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Contribution from the Institute for Organic Chemistry TNO,
Utrecht, The Netherlands

Group 1B Organometallic Chemistry. 18. Novel Routes to Stable Hexanuclear Copper–Silver, Silver–Gold, and Copper–Gold Cluster Compounds Starting from Polymeric 2-(Dimethylamino)phenylcopper and from Bis[(2-dimethylamino)phenyl]goldlithium Dimer¹

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Mixed hexanuclear copper–silver, silver–gold, and copper–gold complexes of the type $\text{R}_4\text{M}_4\text{M}'_2\text{X}_2$ have been prepared via the reaction of 2-(dimethylamino)phenylcopper (RCu) with CuOTf or AgOTf (OTf = trifluoromethanesulfonato) as well as via the reaction of cuprous halide, of CuOTf, or of AgOTf with the novel bis[2-(dimethylamino)phenyl]goldlithium dimer $\text{R}_4\text{Au}_2\text{Li}_2$. IR and NMR spectroscopies reveal a structure for the $\text{R}_4\text{M}_4\text{M}'_2\text{X}_2$ compounds which is similar to the structure of $\text{R}_4\text{Cu}_6\text{Br}_2$ (x ray), i.e., a hexanuclear cluster structure with the (2-dimethylamino)phenyl ligands spanning triangular faces of the mixed $\text{M}_4\text{M}'_2$ core by 2e–3c carbon–metal and by 2e–2c metal–nitrogen bonds. The gold atoms in $\text{R}_4\text{M}_4\text{Au}_2\text{X}_2$ (M = Cu or Ag) occupy apical positions which is in line with the strong preference of gold(I) for a digonal coordination geometry. $\text{R}_4\text{Cu}_4\text{Ag}_2(\text{OTf})_2$ is not stable and decomposes into R–R, $\text{R}_4\text{Cu}_6(\text{OTf})_2$, and metallic silver at room temperature. Dynamic NMR spectroscopy reveals that the NMe_2 grouping is an excellent probe for the detection and elucidation of the dissymmetry in the cluster (R groups bridge unlike metal atoms; metal–N(Me_2) coordination renders the NMe_2 grouping a stable prochiral assembly). NMe resonances in $\text{R}_4\text{Cu}_4\text{Au}_2\text{X}_2$ remain anisochronous up to 90 °C, whereas those of $\text{R}_4\text{Cu}_6\text{X}_2$ coalesce at 40 °C. This has been explained in terms of increased N–Cu_{eq} bond strength in the copper–gold derivative resulting from a contribution to the bonding of canonical structures such as $\text{R}_2\text{Au}^-[\text{Cu}_4\text{X}_2^{2+}]^-\text{AuR}_2$, in which 2e–3c RAuCu bonding has been replaced by 2e–2c RAu interactions. IR spectroscopy reveals that in spite of the weak electron-donor properties of the OTf anion the $\text{R}_4\text{M}_{6-n}\text{M}'_n(\text{OTf})_2$ compounds ($n = 0, 2$) like the halide clusters $\text{R}_4\text{M}_{6-n}\text{M}'_n\text{X}_2$ (X = Br or I) are 84-electron species with each OTf anion contributing 4 electrons to the cluster by bridging two equatorial metal atoms. The similarity of the NMR patterns of $\text{R}_4\text{Cu}_4\text{Au}_2\text{X}_2$ (X = halide or OTf) derivatives in electron-pair-donating solvents such as pyridine can be explained both by metal core–anion dissociation resulting in 84-electron dications $\text{R}_4\text{M}_{6-n}\text{M}'_n(\text{py})_4^{2+}$ or by cluster rearrangement affording $\text{R}_4\text{M}_{4-n}\text{M}'_n$.

Introduction

In previous reports we have shown that arylcopper compounds interact with metal halides. Electron-transfer,^{1,3} transmetalation,^{4,5} and complex formation reactions^{2,3} have been identified for a number of different arylcopper derivatives. Both the substitution pattern of the aryl nucleus and the presence of heteroatoms in the substituents which coordinate with copper have proved to be decisive factors in determining the course of these reactions.

Recently we found² that interaction of polymeric 2-(dimethylamino)phenylcopper (I) with cuprous halides results in the formation of complexes $\text{R}_4\text{Cu}_6\text{X}_2$ which have discrete cluster structures consisting of 2- $\text{Me}_2\text{NC}_6\text{H}_4$ groups bonded to a Cu_6 core by 2e–3c Cu–C and 2e–2c Cu–N bonds. The halide ligands bridge two equatorial Cu^1 atoms by 4e–3c bonds (see Figure 1). In contrast, substitution of MeO for Me_2N results in a less specific aggregate formation,⁶ whereas substitution of Me_2N by Me_2NCH_2 gives rise to the formation of polymeric species with $\text{RCu}\cdot\text{CuX}$ stoichiometry.^{3,6}

The observation that the 2- $\text{Me}_2\text{NC}_6\text{H}_4$ has the unique property of spanning octahedral faces of a Cu_6 core, which for example allows ligand substitution with retention of the R_4Cu_6 skeleton,^{7,8} has provided further impetus to a study of

the factors determining the stability of this type of 1B metal cluster compounds.

