Tri- and Tetra-meric Copper(I) Amides $\{Cu[N(SiMePh_2)_2]\}_3$ and $\{Cu[N(SiMe_2Ph)_2]\}_4$†

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The compounds $\{Cu[N(SiMePh_2)_2]\}_3$ **1** and $\{Cu[N(SiMe_2Ph)_2]\}_4$ **2** have been synthesised by the reaction of CuBr with the appropriate lithium silylamide in diethyl ether solution. Both were characterized by X-ray crystallography, ^{1}H NMR and IR spectroscopy, and elemental analysis. They represent the first copper silylamides to be completely characterized by X-ray crystallography. Compound **1** has a very rare trimeric structure with the metals disposed in a triangular fashion and bridged by amide ligands. The less-crowded derivative **2** has an amide-bridged tetrameric structure and an almost square-planar arrangement of four coppers. The bridging amides are displaced from the Cu_4 plane such that the Cu_4N_4 core possesses a butterfly structure. In **1** the Cu···Cu and Cu–N distances average 2.481(8) and 1.976(8) Å and the corresponding distances in **2** are 2.69(3) and 1.936(6) Å. Crystal data: **1**, orthorhombic, space group *Pbca*, a = 29.421(8), b = 18.630(4), c = 29.971(8) Å, Z = 8, R = 0.069 for 4239 [$I > 3\sigma(I)$] data; **2**, triclinic, space group $P\bar{1}$, a = 15.365(3), b = 15.420(3), c = 17.797(3) Å, α = 67.58(1), β = 64.28(1), γ = 66.95(1)°, Z = 2, R = 0.050 for 10 999 [$I > 2\sigma(I)$] data.

The use of $N(SiMe_3)_2$ [1,2] and the closely related $NBu^t(SiMe_3)$ [2] ligand has played a pivotal role in the synthesis and characterization of compounds with low co-ordination numbers throughout the Periodic Table.[3,4] These ligands have proved particularly useful in the stabilization of the co-ordination number three.[5] It is clear, however, that even these very crowding ligands have steric limits since most of their bivalent metal derivatives are co-ordinatively unsaturated and readily form donor–acceptor complexes with a variety of molecules. Well known examples are the transition-metal derivatives $M[N(SiMe_3)_2]_2$ (M = Mn,[1] Fe[6] or Co[1]) which, although monomeric in the vapour,[6] dimerize with amide bridging in the solid[7–9] and form strong complexes with relatively weak donor ligands as in the species $M[N(SiMe_3)_2]_2(thf)$ (M = Mn[5] or Fe,[9] thf = tetrahydrofuran). Recent work in this laboratory has shown that this type of complexation can be prevented by using more crowding ligands such as $N(SiMePh_2)_2$ [10,11] or $N(SiMe_2Ph)_2$.[11] Moreover, these bulkier ligands permit the isolation of several unassociated, two-co-ordinate crystalline transition-metal compounds.[12] In this paper, the extension of the use of these ligands to isolate new amide derivatives of copper is reported.

Experimental

General Procedures and Techniques.—All reactions were performed by using modified Schlenk techniques under an inert atmosphere of N_2 or a Vacuum Atmospheres HE43-2 dry-box. Solvents were freshly distilled under N_2 from Na/K alloy or sodium/potassium diphenylketyl and degassed twice before use. The compounds $NH(SiMe_2Ph)_2$ [13] and $NH(SiMePh_2)_2$ [14] were synthesised as previously described. Anhydrous CuBr and $LiBu^n$ (1.6 mol dm^{-3} in hexane) were purchased from commercial suppliers and used as received. Proton NMR spectra were recorded in C_6D_6 solution by using a General Electric QE-300 spectrometer, IR spectra (Nujol mull, CsI plates) in the range 4000–200 cm^{-1} with a Perkin-Elmer 1420 spectrometer.

Preparation of Compounds.—$\{Cu[N(SiMePh_2)_2]\}_3$ **1**. Copper(I) bromide (0.574 g, 4 mmol) was suspended in diethyl ether (10 cm^3) and cooled in an ice-bath. A solution of $Li[N(SiMePh_2)_2]$ in diethyl ether (30 cm^3), derived from $NH(SiMePh_2)_2$ (1.639 g, 4 mmol) and a 1.6 mol dm^{-3} $LiBu^n$ hexane solution (2.5 cm^3), was added dropwise. The resultant pale amber solution was stirred for 1 h whereupon the ice-bath was removed. The solution was then stirred for 2 h at ambient temperature. The volatile materials were removed under reduced pressure and the residue was extracted with toluene (15 cm^3). Filtration of the extract gave a clear pale amber solution. This was pumped down to *ca.* 5 cm^3 and hexane ($\approx$ 5–6 cm^3) added slowly. Cooling in a freezer at −20 °C for 36 h gave the product as colourless crystals which were isolated and dried by pumping at 0.02 mmHg (*ca.* 2.66 Pa) for 5 min, yield 3.51 g (57%), m.p. 151–153 °C (Found: C, 68.2; H, 5.2; N, 2.8. Calc.: C, 68.9; H, 5.1; N, 2.7%). ^{1}H NMR: δ 0.72 (s, 9 H, 3 Me), 7.04 (m, 36 H, *o*- and *p*-H) and 7.8 (m, 24 H, *m*-H). IR: ν(Cu–N) 308 cm^{-1}.

