Syntheses and Crystal Structures* of Complexes $[M_2R_2]$ [M = Cu, Ag, or Au; R = 2-$C(SiMe_3)_2C_5H_4N$] and $[Cu_4R'_4]$ [R' = 2-$CH(SiMe_3)C_5H_4N$]; Electrochemical Generation of $[Cu_2R_2]^{2+}$

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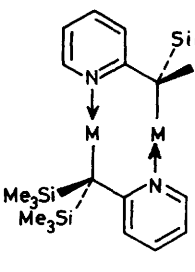
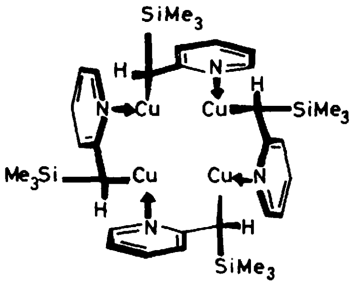
Reaction of 'LiR,' where R = 2-$C(SiMe_3)_2C_5H_4N$, with CuCl, $AgBF_4$, or [Au(CO)Cl] in tetrahydrofuran–hexane yields binuclear complexes $[M_2R_2]$ [M = Cu, (**1**); Ag, (**2**); Au, (**3**)] of relative thermal stabilities (**1**) > (**3**) > (**2**), the copper complex being sublimable *in vacuo*. In the same solvents, 'Li[2-$CH(SiMe_3)C_5H_4N$]' yields a tetranuclear species $[Cu_4\{2\text{-}CH(SiMe_3)C_5H_4N\}_4]$, (**4**), which rapidly decomposes in solution at ambient temperature to elemental copper. Electrochemistry reveals that (**1**) is reversibly oxidized to the formally copper(II) alkyl species $[Cu_2R_2]^{2+}$. The structures of complexes (**1**)—(**4**) have been established from single-crystal *X*-ray diffraction data. Molecules of (**1**)—(**3**) are centrosymmetric with each ligand bridging the two metal centres which are in close proximity [M ··· M 2.412(1) in (**1**), 2.654(1) in (**2**), and 2.672(1) Å in (**3**)]. In (**4**) the ligands bridge successive metal centres, alternating above and below a Cu_4 square, M ··· M 2.668(2) Å.

The structure of coinage metal(I) alkyl or aryl complexes has attracted much attention in recent years. For copper this stems from the widespread application of such complexes in organic synthesis. Cuprates, such as the Gilman reagents, $LiCuR_2$, are mononuclear with respect to copper with σ-bonding hydrocarbyl groups, *viz.* $[CuR_2]^-$ [R = Me, Ph,[1] $C(SiMe_3)_3$,[2] or $C_6H_2Me_3$-2,4,6[3]] and $[Cu\{CH(SiMe_3)_2\}Br]^-$,[1] or have complicated structures with multicentre bonding,[4] a common feature of copper aryls, except for $[CuPh\{(Ph_2PCH_2)_3CMe\}]$.[5] The only simple copper alkyl authenticated prior to this work was $[Cu_4(CH_2SiMe_3)_4]$[6] which also has multicentre bonding. Within the realm of silver(I) chemistry, structural data on alkyl and aryl complexes are sparse, partly as a consequence of the complexes often being thermally unstable and/or susceptible to photolytic decomposition.[7] There are metalate species with σ bonding as in the above copper compounds, *viz.* $[AgR_2]^-$ [R = $\overline{CHSO_2(CH_2)_3SO_2}$,[8] $C(SiMe_3)_3$,[9] or $CF(CF_3)_2$[10]], and aryl complexes having multicentre bonding.[11] Gold(I) alkyl and aryl complexes are in contrast well established,[12,13] encompassing all the structural types discussed for copper and silver. Unlike the lighter coinage metals, however, bi- and trivalent alkyl and aryl complexes are also accessible.[13]

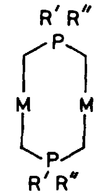
Herein we report the synthesis and structure determinations of the binuclear metal alkyl complexes $[M_2R_2]$ [R = 2-$C(SiMe_3)_2C_5H_4N$; M = Cu (1), Ag (2), or Au (3)], and of the tetranuclear complex $[Cu_4\{2\text{-}CH(SiMe_3)C_5H_4N\}_4]$, (4). The structures of complexes (1)—(3) represent the first complete series of 'isostructural' organocoinage metal complexes thus allowing unique comparison within the group and with the structurally characterized lithium analogue.[14] In complexes (1)—(4) there is no multicentre bonding, the hydrocarbyl group acting as an A-frame ligand. Such ligands have recently become prominent mainly because in their metal complexes the metal centres are forced into close proximity resulting in metal–metal interactions, which has been the subject of theoretical studies,[15,16] and the unusual chemistry their complexes can display. Noteworthy A-frame ligands in coinage metal chemistry related to the present discussion are based on phosphorus ylides, (5) (R', R'' = alkyl or aryl), for copper,[17] and gold for which there has been a flurry of papers mainly from the research groups of Schmidbaur and co-workers[18] and Fackler and co-workers.[19]



	M
(1)	Cu
(2)	Ag
(3)	Au



(4)



(5) M = Cu or Au

We also report the electrochemical generation of the formally copper(II) alkyl species $[(CuR)_2]^{2+}$ from (1). This is significant in that there are no reports of isolable copper(II) alkyls in the literature. Indeed the reaction of Main Group 1 or 2 reagents with copper(II) halides results in oxidative coupling of organic moieties rather than formation of copper(II) hydrocarbyl complexes, a reaction which has application in organic synthesis.[20]