Substitution of copper atoms by silver atoms in $\text{R}_4\text{Cu}_6\text{X}_2$ results in the formation of species $\text{R}_4\text{Cu}_2\text{Ag}_4\text{X}_2$ and $\text{R}_4\text{Cu}_4\text{Ag}_2\text{X}_2$ having exactly the same overall stoichiometry.⁹ NMR spectroscopy unambiguously showed that these mixed-metal species are not stable in solution and enter into interaggregate exchange reactions resulting in an equilibrium mixture of the various possible hexanuclear species $\text{R}_4\text{Cu}_{6-n}\text{Ag}_n\text{X}_2$ ($n = 1\text{--}5$).² These exchange phenomena can be rationalized on the basis of the different coordination symmetry of the apical and equatorial sites in hexanuclear $\text{R}_4\text{M}_6\text{X}_2$ clusters.^{10a} Since both Cu^1 and Ag^1 can have digonal or trigonal coordination symmetries,^{10b} these metals will not have a distinct preference for either the apical or equatorial sites in the $\text{Cu}_{6-n}\text{Ag}_n$ core. As a consequence the various $\text{R}_4\text{Cu}_{6-n}\text{Ag}_n\text{X}_2$ clusters will not differ greatly in stability. However, going down in the 1B metal series the preference for linear, twofold coordination increases. This is reflected in the fact that gold(I) complexes with trigonal coordination symmetry are exceptions.^{10b,11} For this reason we anticipated increased stability for $\text{R}_4\text{Cu}_4\text{Au}_2\text{X}_2$ compounds because the gold(I) atoms can satisfy their preference for digonal coor-

Table I. NMR Data for the Bis[2-(dimethylamino)phenyl(metal 1B)](metal 1B) Salt Compounds^a

Compd	Temp, °C	NMe	H(6)	H(3)	H(4,5)
R ₄ Cu ₆ (OTf) ₂ ^b	10	1.92 s, br 2.96 s, br	8.18 m <i>J</i> _{5,6} = 7 Hz (8.48)	6.44 m <i>J</i> _{3,4} = 8 Hz (6.50)	<i>d</i>
	Ambient	Coalescence (2.86 s)			
	80 ^c	2.50 s			
R ₄ Cu ₄ Ag ₂ (OTf) ₂ ^{c,e}	Ambient	2.40 br ^f	8.23 m		<i>d</i>
R ₄ Cu ₄ Au ₂ (OTf) ₂ ^{c,e}	Ambient	1.84 s (3.08 s) ^g 2.88 s	8.10 m (8.07 m) <i>J</i> _{5,6} = 7 Hz	6.48 m <i>J</i> _{3,4} = 8 Hz	<i>d</i>
	78 ^e	1.89 s 2.95 s			
	Ambient	1.90 s (2.68 s) 2.79 s	8.06 m ⁱ (7.87 m) <i>J</i> _{5,6} ≈ 6.5 Hz <i>J</i> _{H-Ag} ≈ 6 Hz	6.61 m	
R ₄ Cu ₄ Au ₂ Br ₂ ^c	Ambient	1.77 s 2.96 s	8.38 m <i>J</i> _{5,6} = 8 Hz <i>J</i> _{4,6} = 2 Hz	6.66 m <i>J</i> _{3,4} = 8 Hz <i>J</i> _{3,5} = 2 Hz	6.94
	75	1.80 s 2.94 s			
	Ambient	1.77 s (3.06 s) 2.93 s	8.46 m (8.08 m) <i>J</i> _{5,6} = 8 Hz <i>J</i> _{4,6} = 2 Hz	6.63 m <i>J</i> _{3,4} = 8 Hz	
R ₄ Cu ₄ Au ₂ I ₂ ^{c,e}	Ambient	1.77 s (3.06 s) 2.93 s	8.46 m (8.08 m) <i>J</i> _{5,6} = 8 Hz <i>J</i> _{4,6} = 2 Hz	6.63 m <i>J</i> _{3,4} = 8 Hz	
	90 ^b	1.74 s 2.90 s			
	Ambient	1.84 s, br 2.94 s, br 2.42 s	8.48 m	6.64 m	

^a Values in parentheses correspond to the spectra recorded in pyridine-*d*₅. ^b In toluene-*d*₈. ^c In benzene-*d*₆. ^d Masked due to resonances of solvent H. ^e Accumulated spectra (100–110 scans). ^f Decomposes into a 2/1 molar mixture of RR-CuOTf¹⁸ and R₄Cu₆(OTf)₂; see eq 5. ^g Addition of H₂O to this solution afforded after 10 min the resonance patterns of RAu(py) (stable in H₂O), R₄Cu₄Au₂(OTf)₂, and RH. ^h R_nCu_n (in pyridine-*d*₅; ambient): 2.92 s (NCH₃), 8.91 m (H(6)), 6.54 m (H(3)). RAu(py) (in pyridine-*d*₅; ambient): 3.10 (NCH₃), 7.94 m (H(6)); *J*_{5,6} = 7, *J*_{4,6} = 2 Hz, 6.92 m (H(3)); *J*_{3,4} = 6, *J*_{3,5} = 2 Hz). ⁱ Irradiation at the position of H(5) (7.20 ppm) results in a doublet due to *J*[H-^{107,109}Ag] centered at 8.06 ppm. ^j See ref 2.

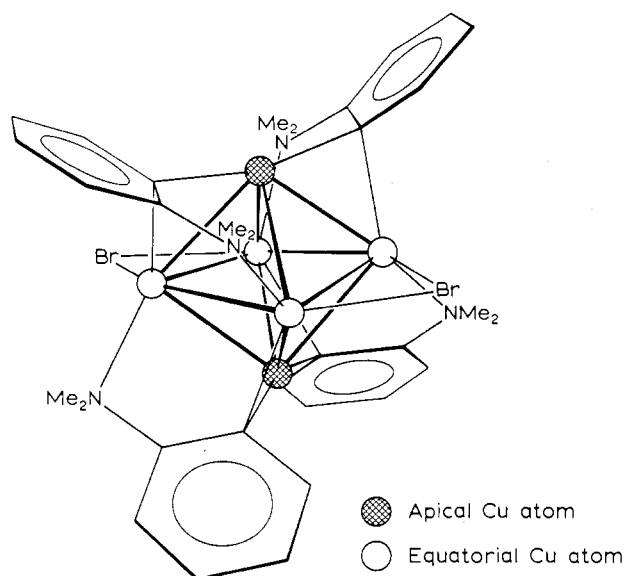


Figure 1. Structure of hexanuclear bis[2-(dimethylamino)phenylcopper]cuprous bromide (cf ref 22).

dination by occupying apical positions.