$\{Cu[N(SiMe_2Ph)_2]\}_4$ **2**. The compound $NH(SiMe_2Ph)_2$ (1.15 g, 4 mmol) in diethyl ether (30 cm^3), cooled in an ice-bath, was treated dropwise with $LiBu^n$ (2.5 cm^3 of a 1.6 mol dm^{-3} solution in hexane). Copper(I) bromide (0.574 g, 4 mmol) was then added through a solid addition funnel. Stirring for 1 h afforded a pale brown solution that was allowed to come to room temperature whereupon stirring was continued for 2 h. Removal of the volatile components under reduced pressure, followed by extraction of the residue with hexane (25 cm^3), gave, upon filtration, a pale amber solution. Reduction of the volume to *ca.* 8–9 cm^3 and cooling in a freezer at −20 °C for 2 d afforded the product as colourless crystals, yield 0.56 g (40%), m.p. 177–181 °C (Found: C, 55.3; H, 6.4; N, 4.00. Calc.: C, 55.2; H, 6.35; N, 4.00%). ^{1}H NMR: δ 0.79 (s, 24 H, 8 Me), 7.1 (m, 12 H, *o*- and *p*-H) and 7.9 (m, 8 H, *m*-H). IR: ν(Cu–N) 312 cm^{-1}.

Crystallographic Studies.—X-Ray data for compounds **1** and **2** were collected at 130 K with either a Siemens P4/RA (**1**) or a Siemens R3m/v (**2**) diffractometer equipped with locally modified LT-2 (**1**) or Enraf–Nonius (**2**) low-temperature devices. Crystals of the compounds were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fibre on a mounting pin and immediately placed in the low-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

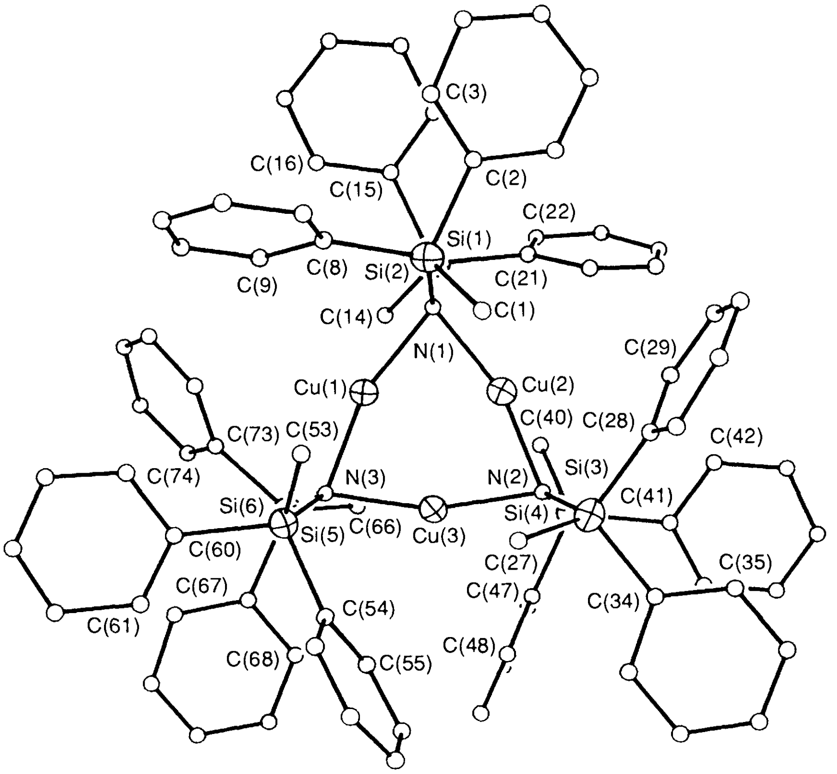

Fig. 1 Thermal ellipsoidal drawing of compound **1**

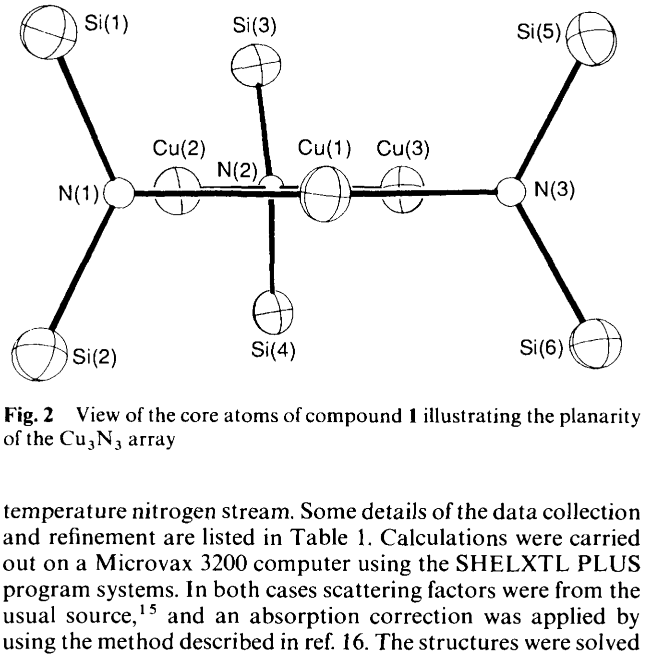

Fig. 2 View of the core atoms of compound **1** illustrating the planarity of the Cu_3N_3 array

temperature nitrogen stream. Some details of the data collection and refinement are listed in Table 1. Calculations were carried out on a Microvax 3200 computer using the SHELXTL PLUS program systems. In both cases scattering factors were from the usual source,[15] and an absorption correction was applied by using the method described in ref. 16. The structures were solved by direct methods and refined by blocked-diagonal least-squares refinement. The H atoms were included by use of a riding model with C–H distances of 0.96 Å and isotropic thermal parameters equal to 1.2 times that of the bonded carbon. The C and N atoms in **1** were refined isotropically, and phenyl rings were refined as rigid hexagons. A weighting scheme of the type $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ [g = 0.0036(**1**) or 0.0203(**2**)] was applied.

