Silylmethyl and Related Complexes. Part 4.[1] Preparation, Properties, and Crystal and Molecular Structure of Tetrakis[(trimethylsilylmethyl)-copper(I)], an Alkyl-bridged, Square-planar, Tetranuclear Copper(I) Cluster †

By **John A. J. Jarvis** and **Ronald Pearce**, Imperial Chemical Industries Limited, Corporate Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE
Michael F. Lappert,* School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Interaction of $Li(CH_2SiMe_3)$ with CuI gives $[\{Cu(CH_2SiMe_3)\}_4]$ a thermally stable, light-petroleum-soluble, colourless copper(I) alkyl, which by cryoscopy is a tetramer in benzene and a hexamer in cyclohexane. An *X*-ray crystal-structure determination at −40 °C shows that the complex consists of discrete centrosymmetric units containing a square plane of copper atoms with the methylene carbons lying in the same plane and bridging the edges. Crystals are monoclinic with $a = 6.355(4)$, $b = 12.636(7)$, $c = 17.938(11)$ Å, $\beta = 90.84(5)°$, space group $P2_1/c$. Relevant distances and angles are: Cu–Cu 2.417 and Cu–C (mean) 2.02 Å; Cu–Cu–Cu 89.8, 90.2, Cu–C–Cu (mean) 73.5, and C–Cu–C (mean) 163.5°. Decomposition (thermal or photochemical) occurs *via* a homolytic path. Reactions with some organic halides (C_3H_5Br, PhI, $SiMe_3Cl$, or $PhCH_2Br$) are outlined, showing for the most part simple metathetical $X–CH_2SiMe_3$ exchange, but less readily than with alkyls of Li or Mg. Addition of $Li(CH_2SiMe_3)$ appears to yield $Li[Cu(CH_2SiMe_3)_2]$.

ALKYLCOPPER(I) complexes are generally unstable, often difficult to obtain in a pure state, and usually insoluble in the ether or hydrocarbon medium employed in their preparation.[2] No stable copper(II) hydrocarbyl complexes have been reported. That organocopper(I) complexes are not inherently thermally unstable is demonstrated by reports that have appeared in the last five years of a range of stable homoleptic (binary) complexes $[(CuR)_n]$.[2,3] Stable species are obtained by a careful choice of ligand. These have latterly included the bidentate phosphorus or arsenic groups, $[CH_2]_2EMe_2$ (E = P or As)[4] and the chelating $C_6H_4CH_2\dot{N}Me_2$-*o*.[5] [In contrast to the alkyls, simple copper(I) aryls show reasonable thermal stability.[2]] We have discussed elsewhere factors affecting the stability of transition-metal hydrocarbyl complexes, and have reviewed the available range of homoleptic complexes, as well as their decomposition paths and those of heteroleptic species.[3] The stability and solubility of copper(I) alkyls is enhanced on reaction with organolithium (or magnesium) reagents, affording the diorganocuprates. These have received considerable attention in recent years as reagents for organic synthesis.[6]

In our researches into the preparation of stable alkyls of the transition metals we have been particularly concerned with homoleptic compounds having trimethylsilyl or related ligands.[3b] These ligands confer the useful properties of good solubility in hydrocarbon media, simple ^1H n.m.r. spectra, and good thermal stability arising from the preclusion of several common decomposition paths. Consequently, a range of complexes with the early transition metals, for example $[Zr(CH_2SiMe_3)_4]$ and $[Cr\{CH(SiMe_3)_2\}_3]$, has been obtained.[3b]

We now report the copper(I) complex, $[\{Cu(CH_2SiMe_3)\}_4]$, which shows remarkable thermal stability and solubility in hydrocarbons and which possesses a novel molecular geometry based on a square plane of copper atoms with single-bridging, coplanar, trimethylsilylmethyl groups between pairs of adjacent copper atoms. There appears to be no precedent for an electron-deficient metal cluster having a single alkyl bridge between adjacent metal atoms. Our findings were summarised in 1973 in preliminary communications.[7,8] This paper presents full details of the preparation, properties, and crystal and molecular structure of $[\{Cu(CH_2SiMe_3)\}_4]$.