This paper deals with a closer study of (i) the consequences of the fact that the apical copper atoms in R₄Cu₆X₂ have digonal and the equatorial atoms have a trigonal coordination geometry (see Figure 1) for the synthesis of mixed copper-silver, silver-gold, and copper-gold cluster compounds and (ii) the possibility to synthesize compounds, which can be formulated as ion pairs R₄M_{6-n}M'_n²⁺·2X⁻, by substituting the halide ligands in these clusters by anions of low coordinating ability.

Experimental Section

General Data. CuOTf·¹/₂C₆H₆ was prepared according to the directions given by Salomon and Kochi.¹² The organo(metal 1B)

compounds were synthesized by published methods.^{3,6} The reactions were carried out under dry oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled before use under nitrogen.

IR spectra were recorded on a Perkin-Elmer 577 Grating IR spectrometer. ¹H NMR spectra were recorded on a Varian Associates HA-100 NMR spectrometer, while in some cases a C-1024 time-averaging computer of Varian was used (cf. Table I). The IR and ¹H NMR spectra were obtained by Mrs. G. M. Bijlsma-Kreuger, Mrs. T. van Montfort-Volp, and Mr. J. W. Marsman. Elemental analyses were carried out under the supervision of Mr. W. J. Buis in the Analytical Department of this institute.

Bis[2-(dimethylamino)phenylcopper]cuprous Trifluoromethanesulfonate. Solid CuOTf·¹/₂C₆H₆ (2.45 mmol) was added at room temperature to a well-stirred suspension of 2-(dimethylamino)phenylcopper⁶ in benzene (25 mL). The resulting brown-yellow reaction mixture was stirred for 48 h. The yellow precipitate was filtered off and extracted twice with benzene (20 mL) and with pentane (2 × 20 mL). The yellow residue (80% yield) was dried in vacuo. Anal. Calcd for C₁₇H₂₀Cu₃F₃O₃N₂S: C, 35.2; H, 3.48; N, 4.83; Cu, 32.8; F, 9.83. Found: C, 34.2; H, 3.5; N, 4.4; Cu, 32.0; F, 9.6. Decomposition (under N₂) starts at 118–122 °C; explosion occurs at 123 °C. IR data are presented in Table II and the NMR data in Table I.

Essentially the same result was obtained when after mixing of the reagents the reaction mixture was stirred in a CO₂ atmosphere for 48 h. Yellow solid was isolated in 82% yield which was identified by IR and NMR spectroscopy and by elemental analysis as the pure product. Anal. Found: C, 34.4; H, 3.7; N, 4.5; Cu, 32.1; F, 10.2.

The reaction of R₄Cu₆(OTf)₂ (0.05 mmol) in benzene (1 mL) with D₂O (1 mL) at room temperature for 5 days afforded a yellow suspension. Subsequent treatment with KCN (100 mg) resulted in clear layers. According to GLC and GC-MS analysis of the benzene layer showed almost quantitative formation of the deuterated arene (100% RD; ratios *m/e* 121/122 and *m/e* 105/106 identical with the ratios observed for 2-deuterio-*N,N*-dimethylaniline⁶ obtained via the reaction of 2-(dimethylamino)phenyllithium with D₂O^{6,9}). Only a trace amount of the dimer 2,2'-bis(dimethylamino)biphenyl could be detected by GC-MS analysis.

Bis[2-(dimethylamino)phenylcopper]silver Trifluoromethanesulfonate. Solid AgOTf (2.73 mmol) was added at room temperature to a stirred suspension of 5.45 mmol of 2-(dimethylamino)phenylcopper in benzene

Table II. IR Spectra^a of Bis[2-(dimethylamino)phenyl(metal 1B)](metal 1B) Trifluoromethanesulfonate Compounds

Assignment (OTf vib ^b)	R ₄ Cu ₄ Au ₂ I ₂ V	R ₄ Cu ₄ Au ₂ (OTf) ₂ VII	R ₄ Au ₂ Ag ₂ (OTf) ₂ VIII	R ₄ Cu ₆ (OTf) ₂ VI	R ₄ Cu ₆ I ₂ X
	1565 w	1570 w	1570 w	1568 w	1565 w
	1552 w	1555 w	1555 sh	1555 sh	
		1296 s ^c	1295 s	1315 s	
ν_4 (E) SO ₃ asym str	1278 vw	1280 sh	1280 sh	1298 sh	
	1253 m	1254 w	1258 w	1280 sh	1250 m
		1218 s	1215 s	1248 vw	1242 m
		1200 sh		1230 m	
		1173 vw	1172 m	1170 m	1175 vw
	1163 vw	1165 sh	1165 s	1160 sh	1157 m
	1152 m	1152 sh	1160 sh	1150 sh	1149 m
	1135 w	1137 sh	1138 sh	1135 sh	1132 w
	1097 m	1096 w	1097 w	1095 w	1092 m
ν_1 (A ₁) SO ₃ sym str	1044 w	1043 vw	1046 w	1042 vw	1039 w
		1024 s	1018 vs	1027 m	
	1012 m	1011 sh		1010 s	1011 m
	918 s	918 m-s	921 m-s	917 m, br	918 s
	868 vw	870 vw			870 vw
	778 sh	780 sh			
ν_2 (A ₁) SX str?	771 vs	775 s	774 s	778 m	777 vs
	768 sh	768 sh			
		760 vw	761 w	758 vw	
	752 m	750 vw	758 w	750 vw	749 w
	727 vs	729 s	730 s		728 vs
	723 sh	721 sh	723 sh	724 m	722 vs
	720 sh			718 vs	
	638 w-m				633 w-m
ν_5 (E) SO ₃ asym def		633 vs	632 s	632 s	
		625 sh	(627 s)		
	595 m	598 vw	585 w	585 sh	588 m
		585 vw	579 sh	571 w-m	
	568 m-s	565 m	559 w		564 m
ν_3 (A ₁) SO ₃ sym def		520 m	523 m	521 m	
	515 vw		514 sh		508 vw
	469 m	478 w	476 w	464 w	452 m

