

Syntheses and structures of lithium cyanocuprates containing the C(SiMe₃)₃, C(SiMe₃)₂(SiMe₂NMe₂) and C(SiMe₃)(SiMe₂OMe)₂ groups

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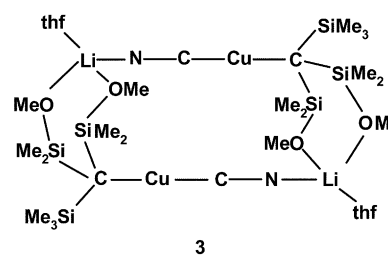
Received 27th June 2002, Accepted 15th August 2002

First published as an Advance Article on the web 2nd October 2002

The 'lower order' lithium cyanocuprates [Li(thf)₂NCCu{C(SiMe₃)₃}]₂ (**1d**), [Li(thf)₂NCCu{C(SiMe₃)₂(SiMe₂NMe₂)}]₂ (**1e**) and [Li(thf)NCCu{C(SiMe₃)(SiMe₂OMe)₂}]₂ (**3**) have been obtained from the reactions between copper(I) cyanide and the corresponding organolithium compounds. The compounds **1d** and **1e** have molecular structures containing four-membered Li₂N₂ rings but in **3** the lithium is coordinated by the methoxy groups of the ligand and almost linear LiNCCu sequences are incorporated into fourteen-membered rings. Attempts to make 'higher order' cyanocuprates containing tri(organosilyl)methyl groups were unsuccessful and no reactions were observed when the cyanocuprate **1d** was treated with alkyl halides or enones.

There is considerable current interest in the structures and reactivity of lithium cyanocuprates.¹⁻⁴ Most of the emphasis has been on the 'higher order' complexes, *i.e.* those with a Li/Cu mole ratio greater than 1;^{4,5} the 'lower order' complexes, with Li/Cu = 1, have been less well studied. They are, however, useful reagents for selective substitutions on haloalkanes⁶ and additions to ynones,⁷ enynes⁸ and enynones.⁹ The lithium *tert*-butyl cyanocuprate is dimeric with structure **1a** in the solid state¹⁰ but monomeric (**2a**) in tetrahydrofuran (thf)¹¹ according to cryoscopic measurements, and the presence of the NCCuR sequence in solutions of the corresponding methyl and ethyl derivatives is confirmed by measurements of ¹³C–¹³C coupling constants.¹² The phenyl compound is dimeric in thf,¹¹ but electrospray mass spectrometry indicates that solutions of substituted lithium ethynyl cyanocuprates contain a mixture of species with various molecular complexities.¹³

silicon affected the aggregation of the corresponding cyanocuprates. We found that compounds **1d** and **1e** have structures like those reported previously, but in the compound [Li(thf)NCCu{C(SiMe₃)(SiMe₂OMe)₂}]₂ (**3**), the oxygen lone pairs in the ligand displace one molecule of thf from the lithium coordination sphere and almost linear LiNCCu sequences are incorporated into fourteen-membered rings.



- 1a** R = Bu^t, L = Et₂O; **1b** R = C(SiMe₂Ph)₃, L = thf **2a** R = Bu^t
1c R = C₆H₃{C₆H₂Prⁱ₃-2,4,6}₂-2,6, L = thf **2b** R = C(SiMe₂Ph)₃
1d R = C(SiMe₃)₃, L = thf
1e R = C(SiMe₃)₂(SiMe₂NMe₂), L = thf

Lower order cyanocuprates are reported to be difficult to crystallise¹ so most of the structural work has been on compounds containing very bulky organic groups, *viz.* **1b**¹⁴ and **1c**.¹⁵ These, like the *tert*-butyl compound **1a**, form lithium-bridged dimers in the solid state but a monomer **2b** has also been isolated.¹⁴ After introduction of the ligands C(SiMe₃)₂(SiMe₂NMe₂)¹⁶ and C(SiMe₃)(SiMe₂OMe)₂,¹⁷ we decided to investigate how the presence of donor groups attached to

Results and discussion

The lower order cyanocuprates **1d**, **1e** and **3** were obtained without difficulty and in reasonable yield by treatment of suspensions of CuCN with stoichiometric quantities of the corresponding organolithium reagents at –78 °C.