EXPERIMENTAL

Synthesis of Tetrakis[(*trimethylsilylmethyl*)*copper*(I)], $[\{Cu(CH_2SiMe_3)\}_4]$.—Trimethylsilylmethyl-lithium (55 mmol) in diethyl ether (95 cm^3) was added dropwise over 3 h at *ca.* −30 °C to a slurry of copper(I) iodide (10.50 g, 55mmol) in diethyl ether (25 cm^3). The mixture was kept at −10 to 0 °C for another hour, giving a green-brown supernatant solution and a green-yellow solid, before removal of the volatiles *in vacuo* at this temperature. Cold pentane

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† No reprints available.

[1] Part 3, C. S. Cundy, M. F. Lappert, and R. Pearce, *J. Organometallic Chem.*, 1973, **59**, 161.

[2] *Cf.*, A. E. Jukes, *Adv. Organometallic Chem.*, 1974, **12**, 215.

[3] *Cf.*, (*a*) P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, 1976, **76**, 219; (*b*) *Accounts Chem. Res.*, 1974, **7**, 209.

[4] *Cf.*, H. Schmidbaur, *Accounts Chem. Res.*, 1975, **8**, 62; *Adv. Organometallic Chem.*, 1976, **14**, 205.

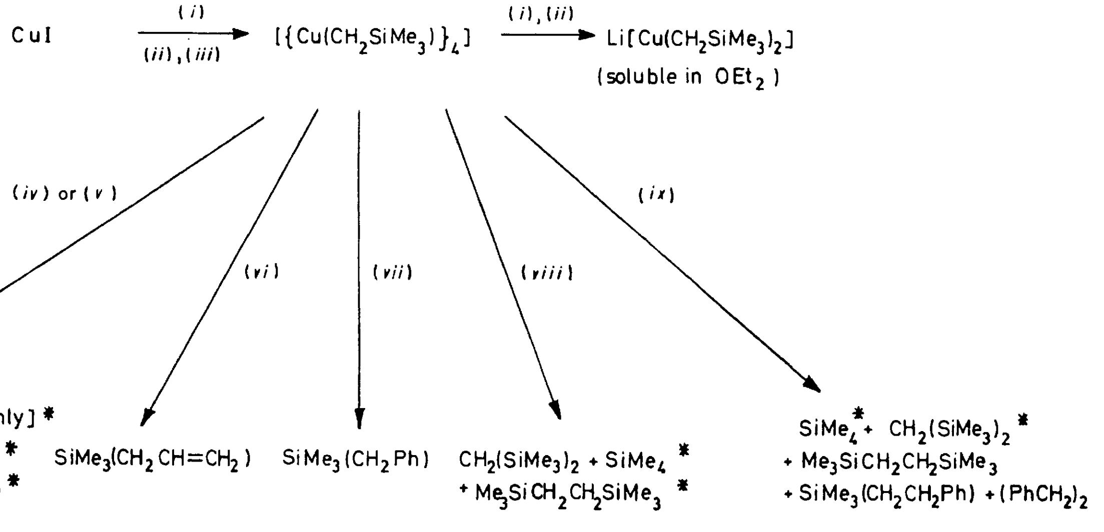
[5] G. van Koten and J. G. Noltes, *J. Organometallic Chem.*, 1975, **84**, 129.

[6] *Cf.* J. F. Normant, *Synthesis*, 1972, 63; G. H. Posner, *Org. Reactions*, 1972, **19**, 1; 1975, **22**, 253.

[7] M. F. Lappert and R. Pearce, *J.C.S. Chem. Comm.*, 1973, 24.

[8] J. A. J. Jarvis, B. T. Kilbourn, R. Pearce, and M. F. Lappert, *J.C.S. Chem. Comm.*, 1973, 475.