Preliminary communications have dealt with the syntheses and structures of complexes (1)[14] and (2).[21] Other chemistry which we have reported for the relatively new hindered ligand R includes the synthesis and structure determinations of (*i*) the lithium analogues of (1)—(3),[14] (*ii*) [LiR(tmen)] (tmen = $Me_2NCH_2CH_2NMe_2$), in which the metal is bound *via* an

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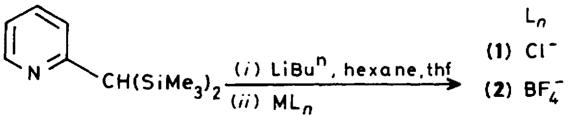
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

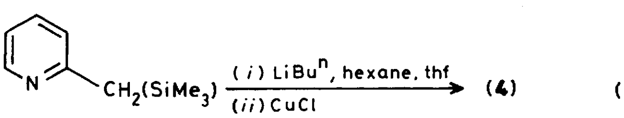
η^3-aza-allyl to the hydrocarbyl group,[22] and (*iii*) $[MR_2]$ (M = Mg, Zn, Cd, or Hg).[23] The last compounds show marked variation in the degree of interaction of the N-functional groups with the metal centre.

Results and Discussion

Synthesis.—Complex (**1**) was prepared by the addition of a stoicheiometric amount of CuCl at *ca.* −78 °C to a thf (tetrahydrofuran) solution of 'LiR' derived from metallation of 2-$CH(SiMe_3)_2C_5H_4N$ using $LiBu^n$ in hexane [equation (1)].[14]



(1)



(2)

The syntheses of complexes (**2**) and (**3**) differed in that the solution of LiR was added to a slurry of a metal substrate, respectively $AgBF_4$ and [Au(CO)Cl], and that light was excluded. Complex (**4**) was prepared by the method devised for (**1**) [equation (2)]; attempts to prepare the corresponding silver and gold complexes were unsuccessful, rapid formation of a silver mirror or colloidal gold resulting. We were also unsuccessful in attempts to prepare a Gilman reagent, $LiCuR_2$, under a variety of conditions including the use of 2 equiv. LiR with CuCl and complex (**1**) with LiR, the only copper-containing species isolated being (**1**).

Complex (**1**) is remarkably stable to thermal and oxidative decomposition, being sublimable *in vacuo* at 160 °C {*cf.* $[Cu_4(CH_2SiMe_3)_4]$ decomposes at *ca.* 80 °C and 'CuMe' decomposes >0 °C}[6] and can be recrystallized from hexane in air. This most likely relates to the protective binding exerted by the bulky $SiMe_3$ groups, and possibly the complexation of the N centres; an earlier attempt to stabilize copper–carbon bonds by complexation of sp^2-N donor ligands failed.[24] The effect of steric hindrance associated with $SiMe_3$ groups in enhancing thermal stability is demonstrated by the greater stability of complex (**1**) compared to (**4**) (decomposes at > *ca.* 0 °C in hexane) which has only one $SiMe_3$ per hydrocarbyl group. The change in steric hindrance is also reflected in the different degrees of aggregation of (**1**) and (**4**). Complex (**2**) is markedly less stable than (**1**), decomposing slowly in hexane at *ca.* 0 °C and yielding a silver mirror. However, in the solid state it is stable in the absence of light for several days. The gold complex is of stability intermediate between (**1**) and (**2**), decomposing at 120 °C, but like (**2**) is photosenstive, slowly darkening on exposure to light and *X*-rays.

Complexes (**1**)—(**4**) were characterized by *X*-ray structure determinations (see below) and, where possible, n.m.r. spectroscopy and mass spectrometry. Of note for (**1**) and (**3**) are their ^{13}C n.m.r. chemical shifts for the carbon atoms bearing the trimethylsilyl groups. At 36.6 and 36.0 p.p.m. respectively these are only slightly downfield from the corresponding value for RH, *viz.* 33.0 p.p.m., and are thus characteristic of a large degree of covalency in the metal–carbon bonding. The value (40.1 p.p.m.) for the analogous lithium complex, $[(LiR)_2]$, is further downfield in agreement with the now widely accepted view that organolithium complexes have a high degree of ionic character.[25]

Electrochemistry.—Cyclic voltammograms of complex (**1**) in thf showed that it undergoes a reversible reduction, $E_{\frac{1}{2}}^{red} = -2.47$ V, close to the solvent reduction potential, and oxidation $E_{\frac{1}{2}}^{ox} = +0.71$ V. The reduced species is of limited stability ($t_{\frac{1}{2}} < 1$ s) whereas the oxidized form is quite stable ($t_{\frac{1}{2}} > 100$ s). Bulk electrolysis[26] using controlled-potential coulometry at +0.64 V *vs.* a saturated calomel electrode (s.c.e.) (*ca.* 1 h) indicates that the oxidation involves the overall loss of two electrons per binuclear unit [equation (3)]. Thus there is

$$[Cu_2R_2] \xrightarrow{-2e} [Cu_2R_2]^{2+} \qquad (3)$$

strong evidence for the formation of the formally copper(II) alkyl species $[Cu_2R_2]^{2+}$ of high stability, in contrast to an earlier report of copper(II) alkyls as transient species.[27] The