^a In Nujol (cm⁻¹). ^b C_{3v} assignment for the F₃CSO₃⁻ anion according to the assignment given in ref 37 for Cu^{II}(OTf)₂. ^c The bands assigned to vibrations of the OTf anion are in italics.

(20 mL). The resulting red solution with a red precipitate was stirred for 1/2 h. The benzene was removed by evaporation at low pressure. Extraction of the orange residue with pentane (2 × 20 mL) afforded R₂Cu₂AgOTf which slowly decomposed at room temperature. An NMR spectrum (benzene-d₆) obtained directly after isolation showed a very broad resonance centered at 2.4 ppm (NCH₃) and a multiplet due to H(6) at 8.23 ppm.

In pyridine immediate decomposition of R₂Cu₂AgOTf occurred affording R₄Cu₆(OTf)₂ and 2,2'-bis(dimethylamino)biphenyl (RR) in a 1/1 molar ratio accompanied by the formation of a metallic mirror (Ag). NMR (pyridine-d₅, δ (ppm)): R₄Cu₆(OTf)₂, 2.88 (NMe, s, 6 H), 8.87 (H(6), d, br, 1 H, J_{ortho} = 7 Hz), 6.52 (H(3), d, br, 1 H, J_{ortho} = 8 Hz); RR, 2.50 (NMe, 12 H).

Bis[2-(dimethylamino)phenylcopper]gold Iodide. Via R₄Au₂Li₂ with CuI/CuOTf·1/2C₆H₆. Solid cuprous iodide (2.36 mmol) was added at room temperature to a suspension of bis[2-(dimethylamino)phenyl]goldlithium (dimer R₄Au₂Li₂;¹³ 2.36 mmol) in benzene (40 mL). The resulting mixture, which was bright yellow, was stirred for 1/2 h. Subsequent addition of CuOTf·1/2C₆H₆ (2.36 mmol) did not change the color of the reaction mixture which was then stirred for another 4 h. The benzene was evaporated at low pressure and the residue was extracted with diethyl ether (2 × 20 mL) and with pentane (2 × 10 mL) and dried in vacuo. IR and NMR spectroscopy showed this yellow solid (92% yield calculated on R₂AuLi) to be almost pure R₄Au₂Cu₄I₂.

Via R₄Au₂Li₂ with CuI. Solid CuI (4.95 mmol) was slowly added to a suspension of R₄Au₂Li₂ (2.48 mmol) in benzene (50 mL). The resulting mixture was stirred at room temperature for 2 days. Similar workup (see above) followed by recrystallization of the yellow solid from hot (50 °C) benzene afforded pure R₄Cu₄Au₂I₂ in 64% yield. Anal. Calcd for C₁₆H₂₀N₂AuCu₂I: C, 27.8; H, 2.89; N, 4.05; Cu, 18.4; Au, 28.5. Found: C, 27.6; H, 3.0; N, 4.0; Cu, 16.9; Au, 28.5. Decomposition starts at 130–131 °C. IR data are presented in Table II and NMR data in Table I; mol wt calcd 1382, found (by osmometry

in C₆H₆) 1136; apparent *n* 1.64 (29.6 mg of R₄Cu₄Au₂I₂ in 10 mL of C₆H₆).

Bis[2-(dimethylamino)phenylcopper]gold Bromide. The synthesis of this complex was carried out as described for the iodide compound R₄Cu₄Au₂I₂ (62% yield). Anal. Calcd: C, 30.3; H, 3.10; N, 4.42; Cu, 20.0; Au, 31.1; Br, 12.6. Found: C, 30.1; H, 3.2; N, 4.3; Cu, 18.0; Au, 27.2; Br, 13.2. For NMR data see Table I. Decomposition occurs at 130 °C. Slow decomposition of R₄Cu₄Au₂Br₂ hampered determination of the molecular weight by ebullioscopy in benzene.

Bis[2-(dimethylamino)phenylcopper]gold Trifluoromethanesulfonate. Solid CuOTf·1/2C₆H₆ (2.48 mmol) was added at room temperature to a solution of R₄Au₂Li₂¹³ (1.24 mmol) in benzene. The yellow reaction mixture was stirred for 2 h. Removal of the benzene at low pressure followed by extraction of the residue with ether (3 × 15 mL) removal of LiOTf and pentane (2 × 10 mL) afforded yellow R₄Cu₄Au₂(OTf)₂ in 91% yield. Anal. Calcd for C₁₇H₂₀N₂AuCu₂O₃F₃S: C, 28.6; H, 2.83; N, 3.93; Cu, 17.8; Au, 27.8; F, 7.99. Found: C, 28.1; H, 2.8; N, 3.7; Cu, 17.8; Au, 27.5; F, 8.0. Slow decomposition starts at 150 °C (heating rate 10 °C/min); explosion occurs at 180 °C. IR data are given in Table II; for NMR data see Table I.