(75 cm^3) was added to the residue and the resulting extract was separated from the remaining grey solid by filtration at *ca.* 0 °C. The clear red-brown filtrate was cooled to *ca.* −70 °C to give off-white needles of the *product* (5.7 g, 70%). Recrystallisation from pentane gave colourless needles (Found: C, 31.45; H, 7.1; Cu, 42.3; Si, 18.35. $C_4H_{11}CuSi$ requires C, 31.9; H, 7.35; Cu, 42.1; Si, 18.6%), m.p. 78—79 °C (decomp.; darkening of the crystals occurs below the m.p.). The molecular weight (by cryoscopy) of *ca.* 10% w/w solutions was determined as 977 (in cyclohexane) or 647 (in benzene) ($C_4H_{11}CuSi$ requires *M* 151).



SCHEME Aspects of the chemistry of $[\{Cu(CH_2SiMe_3)\}_4]$. (*i*) $Li(CH_2SiMe_3)$; (*ii*) OEt_2; (*iii*) −30 °C; (*iv*) 80 °C, PhMe (in the dark); (*v*) $h\nu$; (*vi*) C_3H_5Br; (*vii*) PhI; (*viii*) $SiMe_3Cl$; (*ix*) $PhCH_2Br$

* Minor product in reaction mixture.

Reactions of $[\{Cu(CH_2SiMe_3)\}_4]$.—These were carried out at ambient temperature in diethyl ether solution, under an argon atmosphere, and in the absence of light. Products were established by g.l.c. and ^1H n.m.r. spectroscopy. Details are in the Scheme.

X-*Ray Structure Analysis*.—The complex was obtained in a suitable form by crystallisation from n-pentane at *ca.* −70 °C. Crystals were mounted in capillaries in a nitrogen-filled glove-box under subdued light and care was taken to keep them at low temperatures (<*ca.* 0 °C), except for brief periods during manipulation, by provision of a cooled storage tray in the glove-box.

Crystal Data.—$C_{16}H_{44}Cu_4Si_4$, $M = 603.0$, colourless, Monoclinic, $a = 6.355(4)$, $b = 12.636(7)$, $c = 17.938(11)$ Å, $\beta = 90.84(5)°$, $U = 1\,440(1)$ Å^3, space group $P2_1/c$, $D_c = 1.390$, $Z = 2$, $F(000) = 624$, Mo-K_α radiation (Nb filter), $\mu = 31.8$ cm^{-1}.

After preliminary photography to identify the space group, three-dimensional intensity data ($2\theta \leqslant 50°$) were collected on a card-operated Picker diffractometer. The crystal was kept at *ca.* −40 °C while being orientated, and during data collection.[9] The observed intensities for 2 044 independent reflections with $I \geqslant 3.5\sigma(I)$ were corrected for Lorentz and polarisation factors, but neither absorption nor extinction corrections were computed. The structure was solved by heavy-atom procedures and refined with anisotropic thermal parameters for copper, silicon, and carbon atoms. A difference synthesis revealed the methylene hydrogen atoms, but not those of the methyl groups which have rather high anisotropic thermal parameters. The structure was refined to *R* 0.049 with the four methylene hydrogens treated isotropically. The weights used in the final cycles of refinement were given by $\omega^{-1} = 1 + [(F_o - K_2)/k_1]^2$, where $k_1 = 20$ and $K_2 = 17$; these values were chosen to give reasonably constant average values for $\Sigma\omega\Delta^2$ in different ranges of F_o.