The molecular structures of **1d** and **1e** are shown in Figs. 1 and 2 and selected bond lengths and angles in Table 1. In the structure of **1d** there are two independent molecules, one on an inversion centre and the other in a general position. Bond lengths and angles are identical in the two species within the margin of error, so values are given only for the less symmetrical molecule. The configurations of the central Li₂N₂ rings in **1e** and both conformations of **1d** are almost identical; the adjacent Li–N bond lengths are significantly different (by 4–8 standard deviations) and the Li–N–C angles (154.2–166.9°) involving the shorter Li–N bond are much wider than the other Li–N–C angles (109.6–119.1°). This indicates that the dimers are best regarded as pairs of monomers, loosely held together by electrostatic interactions between lithium and nitrogen or by donation of π-electron density from cyanide into the lithium

Table 1 Bond lengths (Å) and angles (°) in [Li(thf)₂NCCu{C(SiMe₂Ph)₃}]₂ (**1b**), [Li(thf)₂NCCu{C(SiMe₃)₃}]₂ (**1d**), [Li(thf)₂NCCu{C(SiMe₃)₂(SiMe₂NMe₂)}]₂ (**1e**) and [Li(thf)NCCu{C(SiMe₂OMe)₂(SiMe₃)}]₂ (**3**)

	1b ^a	1d ^b	1e ^c	3 ^d
Li1–N1	2.059(10)	2.115(17)	2.133(14)	1.995(8) ^f
Li2–N1	2.062(9)	2.054(18)	2.012(12)	—
Li1–N2		2.020(19)	2.032(13)	—
Li2–N2		2.13(2)	2.144(14)	—
Li–O(thf)	1.905(11) ^e	1.885(17) ^e	1.901(14) ^e	1.950(8)
Cu–CN	1.851(4)	1.871(12) ^e	1.856(7) ^e	1.872(5)
Cu–C	1.933(3)	1.936(9) ^e	1.931(6) ^e	1.955(4)
C–N	1.151(5)	1.136(12) ^e	1.143(8) ^e	1.142(5)
Si–C	1.864(4) ^e	1.850(9) ^e	1.853(7) ^e	1.842(3) ^e
Si–Me	1.885(4) ^e	1.879(12) ^e	1.875(8) ^e	1.877(6) ^e
N–Li–N	97.1(4)	96.3(7) ^e	95.8(6) ^e	—
Li–N–Li	82.9(4)	83.4(7) ^e	83.9(5) ^e	—
Li1–N1–C	138.4(5)	109.6(8)	116.0(6)	163.3(4) ^f
Li2–N1–C	136.0(4)	166.9(9)	155.4(7)	—
Li1–N2–C		154.2(10)	155.8(7)	—
Li2–N2–C		117.5(9)	119.1(6)	—
N–Li–O(thf)	110.3(4)–115.2(5)	108.2(8)–115.6(9)	105.1(7)–120.5(7)	111.1(4) ^f
O–Li–O	109.1(5)	110.8(8), 113.5(9)	110.1(6) ^e	101.6(4), 101.9(4), 118.4(4)
N–C–Cu	174.9(4)	174.5(9) ^e	175.2(7) ^e	177.9(4)
C–Cu–C	173.68(16)	171.8(4), 174.3(4)	173.3(3) ^e	179.60(19)
Cu–C–Si	106.83(16)–101.94(17)	100.4(4)–108.5(4)	99.3(3)–110.4(3)	106.0(2), 103.89(19), 102.42(19)
Si–C–Si	114.52(18) ^e	114.1(5) ^e	114.0(3) ^e	112.0(6)–116.1(2) ^e
Me–Si–Me	102.71(17)–106.65(18)	104.9(7) ^e	105.1(4) ^e	102.9(2)–107.5(3)

^a Ref. 14 and unpublished data. ^b Values for the molecule in the general position. For the centrosymmetrical molecule: Li–N3 1.988(17), Li'–N3 2.119(19) Å, Li–N3–C 163.5(9), Li'–N3–C 111.2(8)° [Symmetry transformation': $-x, -y, -z$]. ^c Mean Si–N 1.725(7); mean C–Si–N 113.0(3). ^d Mean Li–OSi 1.940(8); mean Si–O 1.684(3) Å; N–Li–O 118.7(4) and 105.5(4); C–Si–O 102.9(2)–110.23(17); Li–O1–Si1 129.8(3); Li–O2–Si2 117.2(3)°. ^e Mean values, except where a range is given. E.s.d.s for individual measurements are shown in parentheses; no value differs significantly from the mean. ^f N' Symmetry transformation': $-x + 1, y, -z + \frac{1}{2}$.

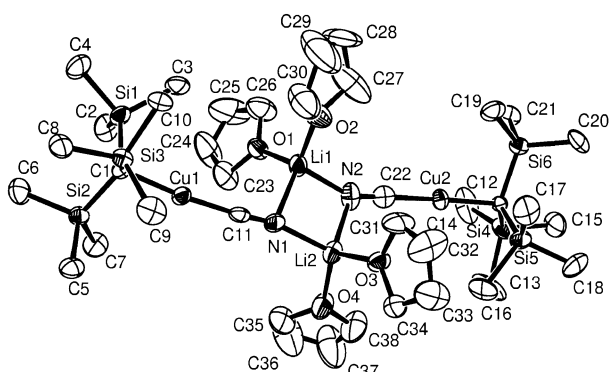


Fig. 1 The structure of one of the molecules in the asymmetric unit of [Li(thf)₂NCCu{C(SiMe₃)₃}]₂ **1d**.