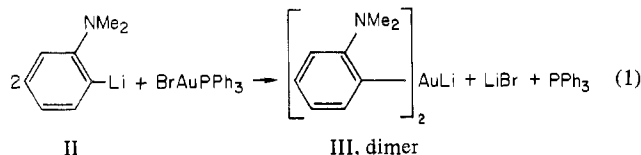
Bis[2-(dimethylamino)phenylsilver]gold Trifluoromethanesulfonate. For the preparative details see the synthesis of R₄Cu₄Au₂(OTf)₂; 91% yield. Decomposition starts at 130 °C (explosion). Anal. Calcd for C₁₇H₂₀N₂AuAg₂O₃F₃S: C, 25.5; H, 2.51; N, 3.49; Ag + Au, 51.5; F, 7.11. Found: C, 26.3; H, 2.8; N, 3.3; Ag + Au, 51.2; F, 6.7. IR data are in Table II and NMR data in Table I. The data for the proton decoupling experiment for the determination of J(H-^{107,109}Ag) are in Table I.

Results

R₄Cu₄Au₂X₂ (X = Br or I) cannot be synthesized via the reaction of 2-Me₂NC₆H₄Cu (I) with AuX because pure Au^IX is difficult to obtain. However, the synthesis of such com-

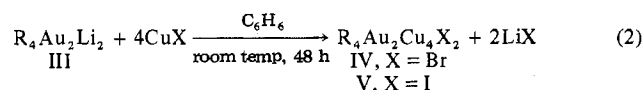
pounds proved to be possible starting from diaryl aurate complexes.¹³

The 2/1 reaction of 2-(dimethylamino)phenyllithium (II) with bromo(triphenylphosphino)gold(I) in ether afforded a colorless solid identified by elemental analysis and NMR spectroscopy as the pure aurate III.¹⁴



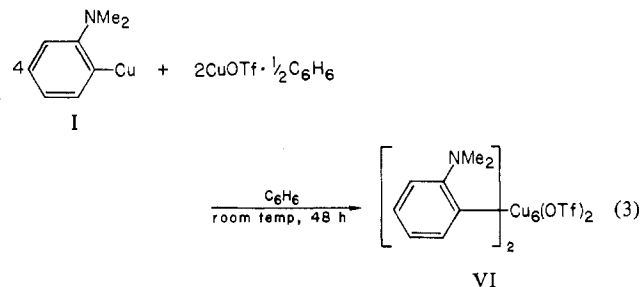
Molecular weight determinations indicated that III exists in benzene as a dimer and has $\text{R}_4\text{Au}_2\text{Li}_2$ stoichiometry.¹⁶

The 1/2 reaction of III with cuprous bromide or cuprous iodide afforded the corresponding mixed AuCu species IV and V.

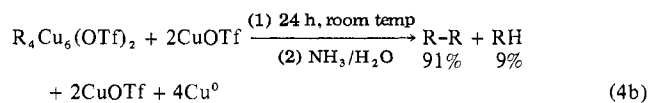
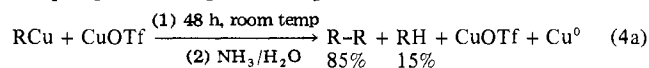


Both compounds, which were isolated as yellow solids in about 60% yield, have low solubility in the common organic solvents and decompose at about 130 °C.

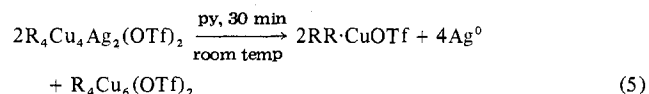
The 2/1 reaction of polymeric 2-(dimethylamino)phenyl-copper (I) with $\text{CuOTf} \cdot \frac{1}{2}\text{C}_6\text{H}_6$ in benzene affords the new compound $\text{R}_4\text{Cu}_6(\text{OTf})_2$ (VI) in 80% yield.¹⁷



For a successful synthesis of VI a 2/1 stoichiometry of the reaction is essential. The 1/1 reaction of I with CuOTf as well as the 1/2 reaction of VI with CuOTf results in C–C coupling according to the equations¹⁸



The 2/1 reaction of I with AgOTf results in the formation of an unstable red solid. An NMR spectrum of a solution of this solid in benzene- d_6 , recorded directly after its isolation, revealed that most probably a 2/1 complex of the stoichiometry $\text{R}_2\text{CuAg}_2\text{OTf}$ was obtained. This was supported by the observation that in pyridine specific decomposition occurred according to the equation (cf. Experimental Section)



The aurate III has also been used for the synthesis of mixed metal compounds $\text{R}_4\text{M}_{6-n}\text{M}'_n\text{X}_2$ in which X represents the OTf anion. The 1/2 reaction of III with CuOTf afforded the yellow 2/1 complex $\text{R}_4\text{Cu}_4\text{Au}_2(\text{OTf})_2$ (VII) in almost quantitative yield.