The final positional parameters are given in Table 1, thermal parameters in Table 2, and bond lengths and angles in Table 3. Final structure factors are listed in Supplementary Publication No. SUP 22000 (15 pp., 1 microfiche).*

TABLE 1

Final positional parameters (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu(1)	−1 879(1)	4 289(1)	5 456(1)
Cu(2)	−0 923(1)	4 525(1)	4 167(1)
Si(1)	−4 512(3)	2 474(1)	5 067(1)
Si(2)	0 013(3)	4 638(1)	2 608(1)
C(1)	−3 340(12)	3 650(6)	4 582(4)
C(2)	1 052(12)	5 273(6)	3 484(4)
C(3)	−5 946(14)	2 865(7)	5 942(5)
C(4)	−2 381(14)	1 501(7)	5 329(5)
C(5)	−6 478(15)	1 806(8)	4 416(5)
C(6)	0 590(19)	3 184(6)	2 616(5)
C(7)	−2 906(12)	4 907(9)	2 485(4)
C(8)	1 349(12)	5 235(6)	1 773(3)
H(11)	−2 773(133)	3 328(70)	4 140(48)
H(12)	−4 544(197)	4 124(102)	4 308(69)
H(21)	0 962(130)	6 155(73)	3 354(47)
H(22)	2 062(182)	5 017(107)	3 495(69)

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[9] G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc.* (*A*), 1970, 1275.

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

TABLE 2

Mean-square atomic vibrations (Å^2; × 10^4 for copper and silicon, × 10^3 for carbon) with estimated standard deviations in parentheses*

Atom	U_{11}	$2U_{12}$	$2U_{13}$	U_{22}	$2U_{23}$	U_{33}
Cu(1)	457(4)	−218(7)	−62(6)	449(4)	−1(6)	302(4)
Cu(2)	479(4)	−215(7)	−23(6)	428(4)	34(6)	300(3)
Si(1)	441(9)	−150(14)	48(14)	413(9)	−34(14)	418(8)
Si(2)	462(9)	−53(14)	−10(13)	444(9)	−39(13)	295(7)
C(1)	59(4)	−45(7)	−4(6)	56(4)	8(6)	38(3)
C(2)	54(4)	−19(7)	−3(6)	58(4)	0(6)	35(3)
C(3)	85(6)	−36(9)	73(9)	80(6)	−31(9)	76(5)
C(4)	85(6)	57(9)	−7(9)	65(5)	17(8)	79(5)
C(5)	90(6)	−82(10)	−36(9)	86(6)	−23(10)	84(6)
C(6)	167(10)	29(10)	30(11)	43(4)	−3(7)	65(5)
C(7)	48(4)	0(10)	−10(7)	145(9)	−13(10)	50(40)
C(8)	64(4)	−11(7)	11(6)	72(5)	7(6)	35(3)

* Isotropic U values for the hydrogen atoms did not converge, but fluctuated between 0.05 and 0.1 Å^2

TABLE 3

Interatomic distances (Å) and angles (°)

Cu(1)–Cu(2)	2.418	Si(1)–C(5)	1.90
Cu(1)–Cu(2′)	2.417	Si(2)–C(2)	1.88
Cu(1)–C(1)	1.98	Si(2)–C(6)	1.87
Cu(2)–C(2)	2.00	Si(2)–C(7)	1.89
Cu(1)–C(2′)	2.04	Si(2)–C(8)	1.89
Cu(2)–C(1)	2.04	C(1)–H(11)	0.97
Si(1)–C(1)	1.88	C(1)–H(12)	1.08
Si(1)–C(3)	1.89	C(2)–H(21)	1.14
Si(1)–C(4)	1.88	C(2)–H(22)	0.72
Cu(1)–Cu(2)–Cu(1′)	90.2	C(1)–Si(1)–C(5)	109.1
Cu(1)–C(1)–Cu(2)	73.8	C(3)–Si(1)–C(4)	108.5
Cu(1′)–C(2)–Cu(2)	73.4	C(3)–Si(1)–C(5)	107.8
C(1)–Cu(1)–C(2′)	163.4	C(4)–Si(1)–C(5)	109.1
C(1)–Cu(2)–C(2)	163.7	C(2)–Si(2)–C(6)	110.3
Cu(1)–C(1)–Si(1)	98.0	C(2)–Si(2)–C(7)	110.7
Cu(2)–C(2)–Si(2)	95.4	C(2)–Si(2)–C(8)	109.7
Cu(2)–C(1)–Si(1)	154.3	C(6)–Si(2)–C(7)	111.6
Cu(1′)–C(2)–Si(2)	168.2	C(6)–Si(2)–C(8)	107.9
C(1)–Si(1)–C(3)	112.1	C(7)–Si(2)–C(8)	106.7
C(1)–Si(1)–C(4)	110.1		