Table 1. Crystal data

	(1)	(2)	(3)	(4)
Formula	$C_{24}H_{44}Cu_2N_2Si_4$	$C_{24}H_{44}Ag_2N_2Si_4$	$C_{24}H_{44}Au_2N_2Si_4$	$C_{76}H_{56}Cu_4N_4Si_4$
M	600.1	688.4	866.6	911.4
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Tetragonal
Space group	$P\bar{1}$, no. 2	*Pcab*, no. 61[a]	*Pcab*, no. 61[a]	$P4_2/n$, no. 86
a/Å	11.227(4)	16.318(9)	16.038(8)	13.349(5)
b/Å	9.153(3)	16.115(10)	16.059(7)	
c/Å	8.691(3)	12.033(6)	12.084(5)	12.430(7)
α/°	111.89(1)			
β/°	100.11(1)			
γ/°	100.59(1)			
U/Å^3	785.3(5)	3 165(3)	3 112(3)	2 215(2)
D_c/g cm^{-3}	1.27	1.44	1.85	1.36
Z	1	4	4	2
F(000)	316	1 408	1 664	1 424
μ_{Mo}/cm^{-1}	15.5	12.2	98.9	20.9
Specimen/mm	Spheroid (diameter 0.25)	Spheroid (diameter 0.37)	0.35 × 0.35 × 0.30	Spheroid (diameter 0.3)
Abs. correction	Spherical	Spherical	Analytical[b]	Spherical
$2\theta_{max.}$/°	45	60	50	50
N	2 059	4 532	2 733	1 967
N_o	1 675	2 183	1 498	1 301
R	0.031	0.039	0.041	0.039
R'	0.036	0.048	0.038	0.046

[a] Variant. [b] min., max. A^* = 1.46, 2.05.

Table 2. Non-hydrogen atom co-ordinates

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Compound (**1**)							
Cu	0.085 41(4)	0.480 49(6)	0.434 47(5)	Si(1)	−0.300 8(1)	0.491 4(1)	0.298 6(1)
N	−0.028 0(3)	0.324 4(4)	0.220 0(4)	C(11)	−0.464 1(4)	0.381 4(6)	0.154 7(7)
C(1)	0.017 0(4)	0.254 3(6)	0.083 9(5)	C(12)	−0.320 7(5)	0.649 3(6)	0.496 3(6)
C(2)	−0.056 2(5)	0.139 9(6)	−0.071 0(5)	C(13)	−0.218 8(5)	0.601 9(6)	0.187 6(7)
C(3)	−0.182 1(5)	0.092 6(6)	−0.090 9(5)	Si(2)	−0.272 6(1)	0.208 3(1)	0.430 3(1)
C(4)	−0.229 9(4)	0.161 7(5)	0.043 6(5)	C(21)	−0.307 8(5)	0.310 1(6)	0.639 9(6)
C(5)	−0.153 5(3)	0.280 8(4)	0.203 6(4)	C(22)	−0.154 8(5)	0.094 7(6)	0.458 8(7)
C(6)	−0.205 8(3)	0.359 3(4)	0.351 0(4)	C(23)	−0.422 5(6)	0.048 6(7)	0.286 7(8)
Compound (**2**)							
Ag	0.517 23(3)	−0.041 56(3)	0.407 70(3)	Si(1)	0.504 2(1)	0.096 4(1)	0.229 4(1)
N	0.394 1(3)	0.105 9(3)	0.490 6(4)	C(11)	0.578 1(5)	0.031 9(5)	0.149 4(6)
C(1)	0.346 0(5)	0.160 4(4)	0.546 5(6)	C(12)	0.566 7(5)	0.164 7(5)	0.321 2(6)
C(2)	0.281 6(5)	0.201 2(4)	0.501 3(7)	C(13)	0.452 4(5)	0.165 8(5)	0.125 3(6)
C(3)	0.263 9(5)	0.185 4(5)	0.392 0(8)	Si(2)	0.370 9(1)	−0.051 3(1)	0.246 8(1)
C(4)	0.312 6(5)	0.131 9(5)	0.334 9(6)	C(21)	0.295 2(5)	−0.020 6(5)	0.136 5(6)
C(5)	0.378 1(3)	0.090 6(3)	0.382 3(4)	C(22)	0.438 9(5)	−0.129 3(4)	0.177 1(6)
C(6)	0.431 5(3)	0.033 2(3)	0.315 5(4)	C(23)	0.311 1(5)	−0.107 6(5)	0.355 8(6)
Compound (**3**)							
Au	0.521 48(3)	−0.039 11(3)	0.406 69(4)	Si(1)	0.508 1(2)	0.095 4(2)	0.226 6(4)
N	0.605 7(6)	−0.102 4(6)	0.507 2(9)	C(11)	0.579 5(8)	0.030 2(9)	0.143(1)
C(1)	0.658 1(9)	−0.155 9(9)	0.455(1)	C(12)	0.572 0(10)	0.163 4(10)	0.314(2)
C(2)	0.720 1(10)	−0.197 9(9)	0.505(1)	C(13)	0.452 6(9)	0.164 9(8)	0.126(1)
C(3)	0.734 0(10)	−0.184 2(11)	0.616(1)	Si(2)	0.373 6(2)	−0.055 4(2)	0.247 8(4)
C(4)	0.682 4(9)	−0.129 2(10)	0.668(1)	C(21)	0.295 4(9)	−0.024 1(9)	0.144(1)
C(5)	0.618 3(8)	−0.086 4(8)	0.619(1)	C(22)	0.440 8(9)	−0.132 3(9)	0.173(1)
C(6)	0.434 3(7)	0.028 7(9)	0.315(1)	C(23)	0.315 5(9)	−0.110 7(10)	0.357(1)
Compound (**4**)							
Cu	0.137 91(4)	0.165 50(4)	0.262 37(4)	C(5)	0.245 3(3)	0.117 8(3)	0.456 3(3)
N	0.156 8(3)	0.146 8(3)	0.415 4(3)	C(6)	0.326 3(3)	0.084 9(4)	0.382 1(4)
C(1)	0.080 7(4)	0.168 7(4)	0.482 6(4)	Si(1)	0.319 9(1)	−0.053 1(1)	0.361 2(1)
C(2)	0.088 2(5)	0.163 0(4)	0.591 7(5)	C(11)	0.200 8(5)	−0.092 5(4)	0.301 5(6)
C(3)	0.178 3(5)	0.137 0(4)	0.635 3(4)	C(12)	0.426 7(6)	−0.092 3(5)	0.273 6(6)
C(4)	0.256 8(4)	0.114 9(4)	0.568 5(4)	C(13)	0.335 6(6)	−0.123 1(5)	0.491 2(5)