Atom coordinates are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis.—The novel copper(I) silyl amides **1** and **2** were synthesised in moderate yield by the reaction of copper(I) bromide and 1 equivalent of the appropriate lithium silylamide in diethyl ether as in equation (1). Although copper(I) amides

$$CuBr + LiNR_2 \xrightarrow{Et_2O} \frac{1}{n}[Cu(NR_2)]_n + LiBr \quad (1)$$
$$n = 3 \text{ or } 4$$

have been known for a long time,[17] the first detailed structural characterization of such a species {involving $[Cu(NEt_2)_4]$} did not appear until 1984.[18] Most of the well characterized copper(I) amides including $\{Cu[N(SiMe_3)_2]\}_4$,[1,*] $Cu[\overline{N(CH_2)_4C}H_2]$,[19] $Cu[\overline{NCH_2CH_2OCH_2C}H_2]$, $[Cu(NEt_2)]_4$,[18] and $[Cu(NRR')]_4$[20] {NRR′ = NMe_2, $\overline{N(CH_2)_3C}H_2$, $NMe(CH_2)_2NMe_2$ or $N[(CH_2)_2NEt_2]_2$} have been synthesised by the transmetallation route described above. However, some copper amides have been synthesised by transamination or by the reaction of amines with organocopper compounds.[21,22]

Structural Descriptions.—$\{Cu[N(SiMePh_2)_2]\}_3$ **1**. The structure of compound **1** is illustrated in Fig. 1 and another perspective of the important core atoms is shown in Fig. 2. Important distances and angles for the molecule are given in Table 3. The structure is composed of well separated non-interacting trimers of formula $\{Cu[N(SiMePh_2)_2]\}_3$. In addition, 1.5 molecules of toluene per trimer are included. Although there are no symmetry restrictions, the molecule comes close to possessing a three-fold axis of symmetry that is perpendicular to the plane defined by the three coppers. The coppers are bridged by amide groups with an average Cu–N bond length of 1.976(8) Å. The metals are separated by an average distance of 2.481(8) Å. The nitrogens of the bridging

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* The structure was cited (work of M. B. Hursthouse) as a planar tetramer on p. 493 of ref. 4. No other details were provided.

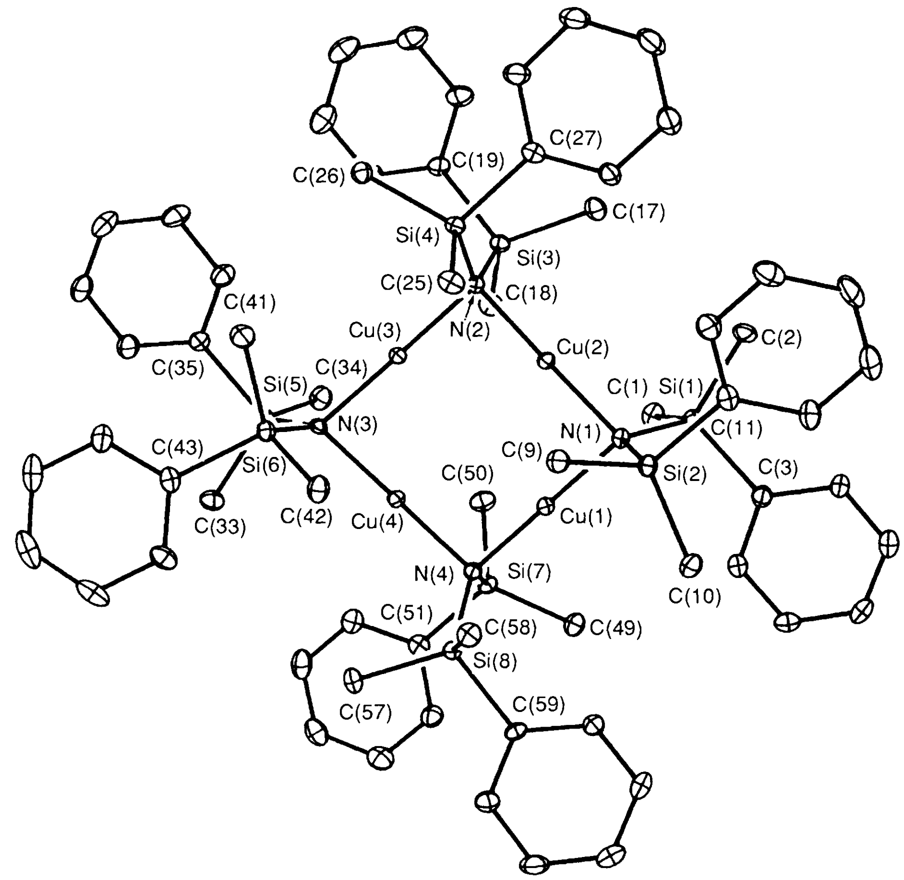

Fig. 3 Thermal ellipsoidal drawing of compound **2**

Table 1 Summary of crystal data collection parameters and structure refinement for compounds **1** and **2**