RESULTS AND DISCUSSION

Preparation and Properties.—Interaction of equimolar quantities of Li(CH_2SiMe_3) and copper(I) iodide in diethyl ether at *ca.* −30 °C gave tetrakis[(trimethylsilylmethyl)copper(I)]. The complex was isolated by evaporation of the ether reaction mixture, extraction of the residue with pentane, followed by crystallisation at low temperature. The colourless crystals of the complex are stable for long periods at ambient temperature, under an inert atmosphere, and in the absence of light, but they darken slowly on exposure to light becoming brown or red-brown. Solutions are markedly more sensitive. Light must be excluded whenever possible during manipulations, the colour of the solutions changing from colourless to yellowish, orange-brown, or red, depending on the degree of exposure to light and/or air. The complex shows considerable thermal stability when compared to the simple copper(I) alkyls,[2] melting with decomposition at 78—79 °C. Solubility in hydrocarbons is very high (extraction is *via* pentane solution) in contrast to simple copper alkyls. This high solubility is a feature of organotransition-metal complexes containing silylmethyl ligands.[3]

Molecular-weight measurements by cryoscopy in benzene and cyclohexane showed mean degrees of association of $[\{Cu(CH_2SiMe_3)\}_n]$ of 4.3 and 6.5 respectively. The former is in fair agreement with the tetranuclear arrangement observed in the mass spectrum and from *X*-ray data (see below). The higher value in cyclohexane suggests the presence of hexanuclear clusters and has a direct parallel with the behaviour of Li(CH_2SiMe_3) which has a mean degree of association of six in cyclohexane and four (in dilute solution) in benzene.[10]

The mass spectrum showed an intense tetranuclear parent ion at *m/e* 600 (for $[\{^{63}Cu(CH_2SiMe_3)\}_4]^+$) with the expected Cu_4 isotope pattern. Fragmentation occurred *via* loss of the species Me, $SiMe_4$, $SiMe_4 + CH_4$, $CH_2(SiMe_3)_2$, and $2SiMe_4$. Lower *m/e* peaks in the spectrum were not assigned. Peaks of considerably lower intensity were also observed at higher *m/e* (centred at 662—663) and are tentatively assigned to a Cu_5 species, $[Cu_5(CH_2SiMe_3)_4]^+$ or $[\{Cu(CH_2SiMe_3)\}_5 - SiMe_4]^+$. The ^1H n.m.r. spectrum at room temperature of a pentane solution (using CH_2Cl_2 as internal standard) was simple, with singlets at τ 9.80 (Si*Me*$_3$) and 10.18 (CuC*H*$_2$Si).

Thermal or Photochemical Decomposition.—Decomposition paths in the thermolysis of organocopper complexes have received considerable attention,[2] the precise course depending markedly on the ligand. It was therefore of interest to examine $[\{Cu(CH_2SiMe_3)\}_4]$ in which the bulky trimethylsilylmethyl ligand is expected to hinder bimolecular paths and for which β-hydrogen elimination is excluded.