Table 3. Interatomic (non-hydrogen) distances (Å) for complexes (**1**)—(**4**)

	(1)	(**2**)	(3)	(**4**)
M–N	1.910(3)	2.160(5)	2.081(11)	1.935(4)
M–C(6)	1.950(4)	2.154(5)	2.094(12)	1.934(5)
N–C(1)	1.353(6)	1.356(8)	1.36(2)	1.347(7)
N–C(5)	1.358(5)	1.352(7)	1.39(2)	1.343(6)
C(1)–C(2)	1.352(5)	1.35(1)	1.34(2)	1.362(8)
C(2)–C(3)	1.359(7)	1.37(1)	1.38(2)	1.365(9)
C(3)–C(4)	1.360(7)	1.36(1)	1.36(2)	1.369(8)
C(4)–C(5)	1.402(5)	1.38(1)	1.37(2)	1.403(6)
C(5)–C(6)	1.495(5)	1.503(7)	1.49(2)	1.487(6)
C(6)–Si(1)	1.877(5)	1.876(6)	1.92(1)	1.862(5)
C(6)–Si(2)	1.859(5)	1.876(6)	1.85(2)	
Si(1)–C(11)	1.875(5)	1.860(8)	1.85(1)	1.833(7)
Si(1)–C(12)	1.869(5)	1.862(8)	1.84(2)	1.868(8)
Si(1)–C(13)	1.871(7)	1.881(8)	1.87(1)	1.879(6)
Si(2)–C(21)	1.862(6)	1.879(8)	1.84(2)	
Si(2)–C(22)	1.864(7)	1.874(8)	1.87(2)	
Si(2)–C(23)	1.877(5)	1.869(8)	1.84(2)	
M···M	2.412(1)	2.654(1)	2.672(1)	2.668(2)

generation of a cationic metal alkyl species is also noteworthy; the only other cationic copper hydrocarbyl species, albeit of Cu^I, are based on phosphonium ylides.[28] Electrochemical reduction of complex (**3**) was also investigated, but did not yield any reduction or oxidation peaks within the limits imposed by the solvent, thf.

Structural Commentary.—X-Ray structure determinations of complexes (**1**)—(**3**) showed that they are comprised of discrete binuclear species lying on inversion centres. Despite the same connectivities, (**2**) and (**3**) crystallize in an orthorhombic cell and are isomorphous whereas (**1**) crystallizes in a triclinic cell; interestingly, the analogous lithium complex crystallizes in a monoclinic cell, also as a centrosymmetric species.[14] Complex (**4**) is comprised of tetranuclear molecules of $\bar{4}$ symmetry. Results are given in Tables 1—4 and Figures 1—3.

In all four compounds each alkyl ligand bridges two metal centres through the nitrogen and the carbon bearing the trimethylsilyl groups, so that there is no multicentre bonding as is usually encountered in coinage metal(I) hydrocarbyl complexes, and the metal centres are two-co-ordinate (ignoring metal–metal interactions, see below. In complex (**4**) the ligands alternate on opposite sides of a Cu_4 plane [Cu–Cu–Cu 89.24(3)°] so that each metal centre is bound by a carbon and the nitrogen of a ligand on the opposite side. Overall the structure resembles that of $[Cu_4(2\text{-}O\text{-}6\text{-}MeC_5H_3N)_4]$.[29] The bulky $SiMe_3$ groups are directed away from the centre of the cluster as expected for the minimization of non-bonding interactions.

The Cu–C distances in (**1**) and (**4**) [1.950(4) and 1.934(5) Å] are similar to those in some copper alkyls,[1] but not in $[Cu\{C(SiMe_3)_3\}_2]^-$ (2.027 Å),[2] the related binuclear ylide complex $[Cu_2\{(CH_2)_2PMe_2\}_2]$ (1.977 Å),[17] and $[Cu_4(CH_2SiMe_3)_4]$ (2.015 Å),[6] although the last has electron-deficient

Table 4. Interatomic (non-hydrogen) angles (°) for complexes (**1**)—(**4**)