	1	**2**
Empirical formula	$C_{88.5}H_{78}Cu_3N_3Si_6$	$C_{64}H_{88}Cu_4N_4Si_8$
Crystal system	Orthorhombic	Triclinic
Colour, habit	Colourless, parallelepipeds	Colourless, parallelepipeds
Space group	*Pbca*	$P\bar{1}$
M	1542.7	1392.3
a/Å	29.421(8)	15.365(3)
b/Å	18.630(4)	15.420(3)
c/Å	29.971(8)	17.797(3)
α/	—	67.58(1)
β/	—	64.28(1)
γ/	—	66.95(1)
U/Å^3	16 379(7)	3380(1)
Z	8	2
D_c/g cm^{-3}	1.251	1.37
Crystal dimensions/mm	0.04 × 0.2 × 0.4	0.52 × 0.71 × 0.86
Radiation	Cu-Kα (λ = 1.541 78 Å)	Mo-Kα (λ = 0.710 69 Å)
2θ range/	0–108.5	0–55
μ/cm^{-1}	2.08	1.43
F(000)	6408	1468
Unique observed data	4239 [$I > 3\sigma(I)$]	10 999 [$I > 2\sigma(I)$]
No. of parameters	438	721
R	0.069	0.050
R'	0.081	0.056
Maximum electron density in difference map/e Å^{-3}	1.09	0.94

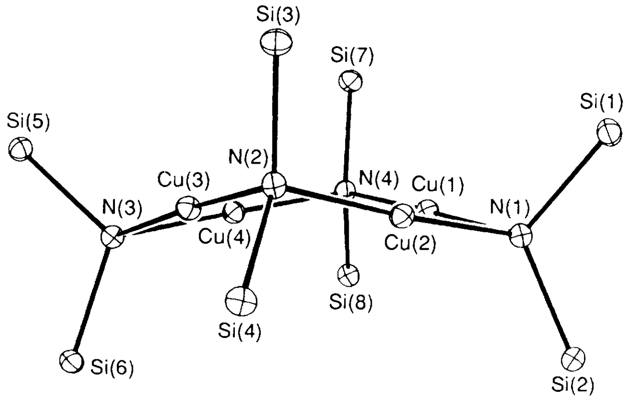

Fig. 4 View of the core atoms of compound **2** illustrating the butterfly structure of the Cu_4N_4 core

amide ligands have almost negligible displacements [+0.018, +0.009 and +0.009 Å for N(1), N(2) and N(3)] from the copper plane. The Cu_3N_3 core may be viewed as a highly distorted, planar hexagon that possesses average internal angles of 162.2(2)° at the coppers and angles averaging 77.8(7)° at the nitrogens. Alternatively, it could be considered an equilateral triangle with nitrogen apices and the copper atoms at the midpoint in each side accounting for the slight outward deviation from strict linearity. The planes defined by the NSi_2 atoms subtend angles of 87.8 [N(1)], 86.5 [N(2)] and 87.9° [N(3)] with respect to the Cu_3N_3 core. The average N–Si distance is 1.754(9) Å and the Si–N–Si angles average 124.2(14)°.

$\{Cu[N(SiMe_2Ph)_2]\}_4$ **2**. The structure of compound **2** is illustrated in Fig. 3 and the core atoms are shown in Fig. 4. Important bond distances and angles are provided in Table 3. The compound crystallizes as tetramers of formula $\{Cu[N(SiMe_2Ph)_2]\}_4$ in the space group $P\bar{1}$, with $Z = 2$. Thus there is no imposed crystallographic symmetry. The four metal atoms display only slight deviation [+0.031 Å for Cu(2) and Cu(4),