Heating a solution of the complex in toluene in the absence of light at *ca.* 80 °C for 16 h gave a mixture of products. The solution became deep red and the glass vessel was coated with a copper mirror. G.l.c. showed the presence of $SiMe_4$ (major product), $CH_2(SiMe_3)_2$, $Me_3SiCH_2CH_2SiMe_3$, $SiMe_3(CH_2CH_2Ph)$, and $(PhCH_2)_2$. These products parallel the fragmentation paths in the mass spectrum, *e.g.* loss of $CH_2(SiMe_3)_2$, and are indicative of a major contribution from a homolytic path ($Me_3SiCH_2CH_2SiMe_3$ may arise *via* radical–radical combination or reductive elimination from a polynuclear aggregate). The related copper neophyl ($PhCMe_2CH_2$) complexes decompose homolytically.[11] Photochemical (u.v.) decomposition afforded a similar product mixture with the exception that $CH_2(SiMe_3)_2$ was absent. Again, a radical path is implicated.

The deep red colour of the solutions was tentatively assigned to the presence of a copper sol. Transmission electron microscopy showed the presence of small particles with sizes in the range 50—100 Å, larger particles being mainly absent in the supernatant liquid. The unusual thermal stability of $[\{Cu(CH_2SiMe_3)\}_4]$ compared with most other copper(I) alkyls is not readily explained by its structure, although the cluster

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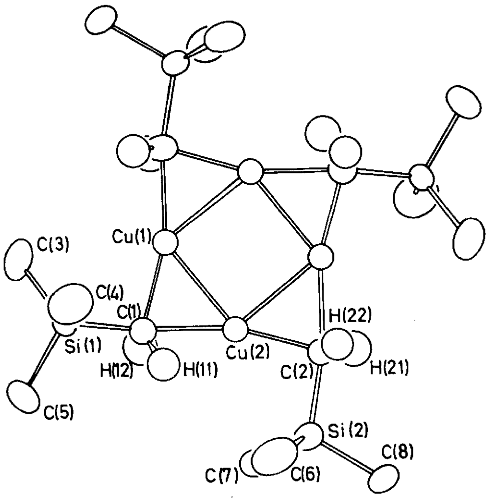
[10] H. L. Lewis and T. L. Brown, *J. Amer. Chem. Soc.*, 1970, **92**, 4664.

[11] G. M. Whitesides, E. J. Panek, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 1972, **94**, 232.

arrangement must be a factor. There is no obvious reason why the unstable $[(CuMe)_n]$ should not adopt a similar structure.

Reaction with Organic Halides.—Reactions of $[\{Cu(CH_2SiMe_3)\}_4]$ with a number of organic halides were briefly investigated in order to study its reactivity as an alkylating agent. The reactions were slow compared with those of corresponding organo-lithium or -magnesium reagents. Allyl bromide gave $SiMe_3(CH_2CH{=}CH_2)$ exclusively, PhI gave $SiMe_3(CH_2Ph)$, and $SiMe_3Cl$ gave $CH_2(SiMe_3)_2$ with minor amounts of $SiMe_4$ and $Me_3SiCH_2CH_2SiMe_3$. Benzyl bromide, which reacted less readily than the above halides, gave a mixture of products, after *ca.* 3 d. These were $SiMe_4$, $CH_2(SiMe_3)_2$ (minor product), $Me_3SiCH_2CH_2SiMe_3$ (minor product), $SiMe_3(CH_2CH_2Ph)$, and $PhCH_2CH_2Ph$. The presence of bibenzyl suggests intermediate benzyl radicals, formed from $[(CuCH_2Ph)_n]$ or from $PhCH_2Br$–R•, or from simple halogen–metal exchange to give $[(CuCH_2Ph)_x]$ and $SiMe_3(CH_2Br)$ followed by the presumably ready reaction $Cu(CH_2Ph) + PhCH_2Br \longrightarrow CuBr + (PhCH_2)_2$.



Crystal and molecular structure of $[\{Cu(CH_2SiMe_3)\}_4]$ showing the atomic numbering

Reaction with $Li(CH_2SiMe_3)$.—Addition of one equivalent of $Li(CH_2SiMe_3)$ to a diethyl ether solution of $[\{Cu(CH_2SiMe_3)\}_4]$ gave a colourless solution which showed increased thermal and photochemical stability. By analogy with the chemistry of simple copper alkyls, the formation of the 'ate' complex $[\{Li[Cu(CH_2SiMe_3)_2]\}_n]$ is inferred, but no attempt at isolation was made.