	(**1**)	(**2**)	(**3**)	(**4**)
N–M–C(6)	178.0(5)	174.5(1)	176.3(5)	165.5(2)
M–N–C(1)	119.8(2)	114.7(4)	116.1(9)	118.9(3)
M–N–C(5)	120.6(2)	126.0(4)	124.9(8)	121.6(3)
C(1)–N–C(5)	119.6(3)	119.0(5)	119(1)	119.4(4)
M–C(6)–C(5)	116.9(2)	116.4(3)	114.5(8)	120.6(4)
M–C(6)–Si(1)	100.5(2)	100.2(2)	99.9(5)	103.6(2)
M–C(6)–Si(2)	98.7(2)	99.4(2)	101.7(6)	
C(5)–C(6)–Si(1)	109.1(3)	109.1(4)	107.5(9)	110.3(3)
C(5)–C(6)–Si(2)	111.0(3)	112.2(4)	113.2(8)	
Si(1)–C(6)–Si(2)	120.4(2)	119.0(3)	119.4(6)	
N–C(1)–C(2)	123.6(4)	124.4(7)	125(1)	123.3(5)
C(1)–C(2)–C(3)	118.2(5)	117.3(7)	118(1)	118.3(6)
C(2)–C(3)–C(4)	119.4(3)	118.7(8)	117(2)	119.2(5)
C(2)–C(4)–C(5)	122.1(4)	123.4(7)	125(1)	120.9(5)
C(4)–C(5)–N	117.1(4)	117.3(5)	116(1)	118.7(4)
C(4)–C(5)–C(6)	122.4(3)	121.1(5)	120(1)	121.9(4)
N–C(5)–C(6)	120.5(2)	121.6(5)	124(1)	119.3(4)
C(6)–Si(1)–C(11)	115.8(2)	113.1(3)	111.6(6)	112.4(2)
C(6)–Si(1)–C(12)	112.0(2)	109.9(3)	110.9(7)	108.9(3)
C(6)–Si(1)–C(13)	109.5(2)	113.9(3)	113.5(6)	111.5(2)
C(11)–Si(1)–C(12)	105.4(2)	106.4(3)	107.8(7)	110.2(3)
C(11)–Si(1)–C(13)	106.4(3)	106.2(3)	106.2(7)	107.6(3)
C(12)–Si(1)–C(13)	107.4(2)	106.9(3)	106.5(7)	106.0(3)
C(6)–Si(2)–C(21)	111.7(2)	117.8(3)	117.1(7)	
C(6)–Si(2)–C(22)	108.1(2)	111.8(3)	112.9(6)	
C(6)–Si(2)–C(23)	116.7(3)	108.5(3)	107.8(7)	
C(21)–Si(2)–C(22)	109.0(3)	104.5(3)	104.3(7)	
C(21)–Si(2)–C(23)	105.1(3)	106.3(4)	105.8(7)	
C(22)–Si(2)–C(23)	106.0(3)	107.3(3)	108.5(7)	

bonding and larger Cu–C distances are expected. The Ag–C distance in (**2**) [2.154(5) Å] is similar to that in various alkylargentate species, *viz.* $[\mathrm{Ag\{CHSO_2(CH_2)_3SO_2\}_2}]^-$ (2.14 Å)[8] and $[\mathrm{Ag\{C(SiMe_3)_3\}_2}]^-$ [2.162(7) and 2.198(7) Å],[9] but is significantly longer than in the silver perfluorinated alkyls $[\mathrm{AgR_2}]^-$ [2.02(4) Å] and [AgR(NCMe)] [2.10(1) Å], R = $\mathrm{CF(CF_3)_2}$.[10] The Au–C distance in (**3**) of 2.094(12) Å is unexceptional, resembling that in $[\mathrm{AuMe(PPh_3)}]$ [2.12(3) Å][30] and $[\mathrm{Ag_2\{(CH_2)_2PEt_2\}_2}]$ [2.07(2) Å].[31]

The Cu–N distances in (**1**) and (**4**) [1.910(3) and 1.935(4) Å] are similar to those reported for related compounds, *e.g.* $[\mathrm{Cu_4(2\text{-}O\text{-}6\text{-}MeC_5H_3N)_4}]$ (1.884 Å)[29] and $[\mathrm{Cu}_n(\mathrm{RN_3R})_n]$ [1.92_3 Å, $n = 2$, R = Ph;[32] 1.87(3) Å, $n = 4$, R = Me[33]]. They are also typical for mononuclear two-co-ordinate species containing pyridine-type ligands.[34] Comparable Ag–N distances to the value in complex (**2**) [2.160(5) Å] are 2.14_9 and 2.17_1 Å in the related complexes $[\mathrm{Ag_2(RN}_n\mathrm{R)_2}]$ ($n = 3$, R = Ph; $n = 5$, R = $\mathrm{C_6H_4Me\text{-}4}$)[35] and again in two-co-ordinate mononuclear species.[34] The Au–N distance in (**3**) [2.081(11) Å] compares with 2.06_6 Å in $[\mathrm{Au_4(PhN_3Ph)_4}]$.[36] The M–C,N distances are significantly different in complex (**1**), but not in (**2**)—(**4**).

We now look at metal–metal distances which are of interest with respect to whether there is any interaction between the formally d^{10} centres. In complex (**1**) the Cu ··· Cu distance is rather short, 2.412(1) Å, *cf.* 2.41_8 Å in $[\mathrm{Cu_4(CH_2SiMe_3)_4}]$,[6] in consequence of the ability of the ligand in its bridging mode to force metal centres into close proximity and/or some metal–metal interaction. The latter would be in agreement with theoretical predictions, namely that mixing of metal *s* and *p* orbitals with *d* orbitals results in a slight attraction between copper(I) centres in binuclear systems.[15] The Cu ··· Cu distance in complex (**4**) [2.668(2) Å] is however much longer and any interaction must be small relative to that in (**1**). The origin of this is unclear, but it is noteworthy that adjacent copper atoms in (**1**) are spanned by two ligands whereas in (**4**) they are spanned by one and thus there is less restriction on Cu ··· Cu interplay. This may be reflected in the greater departure from linear two-co-ordination in (**4**), *viz.* C–Cu–N 165.5(2)° [*cf.* 178.0(5)° in (**1**)], and suggests that the short metal–metal distance in (**1**) is mainly associated with the requirements of the ligand. This is in accord with predictions of Mehrotra and Hoffmann,[37] and that in $[\mathrm{Cu_2\{(CH_2)_2PMe_2\}_2}]$, which has a much larger ligand 'bite,' the Cu ··· Cu distance is much longer [2.84(3) Å].[17] In related tetranuclear complexes the Cu ··· Cu distances, and angles subtended at the metal centres by the ligands, are similar, *e.g.* Cu ··· Cu 2.64(1) and 2.68(1) Å, N–Cu–N 172.5(2)° in $[\mathrm{Cu_4(MeN_3Me)_4}]$,[33] and Cu ··· Cu 2.656(1)—2.709(1) Å and N–Cu–O 166.3(2)—172.6(2)° in $[\mathrm{Cu_4(2\text{-}O\text{-}6\text{-}MeC_5H_3N)_4}]$.[29]