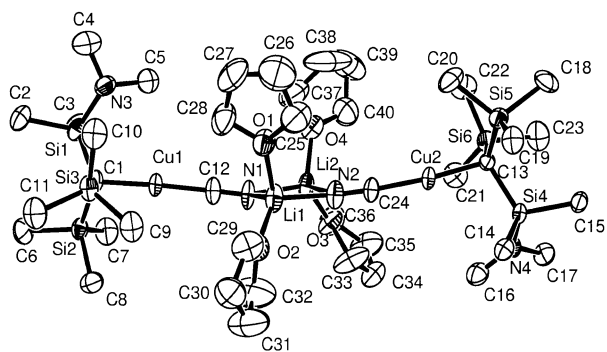


Fig. 2 The molecular structure of [Li(thf)₂NCCu{C(SiMe₃)₂(SiMe₂NMe₂)}]₂ **1e**.

coordination sphere. In contrast, there are no significant differences between Li–N bond lengths or Li–N–C angles (Table 1) in each of the previously determined structures of **1b** and **1c**, so that in these compounds the CN bridges between the pairs of lithium atoms are almost symmetrical.

In all compounds the CCuCN...NCCuC sequences form slightly curved s-shaped skeletons. The N–Li–N angles are wider than the Li–N–Li angles, reflecting the lower inner shell repulsions between lithium than between nitrogen. The Cu–CN [1.851(4)–1.871(12) Å] distances in **1b**, **1d** and **1e** are similar to those in **1a** [1.878(8) Å], **1c** [1.858(5) Å], and the bicyclic guanidine complex [Cu(hppH)CN]_∞ [1.876(5) Å]¹⁸ (hppH = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine). All are shorter than the Cu–alkyl distances [1.931(6)–1.969(7) Å], which are similar to those in the dimeric alkylcopper derivative [CuC(SiMe₃)₂(SiMe₂C₅H₄N-2)]₂ [1.945(12) Å]¹⁹ and to the average of 1.95 Å for two-coordinate copper complexes given in a 1987 survey.²⁰ The Cu–aryl distance in **1c** [1.906(4) Å] is, as expected, shorter.¹⁵ The difference between the Cu–alkyl and Cu–CN distances (0.075–0.083 Å) shown in cyanocuprates is about that expected (0.08 Å) from the difference between the radii of sp³- and sp-hybridised carbon.²¹

Replacement of one methyl group in **1d** by NMe₂ causes essentially no change in molecular structure. The lone pairs on nitrogen are insufficiently basic, or the atoms too crowded, for the displacement of cyanide or thf from the lithium coordination sphere. In contrast, replacement of two methyl groups in **1d** by OMe gives a different structure **3** (see Fig. 3). (Compare the compounds [Li(thf)₂AlH₃C(SiMe₃)₂(SiMe₂X)]; there is no Li–N bond when X = NMe₂, but an Li–O bond when X = OMe.²²) The almost linear Li–N–C–Cu sequences [*cf.* Li–N–C 163.3(4) in **3**, 109.6(8) in **1d** and 116.0(6)° in **1e**] form part of a skewed fourteen-membered ring with a crystallographically-required two-fold axis perpendicular to the C11–C11' vector. The methoxy groups are incorporated into six-membered rings that are reminiscent of those in the dimeric organolithium compounds [LiC(SiMe₃)(SiMe₂OMe)₂]₂ (**4**)¹⁷ and [LiC(SiMe₂OMe)₃]₂ (**5**).²³ The mean Li–OSi distance [1.940(8) Å] is similar to that in **5** [1.925(6) Å] but significantly longer than that in **4** [1.912(6) Å]; the Si–O distance is almost the same in all three compounds [1.684(3) Å in **3**, 1.683(3) Å in **4** and 1.680(2) Å in **5**]. The mean endocyclic Si–C distance in **3** [1.836(4) Å] is longer than those in **4** [1.808(3) Å] or **5** [1.799(2) Å], indicating

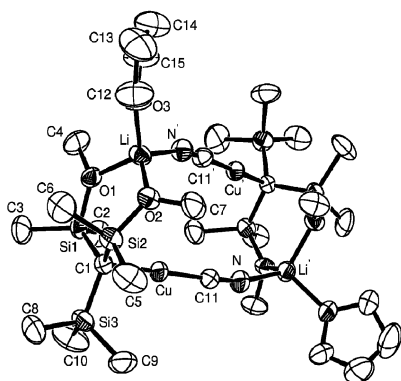
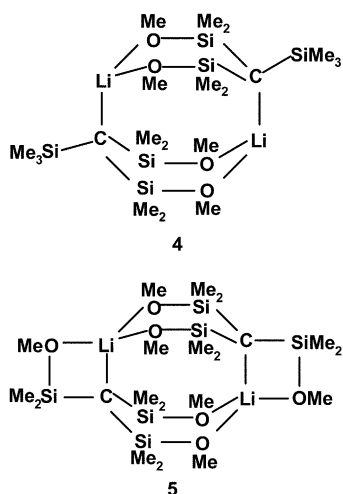