Molecular Structure of Crystalline $[\{Cu(CH_2SiMe_3)\}_4]$.—An *X*-ray structure determination was carried out on a crystal of $[\{Cu(CH_2SiMe_3)\}_4]$ at −40 °C. The molecular geometry is shown in the Figure. The complex exists as discrete centrosymmetric tetrameric units with a square plane of copper atoms. The methylene carbon atoms symmetrically bridge adjacent pairs of copper atoms and lie in the Cu_4 plane (deviations from the plane of 0.06 and 0.02 Å). One silicon atom lies close (0.08 Å) to, and the other slightly out (0.68 Å) of, the Cu_4C_4 plane. The positions of the hydrogen atoms bound to the methylene carbons (but not to the silicon methyl carbons) were determined. To a first approximation, the carbon co-ordination can be considered as tetrahedral with the fourth bonding vector intersecting the Cu–Cu axis off-centre. Alternatively, the carbon [C(1)] may be regarded as the centre of a distorted trigonal bipyramid with a copper atom [Cu(2)] and a silicon [Si(1)] in axial positions and the second copper atom [Cu(1)] with the two hydrogen atoms [H(11) and H(12)] in equatorial positions.

We propose that the alkyl bridge involves a three-centre two-electron bond with linear co-ordination at copper and that copper–copper bonding is relatively unimportant. In such three-centre bonds, the bonding orbitals do not lie along the internuclear axes (see, *e.g.*, Al_2Me_6)[12] and consequently the C–Cu–C angle of 164° in $[\{Cu(CH_2SiMe_3)\}_4]$ does not preclude linear co-ordination at copper. The apparent pinching-in of the copper atoms from a regular Cu_4C_4 square arises from a description using internuclear vectors and is probably not a consequence of Cu–Cu interactions. Bonding in polynuclear clusters has been extensively discussed by Mason and Mingos.[13]

The structure of $[\{Cu(CH_2SiMe_3)\}_4]$ shows two novel features in (*i*) the square plane of Cu_4 atoms (and the planar Cu_4C_4 cluster), and (*ii*) the singly bridging alkyl ligands between adjacent pairs of metal atoms. Planar arrangements of metal atoms in clusters are unusual[14] and, to our knowledge, this is the first example of a square plane. A recent paper has described the structure of the related copper(I) alkoxide, $[\{Cu(OBu^t)\}_4]$, which shows remarkable similarities to $[\{Cu(CH_2SiMe_3)\}_4]$. These include the presence of a planar Cu_4 core, singly bridging alkoxide ligands, and an essentially planar Cu_4O_4 arrangement.[15] Planar arrangements of lower symmetry in Cu_4 clusters are known from *X*-ray studies of $[\{Cu(O_2CCF_3)\}_4]\cdot 2C_6H_6$[16] and $[\{Cu(MeNNNMe)\}_4]$,[17] both of which contain planar parallelograms of copper atoms with the ligands bridging two adjacent metals alternately above and below the Cu_4 plane. As in $[\{Cu(CH_2SiMe_3)\}_4]$, neglecting Cu–Cu interaction, the co-ordination at copper is approximately linear. From spectroscopic data, the structure of a dimeric diaryldicopper complex, $[(o\text{-}CuC_6H_4CH_2NMeCH_2CH_2NMeC_6H_4\text{-}Cu\text{-}o)_2]$, has been interpreted on the basis of a planar Cu_4 core with adjacent pairs of copper atoms bridged by aryl groups of the chelating ligands.[18] On the other hand, the related tetranuclear $[\{\overline{Cu(C_6H_4CH_2N}Me_2\text{-}o)\}_4]$

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[12] P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, 1953, **21**, 986.

[13] R. Mason, *Pure Appl. Chem.*, 1973, **33**, 513; R. Mason and D. M. P. Mingos, *J. Organometallic Chem.*, 1973, **50**, 53.