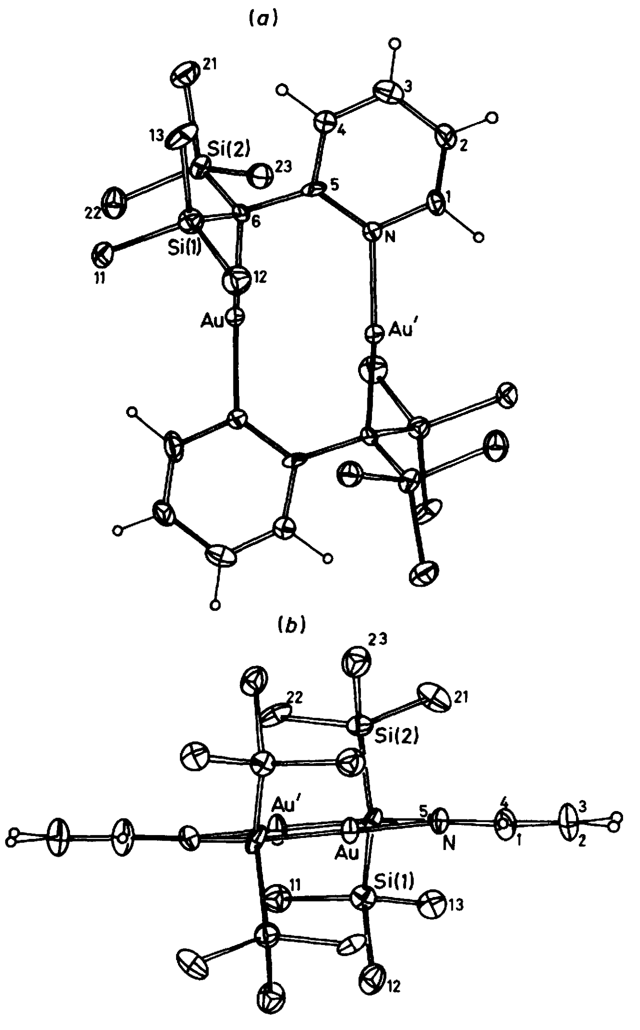


Figure 1. Projections of $[\mathrm{Au_2\{2\text{-}C(SiMe_3)_2C_5H_4N\}_2}]$, (**3**), showing the numbering scheme and 20% thermal ellipsoids: (*a*) normal to the aromatic planes; (*b*) through the plane of the aromatic rings

There are few comparative studies dealing with binuclear silver species. The Ag ··· Ag distance in complex (**2**) [2.654(1) Å] is short, presumably as a consequence of the requirements of the alkyl ligand and/or some metal–metal interaction. In $[\mathrm{Ag_2(PhN_3Ph)_2}]$ the Ag ··· Ag distance is similarly short [2.669(1) Å] and thought to be indicative of some bonding interaction.[35] With a larger ligand 'bite' in $[\mathrm{Ag_2(RN_5R)_2}]$ (R = $\mathrm{C_6H_4Me\text{-}2}$) the corresponding distance is elongated to 3.541 7(5) Å.[35] Other Ag ··· Ag distances approaching that in

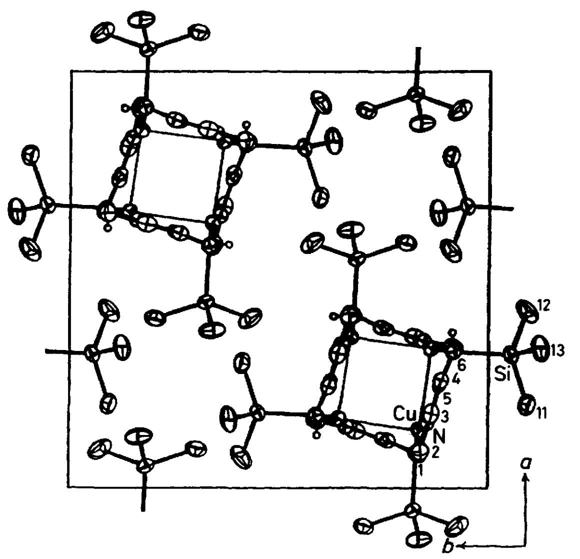


Figure 2. Unit-cell contents of $[Cu_4\{2\text{-}CH(SiMe_3)C_5H_4N\}_4]$, (**4**), down *c* showing 20% thermal ellipsoids for the non-hydrogen atoms; the hydrogen atoms have arbitrary radii