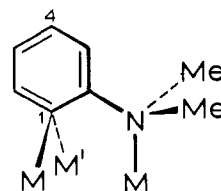
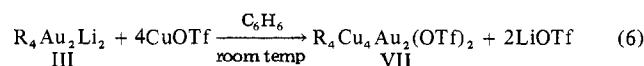
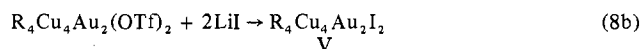
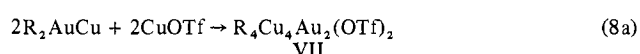
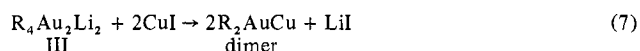


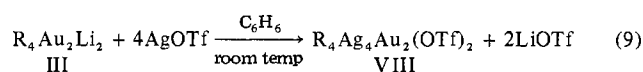
Figure 2. Common structural unit of the compounds IV–VIII (M' represents the apical and M the equatorial atom in $\text{R}_4\text{M}_4\text{M}'_2\text{X}_2$ structures).

Attempts to synthesize VII via the 1/1 reaction of in situ prepared R_2AuCu (from the 1/2 reaction of $\text{R}_4\text{Au}_2\text{Li}_2$ with CuI , eq 7) with CuOTf failed. Instead, $\text{R}_4\text{Cu}_4\text{Au}_2\text{I}_2$ was isolated in 92% yield. A plausible reaction sequence is given in eq 7 and 8. In the first step (eq 7) the mixed copper–gold



compound is formed. We have recently reported the synthesis of $\text{Ar}_4\text{Cu}_2\text{Au}_2$ from $\text{Ar}_4\text{Au}_2\text{Li}_2$ and CuBr in which Ar represents 2- $\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4$.¹³ Reaction with CuOTf most probably involves intermediate formation of VII (eq 8a) which undergoes ligand exchange to V (cf. ref 19). The occurrence of OTf-I exchange is expected because of the lower capacity of the OTf anion to bridge equatorial Cu^I atoms (cf. ref 12 and 20).

The mixed silver–gold cluster $\text{R}_4\text{Ag}_4\text{Au}_2(\text{OTf})_2$ (VIII) was synthesized without complications via the 1/2 reaction of the aurate III with AgOTf



Both compounds VII and VIII decompose above 130 °C and are stable in air.

The spectroscopic data for the various compounds are presented in Tables I and II.

Discussion

The determination of the aggregation state of compounds IV–VIII in solution by cryometry or ebullioscopy was hampered by limited solubility and low thermal stability in solution. An osmometric molecular weight determination revealed that V has a molecular weight of at least 1136 providing strong indication that in analogy with the earlier reported compounds $\text{R}_4\text{Cu}_6\text{X}_2$ and $\text{R}_4\text{Cu}_{6-n}\text{Ag}_n\text{X}_2$,⁹ V also has a dimeric structure with $\text{R}_4\text{Cu}_4\text{Au}_2\text{I}_2$ stoichiometry. An IR and NMR spectroscopic study of compounds IV–VIII provided more conclusive evidence for their structure.

The Structure of $\text{R}_4\text{Cu}_4\text{Au}_2\text{X}_2$ (X = Br or I). The IR spectra of the copper–gold compounds IV and V are superimposable (1600–ca. 200 cm^{-1}) with the spectra of $\text{R}_4\text{Cu}_6\text{Br}_2$ (IX) and $\text{R}_4\text{Cu}_6\text{I}_2$ (X)²¹ the structure of which has been established by x-ray analysis.^{2,22} The striking similarity of these spectra shows that the 2-(dimethylamino)phenyl groups in these compounds are bound to the metal core in the same way. This observation indicates that the structural unit shown in Figure 2, which is well documented for the Cu_6 clusters IX and X,^{2,23} is also present in the copper–gold cluster compounds IV and V.

The NMR data for compounds IV and V are given in Table I. In toluene or benzene the respective proton resonances of the NMe and aromatic protons H(3) and H(6) of each of the compounds IV and V and the parent complex $\text{R}_4\text{Cu}_6\text{X}_2$ (IX)²⁴ appear at almost the same chemical shift positions. This

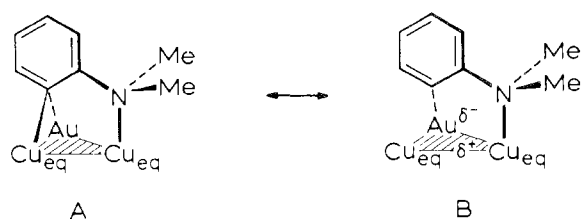


Figure 3. Canonical structures for the $2\text{-Me}_2\text{NC}_6\text{H}_4\text{AuCu}_2$ unit of the hexanuclear $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Au}_2\text{M}_4\text{X}_2$ compounds.

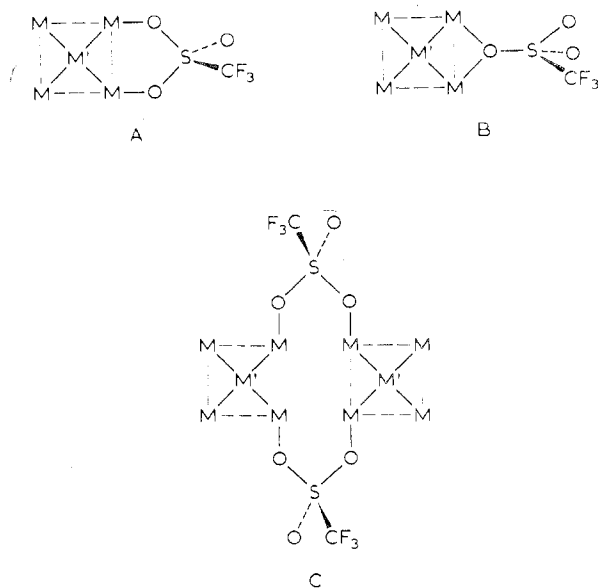
indicates that these compounds have similar overall structures consisting of an R_4M_6 skeleton with the halides bridging equatorial positions. The fact that also for the mixed metal complexes only one resonance pattern for the R group has been found points to identical environments for each of these groups and thus to a symmetrical Cu_4Au_2 core in which the Au atoms occupy apical positions. Thus the aryl group bridges $\text{Cu}_{\text{eq}}\text{Au}_{\text{ap}}$ edges while the NMe_2 ligand coordinates with Cu_{eq} . Further structural information is provided by an analysis of the respective NMe_2 patterns.