[14] *Cf.*, R. B. King, *Progr. Inorg. Chem.*, 1972, **15**, 287.

[15] T. Greiser and E. Weiss, *Chem. Ber.*, 1976, **109**, 3142.

[16] P. F. Rodesiler and E. L. Amma, *J.C.S. Chem. Comm.*, 1974, 599.

[17] J. E. O'Connor, G. A. Janusonis, and E. R. Corey, *Chem. Comm.*, 1968, 445.

[18] G. van Koten and J. G. Noltes, *J. Organometallic Chem.*, 1976, **104**, 127.

has a Cu_4 core of a configuration intermediate between planar and tetrahedral, which may be a consequence of additional constraints imposed by the donor NMe_2 groups.[5,19]

While hydrocarbyl bridges are a feature of the chemistry of some of the main-group metals, in particular of Be and Al,[20] they are less well established in the transition series. Moreover, single alkyl bridges between a pair of metals are without precedent; double alkyl bridges, both between two transition metals (M–M) or between a transition metal and a main-group metal (M–M′), while rare, are better known. In this context, we are concerned with alkyl bridges where the binding is formally electron deficient and thus we exclude complexes such as $[\mathrm{Mn}_2(\mu\text{-}\mathrm{CH}_2)(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2(\mathrm{CO})_4]$ [21] and $[\mathrm{Zr}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2(\mathrm{CH}_2\mathrm{CH}_2\mathrm{AlEt}_2)\mathrm{Cl}]$.[22] By singly bridged alkyl we refer to situations where the alkyl group is the sole binding ligand between two metals, and by doubly bridged where there are two bridging ligands between metals, generally both being alkyl.

Structures where a single alkyl group forms part of a double bridge, with as partner a halide or alkoxo-group, enter into much speculative discussion on the nature of the intermediates in Ziegler–Natta catalysis [23] and of transalkylation reactions. For the latter, supporting evidence for such intermediates comes from recent studies of alkyl-exchange reactions in gold, platinum, and palladium systems.[24] Single hydrocarbyl bridges were formerly restricted to examples of aryl and cyclopentadienyl groups, as in, *e.g.*, $[\{\overline{\mathrm{Cu}(\mathrm{C}_6\mathrm{H}_4\mathrm{CH}_2\mathrm{N}}\mathrm{Me}_2\text{-}o)\}_4]$,[5,19] $[\mathrm{Au}_2\{\mu\text{-}\mathrm{Fe}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)(\eta\text{-}\mathrm{C}_5\mathrm{H}_4)\}(\mathrm{PPh}_3)_2]^+$,[25] and $[\mathrm{Os}_3\mathrm{Ph}(\mathrm{CO})_8(\mathrm{PPh}_2)\{\mathrm{PPh}(\mathrm{C}_6\mathrm{H}_4)\}]$.[26] Examples of double alkyl bridges are to be found in complexes of the Group 3A and lanthanoid metals and of nickel. For the type $[\mathrm{M}_2(\mu\text{-}\mathrm{R})_2]$ these are $[\{\mathrm{MMe}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2\}_2]$ (M = Y, Dy, Ho, Er, or Yb) [27] and $[\{\mathrm{NiMe}(\eta\text{-allyl})\}_2]$ (allyl = C_3H_5, C_4H_7, or C_5H_9).[28] For the type $[\mathrm{M}(\mu\text{-}\mathrm{R})_2\mathrm{M}']$ these are $[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2(\mu\text{-}\mathrm{Me})_2\mathrm{AlMe}_2]$ (M = Ti, Sc, Y, Gd, Dy, Ho, Er, Tm, or Yb) [29] and $[\mathrm{Ni}(\eta\text{-allyl})(\mu\text{-}\mathrm{Me})_2\mathrm{AlMe}_2]$ (allyl = C_3H_5, C_4H_7, or C_5H_9).[28]

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