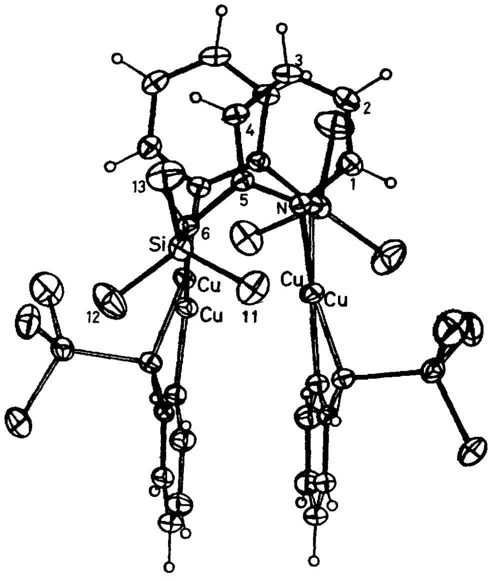


Figure 3. Projection of $[Cu_4\{2\text{-}CH(SiMe_3)C_5H_4N\}_4]$, (**4**), showing the numbering scheme and 20% thermal ellipsoids: the hydrogen atoms have arbitrary radii

(**2**), albeit in higher oligomeric compounds, include 2.733(3) Å in $[Ag_4(C_6H_2Me_3\text{-}2,4,6)_4]$[38] and 2.740(2) Å in $[\{Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_3CH_2Ag\text{-}2)\}_4]$.[39]

The Au ••• Au separation in (**3**) [2.672(1) Å] is the shortest yet observed for binuclear monovalent gold complexes, the previous shortest being 2.76(1) Å in a dithiocarbamate complex,[40] although lower values have been reported for tetranuclear gold(I) species, *e.g.* 2.692(4)—2.710(3) Å in $[Au_5(C_6H_2Me_3\text{-}2,4,6)_5]$.[12] Indeed the distance in the present study is more akin to those in formally gold(II) complexes (2.6—2.7 Å).[41] Again the short metal–metal distance is likely to be a consequence of the geometrical requirements of the alkyl ligand (as above for the analogous copper and silver compounds) possibly coupled with some metal–metal bonding as suggested by theoretical studies similar to that for copper systems,[16] and relativistic effects.[42]

In complexes (**1**)—(**4**) the ligand geometries are unexceptional. The angles subtended at the ligating carbon by the silicon atoms in (**1**)—(**3**) are close to 120°, the silicon atoms being positioned approximately equidistant above and below the plane of the aromatic rings. The metal atoms reside only 0.14, (**1**), 0.30, (**2**), and 0.18 Å, (**3**), out of the aromatic plane and thus have almost planar eight-membered rings (ignoring any metal–metal interaction). This contrasts with a deviation of 1.21 Å leading to a step structure with some close metal ••• methyl hydrogen contacts for the corresponding lithium complex.[14] Other structural differences evident in complexes (**1**)—(**3**) include metal–ligand, metal distances discussed above, and the N–M–C angle, respectively 178.0(5), 174.5(1), and 176.3(5). In (**1**) the bisector of this angle is directed towards the other metal centre whereas in (**2**) and (**3**) it is directed away. This suggests that any metal ••• metal bonding in (**2**) and (**3**) is at a maximum.

Experimental

General Procedures.—All manipulations were carried out under a dry and oxygen-free argon atmosphere or *in vacuo* using standard Schlenk techniques. Solvents were dried over and distilled from $LiAlH_4$ (thf), CaH_2 (hexane), and $LiAlH_4$ (pentane).

Materials.—2-Trimethylsilylmethylpyridine and 2-bis(trimethylsilyl)methylpyridine were prepared according to literature methods.[14,22] Silver tetrafluoroborate was recrystallized prior to use and [Au(CO)Cl] was prepared from elemental gold by the literature procedure.[43]

Physical and Analytical Measurements.—Proton and ^{13}C n.m.r. spectra were recorded on Hitachi Perkin-Elmer R-24B (60 MHz) or Bruker WP-80 spectrometers, mass spectra using a Varian CH7 spectrometer operating at 70 eV (1.12×10^{-17} J). The electrochemical experiments were carried out using a P.A.R. 173 potentiostat, 175 programmer, and a Bryans 26000 X-Y chart recorder. Details of the cell, fitted with a Ag–Ag^+ reference electrode, have been described elsewhere.[44] Solutions were prepared to be 0.2 mol l^{-1} in $[NBu^n_4][BF_4]$ and 1.0×10^{-3} mol l^{-1} in the active species. Potentials were internally referenced by adding ferrocene or bis(biphenyl)-chromium(I) tetraphenylborate and are reported with reference to the s.c.e. Half-lives for unstable species were determined by cyclic voltammetry using Nicholson and Shain's method.[45] Bulk electrolysis measurements were made on a divided electrolysis cell with a large-area platinum-cage working electrode, platinum-coil counter electrode, and the usual Ag–Ag^+ reference electrode. These were connected to an Amel model 551 potentiostat along with a Houston chart recorder and a digital coulometer constructed in our workshops.