At room temperature anisochronous NMe resonances are observed for IV, V, and IX in toluene- d_8 or benzene- d_6 . Only the NMe resonances of the $\text{R}_4\text{Cu}_6\text{Br}_2$ compound IX coalesce to one singlet on raising the temperature.²⁴ The NMe resonances of the copper-gold cluster compounds IV and V remain anisochronous over the whole temperature range (25–70 or 90 °C) studied.²⁵ These NMe resonance patterns can be interpreted in terms of rate-determining (on the NMR time scale) Cu–N coordination. Figures 1 and 2 show that the bridging C atom, C(1), in IV, V, and IX is a center of chirality. In the $\text{R}_4\text{Cu}_6\text{X}_2$ cluster IX this is a consequence of the different coordination symmetry of Cu_{eq} and Cu_{ap} . In the $\text{R}_4\text{Cu}_4\text{Au}_2\text{X}_2$ clusters IV and V not only do the coordination symmetries at the equatorial and apical positions differ but here also the aryl groups bridge unlike metal atoms. Cu–N coordination renders the NMe_2 grouping a stable prochiral assembly (in the coordinated situation inversion at N is blocked). Accordingly, the NMe groups are diastereotopic and thus anisochronous. A process by which the methyl groups can become homotopic and isochronous²⁶ involves dissociation of the Cu–N bond, inversion at N²⁷ with concomitant rotation around the C–N bond (cf. related processes in chiral pentacoordinate triorganotin halides⁵). The observation of different coalescence temperatures for the NMe resonances in $\text{R}_4\text{Cu}_4\text{Au}_2\text{X}_2$ ($T_c > 70$ °C; $\Delta\delta = 1.19$ ppm) and in $\text{R}_4\text{Cu}_6\text{Br}_2$ ($T_c \approx 40$ °C; $\Delta\delta = 1.10$ ppm) points to a stronger coordination bond in the copper-gold clusters IV and V than in the copper cluster IX. This is ascribed to a shift of electron density in the $2e\text{-}3c$ bond toward the apical Au atoms thereby increasing the electron-acceptor properties of Cu_{eq} and thus the N–Cu bond strength (Figure 3). Canonical structure B, in which the $2e\text{-}3c$ ArCuAu bridge bonds are replaced by formal $2e\text{-}2c$ ArAu bonds,²⁸ represents an extreme bonding situation ($\text{R}_4\text{Cu}_4\text{Au}_2\text{X}_2 \leftrightarrow \text{R}_2\text{Au}^+[\text{Cu}_2\text{X}_2^{2-}]^-\text{AuR}_2$; Figure 3 shows only one structural unit).³⁰ Similar canonical structures have been proposed to contribute to the bonding in other aryl(metal B) compounds, e.g., in the phenylcopper polymer $\text{Ph}_2\text{Cu}\text{-Cu}^+$ ³¹ and in $[\text{CpFeC}_5\text{H}_4(\text{AuPPh}_3)_2]^+\text{BF}_4^-$.³²

The Structure of $\text{R}_4\text{M}_4\text{M}'_2(\text{OTf})_2$ Clusters. The NMR spectra of VI–VIII in toluene- d_8 (see Table I) show only one resonance pattern for the 2-(dimethylamino)phenyl group with chemical shift positions similar to those observed for the halogen complexes IX and X. This observation points to an M_6 cluster structure with symmetrical arrangement of the metal atoms in the mixed metal cores Cu_4Au_2 and Ag_4Au_2 (Au atoms in apical positions). In $\text{R}_4\text{Ag}_4\text{Au}_2(\text{OTf})_2$ the proton ortho with respect to the carbon atom bridging the metals, H(6), couples not only with H(5) (6.5 Hz) but also with one

Ag atom (6.0 Hz) as demonstrated in a proton-decoupling experiment (see Table I). The observed $^3J[\text{H}(6)\text{-}^{107,109}\text{Ag}]$ of 6.0 Hz³³ is of the same magnitude as $^3J[\text{H}(6)\text{-}^{107,109}\text{Ag}]$ observed in bis[2-[(dimethylamino)methyl]phenyl]silverlithium ($\text{Ar}_4\text{Ag}_2\text{Li}$)³⁴ but is smaller than the $^2J[\text{H}\text{-}^{107,109}\text{Ag}]$ values in $\text{Ph}_3\text{PCH}_2\text{AgCH}_2\text{PPh}_3$ ³⁵ (12 Hz) and $[\text{Ph}_3\text{PCH}_2\text{AgCl}]_4$ (14.4 Hz).³⁶