Table 2 Atomic coordinates (× 10^4) for compounds **1** and **2**

Atom	*x*	*y*	*z*
Compound **1**			
Cu(1)	2 102(1)	5 833(1)	4 263(1)
Cu(2)	2 849(1)	5 874(1)	3 885(1)
Cu(3)	2 808(1)	5 829(1)	4 715(1)
Si(1)	2 076(1)	6 718(2)	3 405(1)
Si(2)	2 121(1)	5 072(2)	3 336(1)
Si(3)	3 621(1)	6 699(2)	4 336(1)
Si(4)	3 618(1)	5 018(2)	4 363(1)
Si(5)	2 039(1)	6 623(2)	5 173(1)
Si(6)	2 014(1)	4 966(2)	5 136(1)
N(1)	2 237(3)	5 881(5)	3 614(3)
N(2)	3 351(3)	5 870(5)	4 326(3)
N(3)	2 177(3)	5 805(5)	4 918(3)
C(1)	2 493(4)	7 415(7)	3 569(4)
C(2)	2 050(4)	6 772(7)	2 777(4)
C(3)	1 649(5)	6 804(7)	2 545(5)
C(4)	1 624(5)	6 926(8)	2 089(5)
C(5)	2 016(5)	6 997(8)	1 864(5)
C(6)	2 431(5)	6 976(8)	2 063(5)
C(7)	2 451(5)	6 869(8)	2 520(5)
C(8)	1 498(4)	6 997(7)	3 602(5)
C(9)	1 194(4)	6 532(8)	3 840(4)
C(10)	772(5)	6 787(9)	3 995(5)
C(11)	651(5)	7 473(9)	3 927(5)
C(12)	936(6)	7 932(9)	3 707(5)
C(13)	1 349(5)	7 698(8)	3 551(5)
C(14)	1 985(4)	4 346(7)	3 736(4)
C(15)	1 611(4)	5 082(7)	2 945(5)
C(16)	1 167(4)	5 109(7)	3 101(5)
C(17)	798(5)	5 078(8)	2 824(5)
C(18)	878(6)	4 998(9)	2 374(6)
C(19)	1 293(5)	4 973(8)	2 193(6)
C(20)	1 672(6)	5 029(8)	2 479(6)
C(21)	2 628(4)	4 768(6)	2 999(4)
C(22)	2 638(5)	4 068(8)	2 833(4)
C(23)	3 016(5)	3 797(8)	2 594(5)
C(24)	3 392(5)	4 215(8)	2 553(5)
C(25)	3 387(5)	4 903(8)	2 710(5)
C(26)	3 008(4)	5 177(7)	2 929(4)
C(27)	3 283(4)	7 369(7)	4 652(4)
C(28)	3 691(4)	7 045(7)	3 749(4)
C(29)	3 672(4)	6 604(8)	3 376(4)
C(30)	3 719(5)	6 887(9)	2 953(6)
C(31)	3 766(5)	7 610(9)	2 878(6)
C(32)	3 771(6)	8 042(11)	3 245(6)
C(33)	3 757(5)	7 779(9)	3 683(5)
C(34)	4 190(4)	6 691(7)	4 601(4)
C(35)	4 589(5)	6 680(7)	4 346(5)
C(36)	5 028(5)	6 709(8)	4 536(5)
C(37)	5 068(6)	6 733(8)	4 990(6)
C(38)	4 684(5)	6 761(8)	5 260(5)
C(39)	4 248(5)	6 756(7)	5 063(5)
C(40)	3 277(4)	4 334(7)	4 044(4)
C(41)	4 210(4)	4 995(7)	4 137(4)
C(42)	4 283(4)	5 002(7)	3 670(4)
C(43)	4 718(5)	4 952(7)	3 494(5)
C(44)	5 093(5)	4 898(8)	3 783(5)
C(45)	5 027(5)	4 887(7)	4 227(5)
C(46)	4 592(4)	4 937(7)	4 404(5)
C(47)	3 662(4)	4 707(7)	4 954(4)
C(48)	3 664(4)	5 156(7)	5 337(4)
C(49)	3 703(4)	4 894(7)	5 760(5)
C(50)	3 753(4)	4 170(7)	5 829(4)
C(51)	3 768(4)	3 685(8)	5 476(4)
C(52)	3 718(4)	3 956(7)	5 041(4)
C(53)	1 952(4)	7 333(6)	4 753(4)
C(54)	2 513(4)	6 935(7)	5 550(4)
C(55)	2 865(4)	6 493(8)	5 713(4)
C(56)	3 219(5)	6 788(7)	5 958(4)
C(57)	3 232(5)	7 477(8)	6 079(5)
C(58)	2 875(4)	7 919(7)	5 939(4)
C(59)	2 527(5)	7 655(7)	5 688(4)
C(60)	1 503(5)	6 608(7)	5 520(5)
C(61)	1 515(5)	6 632(8)	5 971(5)
C(62)	1 101(6)	6 701(9)	6 228(6)
C(63)	710(7)	6 713(10)	5 992(6)
C(64)	679(7)	6 693(10)	5 537(7)
C(65)	1 082(5)	6 656(9)	5 308(6)
C(66)	2 399(4)	4 237(7)	4 928(4)
C(67)	2 054(4)	4 920(7)	5 762(4)
C(68)	2 484(4)	4 800(7)	5 950(4)
C(69)	2 530(5)	4 715(8)	6 411(5)
C(70)	2 166(5)	4 751(7)	6 687(5)
C(71)	1 755(5)	4 845(7)	6 508(5)
C(72)	1 687(4)	4 919(7)	6 048(4)
C(73)	1 412(4)	4 712(7)	4 976(4)
C(74)	1 247(5)	4 046(8)	5 109(5)
C(75)	814(5)	3 821(9)	4 967(5)
C(76)	567(6)	4 229(9)	4 669(6)
C(77)	718(6)	4 878(9)	4 535(6)
C(78)	1 135(5)	5 105(8)	4 687(5)
C(79)	5 201(7)	7 292(8)	2 821(7)
C(80)	4 941	7 751	3 086
C(81)	4 925	8 483	2 990
C(82)	5 169	8 756	2 629
C(83)	5 430	8 298	2 364
C(84)	5 446	7 565	2 460
C(85)	5 181(12)	6 684(19)	3 035(11)
C(86)	4 453(9)	6 923(10)	1 578(10)
C(87)	4 470	6 569	1 168
C(88)	4 522	5 825	1 154
C(89)	4 556	5 435	1 550
C(90)	4 539	5 789	1 960
C(91)	4 487	6 533	1 974
C(92)	4 446(8)	7 653(13)	1 589(9)
Compound **2**			
Cu(1)	1 416(1)	8 610(1)	2 573(1)
Cu(2)	491(7)	7 557(1)	2 432(1)
Cu(3)	2 178(1)	6 052(1)	2 288(1)
Cu(4)	3 070(1)	7 053(1)	2 506(1)
N(1)	35(3)	8 786(2)	2 730(2)
N(2)	952(2)	6 378(2)	2 060(2)
N(3)	3 365(2)	5 682(2)	2 587(2)
N(4)	2 780(2)	8 424(2)	2 442(2)
Si(1)	−378(1)	9 691(1)	1 893(1)
Si(2)	−722(1)	8 832(1)	3 805(1)
Si(3)	1 062(1)	6 634(1)	970(1)
Si(4)	293(1)	5 513(1)	2 827(1)
Si(5)	4 502(1)	5 276(1)	1 779(1)
Si(6)	3 206(1)	4 903(1)	3 646(1)
Si(7)	3 425(1)	9 074(1)	1 408(1)
Si(8)	2 934(1)	8 479(1)	3 347(1)
C(1)	651(3)	9 671(3)	832(3)
C(2)	−1 502(3)	9 562(3)	1 826(3)
C(3)	−684(3)	10 949(3)	2 007(3)
C(4)	−1 600(4)	11 649(3)	2 001(3)
C(5)	−1 752(4)	12 595(4)	2 013(4)
C(6)	−1 017(4)	12 857(4)	2 040(4)
C(7)	−125(4)	12 194(4)	2 050(4)
C(8)	43(3)	11 248(3)	2 037(3)
C(9)	−295(3)	7 657(3)	4 561(3)
C(10)	−707(3)	9 853(3)	4 115(3)
C(11)	−2 074(3)	9 020(3)	3 981(3)
C(12)	−2 452(3)	8 241(3)	4 188(3)
C(13)	−3 446(4)	8 362(4)	4 318(3)
C(14)	−4 091(4)	9 279(4)	4 222(4)
C(15)	−3 748(4)	10 072(4)	4 019(4)
C(16)	−2 759(3)	9 945(4)	3 909(3)
C(17)	−116(3)	7 442(3)	731(3)
C(18)	2 071(3)	7 244(3)	231(3)