Preparation of Complexes.—$[Cu_2\{2\text{-}C(SiMe_3)_2C_5H_4N\}_2]$, (**1**). A solution of 2-bis(trimethylsilyl)methylpyridine (0.5 g, 2.1 mmol) in thf (10 cm^3) was cooled to *ca.* 0 °C and $LiBu^n$ (1.38 cm^3, 1.6 mol l^{-1} in hexane, 2.2 mmol) added dropwise. The resulting orange solution was warmed to room temperature, a slurry of copper(I) chloride (0.25 g, 2.5 mmol) in thf (2 cm^3) added, and the mixture stirred for 15 min, during which time the solution became yellow-green and a grey precipitate was formed. The solvent was then removed *in vacuo*, the product extracted with pentane (20 cm^3), filtered, concentrated to 5 cm^3, and cooled to −30 °C, yielding yellow-green plates of the required *compound.* These were collected, washed with pentane (5 cm^3), and dried *in vacuo*. Yield 0.5 g, 79%. M.p. 162—164 °C (decomp.). N.m.r. (C_6D_6): ^1H, δ 0.39 (s, 18 H, $SiMe_3$), 6.22 (m, 1 H, C_5H_4N), 7.0 (m, 2 H, C_5H_4N), and 7.8 (m, 1 H, C_5H_4N); ^{13}C (^1H decoupled), δ 4.1 ($SiMe_3$), 36.6 (CCu), 118.0, 129.0, 135.6, 148.4 (CH, C_5H_4N), and 176.7 (C, C_5H_4N). Mass spectrum: m/z 600 (P^+), 585 ($P - CH_3^+$), 527 ($P - SiMe_3^+$), and 300.

$[Ag_2\{2\text{-}C(SiMe_3)_2C_5H_4N\}_2]$, (**2**). An ice-cold solution of 2-bis(trimethylsilyl)methylpyridine (0.5 g, 2.1 mmol) in thf (10 cm^3) was added to LiBu^n (1.3 cm^3, 1.6 mol l^{-1} in hexane, 2.2 mmol). The resulting red solution was stirred for 10 min, then added to a slurry of $AgBF_4$ (0.5 g, 2.4 mmol) in thf (10 cm^3) at −80 °C yielding a brown solution. After 5 min the solvent was removed *in vacuo* and the resulting brown oil extracted with cold pentane (20 cm^3), filtered, then cooled to −30 °C. Colourless prisms of the required *compound* formed after 5 d. These were isolated, washed with pentane (2×5 cm^3), then dried *in vacuo*. Yield 0.10 g, 37%. M.p. (decomp.) 29 °C.

$[Au_2\{2\text{-}C(SiMe_3)_2C_5H_4N\}_2]$, (**3**). To an ice-cooled solution of 2-bis(trimethylsilyl)methylpyridine (0.3 g, 1.2 mmol) in thf (10 cm^3) was added LiBu^n (0.80 cm^3, 1.6 mol l^{-1} in hexane, 1.3 mmol). After 10 min the solution was added to [Au(CO)Cl] (0.35 g, 1.3 mmol) in thf (10 cm^3) at −80 °C yielding a brown solution. The solvent was removed *in vacuo* after 5 min and the product extracted with hexane (10 cm^3). The yellow solution was filtered and gave pale yellow crystals of the required *compound* overnight at −30 °C. These were collected, washed with pentane (5 cm^3), and dried *in vacuo*. Yield 0.21 g, 40%. M.p. 122 °C (decomp.). N.m.r. (C_6D_6): ^{1}H δ 0.5 (s, 18 H, SiMe$_3$), 6.2 (m, 1 H, C_5H_4N), 6.7 (m, 1 H, C_5H_4N), 7.4 (m, 1 H, C_5H_4N), and 8.2 (m, 1 H, C_5H_4N); ^{13}C (^{1}H decoupled), δ 4.6 (SiMe$_3$), 36.0 (CAu), 119.4, 130.6, 135.2, and 151.7 (CH, C_5H_4N).

$[Cu_4\{2\text{-}CH(SiMe_3)C_5H_4N\}_4]$, (**4**). An ice-cold solution of 2-trimethylsilylmethylpyridine (0.3 g, 1.25 mmol) in thf (10 cm^3) was added to LiBu^n (0.83 cm^3, 1.6 mol l^{-1} in hexane, 1.3 mmol) and the solution added to a slurry of CuCl (0.15 g, 1.5 mmol) in thf (3 cm^3). After 15 min the solvent was removed *in vacuo* from the resulting brown solution and the residue was extracted with hexane (20 cm^3), filtered, and cooled to −30 °C yielding large red prisms of the required *compound*. These were collected, washed with pentane (5 cm^3), and dried *in vacuo*. Yield 0.13 g, 86%. M.p. 58 °C (decomp.). ^{1}H N.m.r. (C_6D_6): δ 0.47 (s 9 H, SiMe$_3$), 1.9 (s, 1 H, CH), 6.2 (m, 1 H, C_5H_4N), 7.0 (m, 2 H, C_5H_4N), and 8.0 (m, 1 H, C_5H_4N).

Crystallography.—Unique data sets were measured to the specified $2\theta_{max.}$ limit using Syntex $P2_1$ and $P\bar{1}$ four-circle diffractometers, fitted with monochromatic Mo-K_α radiation sources and operating in conventional 2θ—θ scan mode. N Independent reflections were measured, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement with statistical weights, after solution of the structure by the heavy-atom method and absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included at idealized values, although in some cases it was possible meaningfully to refine $(x, y, z)_H$ (see below). Residuals R, R' on $|F|$ at convergence are quoted in Table 1. Neutral complex scattering factors were used.[46] The XTAL-83 program system was implemented by S. R. Hall on a Perkin-Elmer 3240 computer.[47] Skeletal atom numbering is given in the Figures.

Variations in procedure. For complexes (**1**), (**2**), and (**4**), $(x, y, z)_H$ were refined for the ring hydrogen atoms. A few reflections for complex (**3**) were affected by a diffractometer malfunction and were deleted from the refinement; the data were otherwise of good quality and it is unlikely that the geometrical parameters are significantly affected.

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