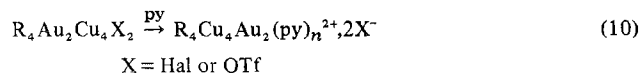
Comparison of the IR spectra of the OTf complexes VI–VIII with those of $\text{R}_4\text{Cu}_4\text{Au}_2\text{I}_2$ and $\text{R}_4\text{Cu}_6\text{I}_2$ reveals that these spectra are superimposable in the 1600–500 cm^{-1} region except for some strong bands in the OTf complexes VI–VIII at 1200–1300, 1000–1030, 630–635, and 520–525 cm^{-1} (see Table II). The observation that the vibrations due to the 2-(dimethylamino)phenyl group are insensitive to the type of anion points to a similar structure in the solid of the R_4M_6 skeleton in the halogen and OTf complexes.² The mode of interaction of the R_4M_6 skeleton with the OTf (O_3SCF_3) anions can be deduced from the observed vibrations for the anion (additional bands observed in the IR spectra of VI–VIII; see Table II, data in italics). An identical pattern has been found for the OTf bands in $\text{R}_4\text{Cu}_4\text{Au}_2(\text{OTf})_2$ and $\text{R}_4\text{Ag}_4\text{Au}_2(\text{OTf})_2$ which points to a similar metal core–anion interaction in these compounds. The assignments have been based on the earlier reported and analyzed spectra of $\text{Cu}^{\text{II}}(\text{XSO}_3)_2$ salts.³⁷ The $\nu_4(\text{E})$ mode is split in two bands at ~ 1218 and 1296 cm^{-1} while the $\nu_5(\text{E})$ mode is observed as a single band at 633 cm^{-1} . This indicates that in the solid the OTf anion has a symmetry below C_{3v} suggesting an interaction with the metal core as in A or B.



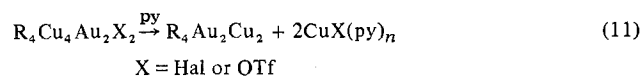
The IR spectrum of $\text{R}_4\text{Cu}_6(\text{OTf})_2$ is much more complex than the spectra of VII and VIII. Two sets of vibrations with separations of 68 and 116 cm^{-1} , respectively, are observed in the region of the $\nu_4(\text{E})$ mode. Also two $\nu_1(\text{A}_1)$ modes are found at 1027 and at 1010 cm^{-1} . These observations indicate that in VI two types of $\text{R}_4\text{Cu}_6\cdots\text{OTf}$ interactions are present in the lattice. A polymeric structure containing both bridging (C) and chelating (A) OTf anions may account for this observation.

In conclusion these IR studies reveal that the occurrence of ionic structures $\text{R}_4\text{M}_4\text{M}'_2(\text{OTf})_2$, in which the OTf anion has C_{3v} symmetry, in the solid can be excluded. However, dissolution of $\text{R}_4\text{Cu}_4\text{Au}_2\text{Br}_2$ (IV) and $\text{R}_4\text{Cu}_4\text{Au}_2(\text{OTf})_2$ (VII) in a strong base like pyridine gives rise to similar species (for NMR data see Table I). Breakdown of the cluster structures can be excluded because the breakdown products $\text{RAu}(\text{py})$ and RCu , which have been separately characterized by NMR, are not observed in these solutions.³⁸ The following possibilities

account for these observations: (i) formation of a solvated ion pair



or (ii) cluster rearrangement



Dissociation of two X groups from $R_4Cu_4Au_2X_2$ (84-electron structure) results in the formation of a 76-electron dication which, however, upon coordination with four pyridine molecules reverts to a 84-electron structure. Other examples of 84-electron clusters are $R_4Cu_6R'_2$ ($R' = \text{arylacetylide}^8$) and $H_6Cu_6(PPh_3)_6$ ³⁹ whereas a 76-electron cluster structure has been established for $[(Ph_3P)_6Au_6^{2+}](BPh_4^-)_2$.⁴⁰ On the other hand also eq 11 can account for the observed NMR pattern in pyridine. $CuX(py)_n$ complexes are well established,⁴¹ whereas an example of an $Ar_4Cu_2Au_2$ species ($Ar = 2-Me_2NCH_2C_6H_4$) has recently been reported.¹³

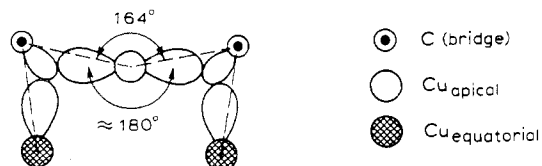
Acknowledgment. Financial support by Borg-Warner Chemicals, Borg-Warner Corp., and stimulating discussions with Dr. M. S. Cohen are gratefully acknowledged.

Registry No. I, 32691-15-9; III, 62549-80-8; IV, 62609-08-9; V, 62682-86-4; VI, 62532-80-3; VII, 62532-79-0; VIII, 62532-78-9; IX, 58616-70-9; X, 54633-67-9; $RuCu_4Ag_2(OTf)_2$, 62562-22-5; $CuOTf$, 42152-44-3; $AgOTf$, 2923-28-6.

Supplementary Material Available: Table listing IR data of compounds IV and V and of $(2-Me_2NC_6H_4)_4Cu_6X_2$ ($X = Br$ or I) and figures showing the IR spectra of these compounds (1600–200-cm⁻¹ region) (3 pages). Ordering information is given on any current masthead page.

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(b) The coordination geometries of metal 1B atoms in their complexes are discussed by F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, London, 1972, p 1053.

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- (19) Quantitative Cl–I exchange takes place with retention of the cluster structure in the 1/2 reaction of $(2-Me_2NC_6H_4)_4Cu_6Cl_2$ with LiI .²
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- (28) Rice and Tobias¹⁴ have formulated Me_2AuLi as a solvent-separated ion pair $Me_2Au^+Li^-$ in which the coordinatively saturated anion has a linear skeletal structure with two 2e–2c Au–C bonds. In contrast, Me_2CuLi most probably consists of a tetrahedral Cu_2Li_2 core with face-centered, bonded Me groups.³⁹ (i.e., 2e–4c Cu_2Li_2C bonds.) Similar subtle shifts of the type of metal 1B–carbon bonding interactions from 2e–3c to 2e–2c have been observed in a series of aryl cuprate, argentate, and aurate cluster compounds.¹⁶
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