered with respect to the central core, which shows two orientations of the planar $\{Cu_2N_6\}$ unit rotated by 90°. This disorder was modeled such that the $\{N_3\}$ unit and the Cu centers were modeled over two positions, in a 19:1 ratio, relative to the 2,6-di-isopropyl rings, which are not disordered. The major component of the disorder was refined using anisotropic displacement parameters. To obtain a stable convergence, refinement of the minor component of disorder was refined with isotropic displacement parameters.

Acknowledgment. We acknowledge the financial support of the University of Bath and the EPSRC for the award of a CASE for New Academics (A.M.W.). We thank UMICORE AG & Co. KG for a generous gift of precious metal compounds. A.L.J. thanks Prof. P. Raithby (UoB) and Dr. M. S. Hill (UoB) for helpful comments and fruitful discussions.

Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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