Table 2 (*continued*)

Atom	*x*	*y*	*z*
C(19)	1 368(3)	5 466(3)	692(3)
C(20)	613(4)	5 150(4)	720(3)
C(21)	815(5)	4 245(4)	598(3)
C(22)	1 764(5)	3 633(4)	441(3)
C(23)	2 538(4)	3 936(4)	378(3)
C(24)	2 343(4)	4 850(3)	493(3)
C(25)	23(3)	5 571(3)	3 935(3)
C(26)	973(3)	4 223(3)	2 755(3)
C(27)	−989(3)	5 779(3)	2 779(3)
C(28)	−1 709(3)	6 650(3)	2 892(1)
C(29)	−2 698(4	6 815(4)	2 962(3)
C(30)	−2 977(4)	6 105(4)	2 905(4)
C(31)	−2 280(4)	5 234(4)	2 786(4)
C(32)	−1 301(4)	5 069(4)	2 732(3)
C(33)	5 641(3)	5 308(3)	1 896(3)
C(34)	4 489(4)	6 014(3)	679(3)
C(35)	4 668(3)	3 994(3)	1 776(3)
C(36)	5 578(4)	3 283(3)	1 712(3)
C(37)	5 693(4)	2 356(4)	1 671(4)
C(38)	4 917(4)	2 131(4)	1 695(3)
C(39)	4 004(4)	2 819(3)	1 751(3)
C(40)	3 894(4)	3 748(3)	1 785(3)
C(41)	2 614(4)	3 937(3)	3 881(3)
C(42)	2 427(3)	5 593(3)	4 483(3)
C(43)	4 433(3)	4 234(3)	3 853(3)
C(44)	4 931(3)	3 273(3)	3 792(3)
C(45)	5 841(4)	2 790(4)	3 917(4)
C(46)	6 283(4)	3 243(5)	4 122(3)
C(47)	5 809(4)	4 185(5)	4 218(3)
C(48)	4 885(3)	4 673(4)	4 081(3)
C(49)	2 887(3)	10 422(3)	1 143(3)
C(50)	3 445(4)	8 652(3)	542(3)
C(51)	4 755(3)	8 858(3)	1 316(3)
C(52)	5 480(3)	7 997(3)	1 161(3)
C(53)	6 452(4)	7 798(4)	1 130(3)
C(54)	6 725(4)	8 481(4)	1 248(3)
C(55)	6 021(4)	9 338(4)	1 415(3)
C(56)	5 053(3)	9 532(3)	1 440(3)
C(57)	4 173(3)	7 670(3)	3 456(3)
C(58)	1 911(3)	8 138(3)	4 369(3)
C(58)	2 815(3)	9 747(3)	3 338(3)
C(60)	3 496(4)	9 935(3)	3 531(3)
C(61)	3 322(4)	10 835(4)	3 661(3)
C(62)	2 462(4)	11 558(4)	3 591(3)
C(63)	1 776(6)	11 400(3)	3 391(3)
C(64)	1 953(3)	10 500(3)	3 273(3)

Table 3 Important distances (Å) and angles (°) in compounds **1** and **2**

Compound **1**		Compound **2**	
Cu(1)–N(1)	1.987(10)	Cu(1)–N(1)	1.936(4)
Cu(1)–N(3)	1.979(9)	Cu(1)–N(4)	1.920(4)
Cu(2)–N(1)	1.975(9)	Cu(2)–N(1)	1.941(4)
Cu(2)–N(2)	1.982(9)	Cu(2)–N(2)	1.935(4)
Cu(3)–N(2)	1.980(9)	Cu(3)–N(3)	1.932(4)
Cu(3)–N(3)	1.954(9)	Cu(3)–N(3)	1.931(4)
av. Cu–N	1.976(8)	Cu(4)–N(3)	1.941(4)
		Cu(4)–N(4)	1.951(4)
		av. Cu–N	1.936(6)
N(1)–Cu(1)–N(3)	162.0(4)	N(1)–Cu(1)–N(4)	178.9(1)
N(1)–Cu(2)–N(3)	162.5(4)	N(1)–Cu(2)–N(2)	176.4(1)
N(2)–Cu(3)–N(3)	162.1(4)	N(2)–Cu(3)–N(3)	176.4(1)
av. N–Cu–N	162.2(2)	N(3)–Cu(4)–N(4)	179.0(2)
		av. N–Cu–N	177.7(13)
Cu(1)–N(1)–Cu(2)	77.3(3)	Cu(1)–N(1)–Cu(2)	87.2(1)
Cu(2)–N(2)–Cu(3)	77.9(3)	Cu(2)–N(2)–Cu(3)	88.9(2)
Cu(1)–N(3)–Cu(3)	78.2(3)	Cu(3)–N(3)–Cu(4)	86.1(1)
av. Cu–N–Cu	77.8(7)	Cu(1)–N(4)–Cu(4)	89.4(2)
		av. Cu–N–Cu	87.9(13)
Cu(1) ··· Cu(2)	2.473(2)	Cu(1) ··· Cu(2)	2.674(1)
Cu(1) ··· Cu(3)	2.480(2)	Cu(1) ··· Cu(4)	2.724(1)
Cu(2) ··· Cu(3)	2.491(2)	Cu(2) ··· Cu(3)	2.709(1)
av. Cu ··· Cu	2.481(8)	Cu(3) ··· Cu(4)	2.642(1)
		av. Cu ··· Cu	2.687(29)
N(1)–Si(1)	1.746(11)	N(1)–Si(1)	1.764(3)
N(1)–Si(2)	1.755(11)	N(1)–Si(2)	1.768(3)
N(2)–Si(3)	1.736(10)	N(2)–Si(3)	1.769(4)
N(2)–Si(4)	1.774(10)	N(2)–Si(4)	1.772(3)
N(3)–Si(4)	1.753(10)	N(3)–Si(5)	1.779(3)
N(3)–Si(6)	1.759(10)	N(3)–Si(6)	1.777(3)
av M–Si	1.754(9)	N(4)–Si(7)	1.778(3)
		N(4)–Si(8)	1.763(5)
		av. N–Si	1.771(7)
S(1)–N(1)–Si(1)	122.9(6)	Si(1)–N(1)–Si(2)	118.0(2)
Si(3)–N(2)–Si(4)	126.3(5)	Si(3)–N(2)–Si(4)	117.4(2)
Si(5)–N(3)–Si(6)	123.3(5)	Si(5)–N(3)–Si(6)	115.4(2)
av. Si–N–Si	124.2(14)	Si(7)–N(4)–Si(8)	117.8(3)
		av. Si–N–Si	117.2(9)

−0.030 Å for Cu(1) and Cu(3)] from a calculated least-squares plane. The nitrogens from the four bridging amide groups, however, display much greater deviation [+0.32 Å for N(1) and N(3), −0.32 Å for N(2) and N(4)] from the copper plane. In effect the four nitrogen atoms of the Cu_4N_4 array describe a butterfly shape (fold angle 153.8°), which is seen to best advantage in Fig. 4. The co-ordination at the metals is almost linear with an average internal angle at copper of 177.7(13)°. The corresponding average angle at nitrogen is 87.9(13)°. The average Cu–N distance is 1.936(6) Å and the coppers are separated by a mean distance of 2.687(29) Å. The average N–Si bond length and Si–N–Si angle are 1.771(7) Å and 117.2(9)°. The planes defined by the NSi_2 atoms subtend angles to the corresponding NCu_2 planes of 84.7, 86.4, 87.2 and 87.6° at N(1), N(2), N(3) and N(4).

The different degrees of aggregation seen in compounds **1** and **2** are, most probably, a consequence of the different sizes of the amide ligands. The structure of **2** confirms that the tetrameric structure, featuring almost linearly co-ordinated coppers, is clearly preferred for copper(I) amides. This is true for the fairly broad range of substituent sizes encompassed by the sterically disparate ligands NMe_2 and $N(SiMe_2Ph)_2$. The butterfly-shaped Cu_4N_4 arrangement in **2** is quite similar to the Cu_4N_4 array in the original copper amide structure $[Cu(NEt_2)]_4$.[18] However, the average Cu–N distances in **2** are somewhat longer (≈0.03 Å) than those observed in the latter[18] and in the compounds $[Cu(NRR')]_4$ [NRR′ = NMe_2, $\overline{N(CH_2)_3C}H_2$, or $NMe(CH_2)_2NMe_2$] which have Cu–N distances in the range 1.885(4)–1.913(4) Å.[20] It is interesting that the structures of the compounds $[Cu(NMe_2)]_4$ and $\{Cu[\overline{N(CH_2)_3C}H_2]\}_4$[20] (and apparently $\{Cu[N(SiMe_3)_2]\}_4$) have planar (rather than butterfly) Cu_4N_4 arrays. The main effect of this structural difference is that the Cu ··· Cu distances in the molecules with planar Cu_4N_4 cores are longer, 2.702(2)–2.742(2),[20] than those in the butterfly species, 2.611(2)–2.724(1) Å.[18,20] These Cu ··· Cu separations are considerably longer than those observed (≈2.4 Å) in the corresponding tetrameric copper alkyls[23] and aryls,[24,25] and marginally shorter than those in tetrameric copper alkoxides.[26] Attention has already been drawn to the large effects of different bridging groups on the Cu ··· Cu separation.[18] The reasons for these differences are complex. In the structures of heavier main-group element derivatives such as $[Cu(PBu^t_2)]_4$,[27] $[Cu(SR)]_4$ [R = $C_6H_3(SiMe_3)_2$-2,6[28] or $Si(OBu^t)_3$[29]] or $[Cu(SBu^t)]_4(PPh_3)_2$[30] much longer Cu ··· Cu interactions are seen, for example, *ca.* 3.16 Å in $[Cu(PBu^t_2)]_4$[27] and *ca.* 2.85 Å in $\{Cu[SSi(OBu^t)_3]\}_4$.[29] In addition, calculations have shown that weak attractive forces can exist between d^{10} systems.[31–33] This seems to be the case in the structure of $[Cu(CH_2SiMe_3)]_4$[23] where the copper atoms are 'pinched in' so that the internal ring angles at the metals are greater than 180°. In the closely related amide and alkoxide derivatives it appears that the aggregates are held together by ligand donor interactions.[18,20,26] Both of these ligands have two or more lone pairs which may behave as the donors. Moreover, the lone pairs are in orbitals that are separated by an approximately tetrahedral angle. Thus, a bridging angle that is close to this value is preferred for these ligands. In contrast, a bridging alkyl ligand with a single bridging donor orbital is relatively free of these angular restrictions. A narrower angle Cu–C–Cu is permitted at the bridging carbon and the coppers are able to approach each other much more closely than in the amide and alkoxide complexes.

In compound **1** the replacement of a methyl group on each silicon by a phenyl substituent affords a reduction in the aggregation number of the $CuNR_2$ units from four to three. The extremely crowded nature of this molecule is apparent from Fig. 1. A triangular arrangement of this type for three coppers is extremely rare. Previously reported examples include chelating ligands as exemplified by compounds $(Cu\{SC_6H_4\text{-}[CH(Me)NMe_2]\text{-}o\})_3$[34] and $[Cu_3(C_6H_2Me_3\text{-}2,4,6)(\mu\text{-}O_2CPh)_2]$.[35] Thus, the trimeric structure of **1** is unique in the sense that the degree of aggregation is determined by steric factors alone. As can be seen in Fig. 1, a large portion of the space surrounding the Cu_3 triangle is occupied by the twelve outwardly directed Ph groups. The less sterically demanding Me groups are directed toward the core of the molecule. A similar orientation of Me and Ph groups is seen in **2**. The $N(SiMePh_2)_2$ ligand was introduced some years ago[10] in order to stabilize crystalline two-co-ordinate transiton-metal compounds. The structure of **1**, however, shows that even this very large group is capable of bridging behaviour under suitable conditions.

Although the Cu_3N_3 core in compound **1** was described above as a very distorted planar hexagon, an equally apt description is of an equilateral triangle with nitrogen apices and bent sides arising from distortions from strict linearity* in the copper co-ordination. These distortions are quite significant as indicated by an average internal angle of 162.2(2)° at the coppers. This deviation from strict linear co-ordination at the metal is probably a result of the ring strain in the molecule. The three-fold aggregation which imposes the equilateral triangle structure implies 60° internal angles at the nitrogens if linearity is to be preserved at the coppers. The 60° internal angle is at great variance with the previously mentioned, approximately tetrahedral, disposition of the lone pairs of the nitrogens. Thus, the structure of **1** may be described as a compromise between the conflicting tendencies toward linearity at copper and a wider angle at nitrogen.

Further evidence of the crowding and the resultant steric strain in compound **1** is to be seen in the rather long Cu–N bonds of 1.976(8) Å which are the longest Cu–N amide bonds reported to date. In contrast, the intermetallic distances are considerably shorter (by ≈0.2 Å) than those observed in the tetrameric analogues. These separations are very similar to those observed in the copper alkyls[23] and aryls.[24,25] The reduced separation between the coppers is a consequence of the lower aggregation and the more acute angles at the bridging nitrogens. A comparison of the IR spectra of the ligands $NH(SiMePh_2)_2$ and $NH(SiMe_2Ph)_2$ with those of **1** and **2** leads to assignment of the medium-intensity band near 310 cm^{-1} to the Cu–N stretching frequency. This appears to be reasonable in comparison with the IR spectra of other first-row transition-metal amides which generally have M–N stretching frequencies in the region of 300–400 cm^{-1}.[6] The bridged nature of **1** and **2** implies a lower frequency for the M–N stretch in these cases.

In summary, the synthesis and structures of two new copper amides have been described. Moreover, the effectiveness of the $N(SiMePh_2)_2$ group in stabilizing hitherto unknown types of compound such as **1** has been demonstrated. Lower degrees of aggregation than three might be expected with larger amide substituents. In view of the constraints imposed by the tendency of copper to preserve approximately linear co-ordination, a dimeric aggregate with equivalent copper atoms is strongly disfavoured since this would impose a very low (ideally 0°) angle for Cu–N–Cu. Instead, a monomeric structure similar to that observed for the unique species $Cu(C_6H_2Ph_3\text{-}2,4,6)$ might be expected.[37] Attempts to synthesise such a species by using the ligand $N(SiPh_3)_2$ have not been successful to date.

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* Linear or near-linear co-ordination is commonly observed in two-co-ordinate copper(I) compounds. However, large distortions from linearity may be observed if weakly co-ordinating ligands, such as ClO_4^-, are included in the co-ordination sphere. See, for example, ref. 36.

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