Fig. 3 The molecular structure of $[\text{Li}(\text{thf})\text{NCCu}\{\text{C}(\text{SiMe}_3)(\text{SiMe}_2\text{OMe})_2\}_2]_2$ **3**.

that there is less delocalisation of carbanionic charge into Si–C bonds. This reflects the fact that the carbanion is coordinated to copper in **3** but to the more electropositive lithium in **4** and **5**. The mean Si–C distance in **3** [1.842(4) Å] may be compared with those in **1b** [1.864(4)], **1d** [1.850(9)] and **1e** [1.853(7) Å]. The endocyclic O–Li–O angles range from 101.6(3)° in **3** to 98.5(4)° in **5** and the endocyclic Si–C–Si angles from 112.0(2)° in **3** to 117.2(2)° in **5**. The space required in the lithium coordination sphere by the isocyanide ligand in **3** is less than that by the tri(organosilyl)methyl ligand in **4**, so that there is room for coordination of an extra molecule of thf.



The IR spectrum of the crude product from the reaction between $[\text{LiC}(\text{SiMe}_3)(\text{SiMe}_2\text{OMe})_2]_2$ and CuCN showed a sharp peak at 2129 cm^{-1} ; cf., the values 2122–2123 cm^{-1} for **1c–1e**. The spectrum from a sample of **3**, obtained after recrystallisation of this crude product from toluene, had different peaks in the fingerprint region (600–1000 cm^{-1}) and ν_{CN} 2140 cm^{-1} . It is possible that the initial kinetic product has a bridged structure **1**, and is slowly converted into the thermodynamic product **3** during recrystallisation. There are two equal ^1H peaks and two equal ^{13}C signals from the SiMe_2 groups in the NMR spectra of **3** in benzene at room temperature, consistent with the preservation of the dimeric structure in solution. However, more work is required to substantiate these hypotheses and at present other less simple explanations for the IR and NMR data cannot be completely ruled out.

The compounds $[\text{LiNCCuR}]_2$, **1d**, **1e** and **3**, were also obtained when CuCN was treated with an excess of the lithium derivative LiR. When **1d** was treated with $\text{LiC}(\text{SiMe}_3)_3(\text{thf})_2$ there was no evidence for the formation of a higher order cyanocuprate $\text{Li}_2[\text{CN}][\text{CuR}_2]$ like those obtained with smaller R groups and shown to contain diorganocuprate ions when

$\text{R} = \text{Bu}^t$ ¹⁰ or $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$.²⁴ Diorganocuprate ions have also been structurally characterised in Gilman reagents $[\text{LiL}_n][\text{CuR}_2]$ with $\text{R} = \text{Me}$, $\text{L}_n = (12\text{-crown-4})_2$; $\text{R} = \text{C}(\text{SiMe}_3)_3$, $\text{L}_n = (\text{thf})_4$ (**6**); or $\text{R} = \text{Ph}$, $\text{L}_n = (12\text{-crown-4})_2(\text{thf})$ ^{25,26} or Et_2O ;²⁷ in $[\text{Cudppe}]_2[\text{CuMe}_2]$ [dppe = 1,2 bis(diphenylphosphino)ethane]²⁸ or in $[\text{Cu}(\text{PMe}_3)_4][\text{CuMe}_2]$.²⁹ The common formation of higher from lower order cyanocuprates indicates that this reaction is thermodynamically possible, and the isolation of the Gilman reagent $[\text{Li}(\text{thf})_4][\text{CuR}_2]$ (**6**) $\text{R} = \text{C}(\text{SiMe}_3)_3$ from LiR and CuI²⁵ shows that the existence of the dialkylcuprate ion $[\text{Cu}\{\text{C}(\text{SiMe}_3)_3\}_2]^-$ is not precluded on steric grounds. The failure to obtain higher order cyanocuprates from **1d** and **1e** must therefore be attributed to the greater difficulty in displacing cyanide than iodide from copper. In part this may be a reflection of the short Cu–CN distances in **1b**, **1d** and **1e**; typical Cu–I distances are 2.50–2.80 Å.^{30,31} We were also unable to detect any reaction between methyl-lithium and the cyanocuprate **1d**. The presence of only one bulky tri(organosilyl)methyl ligand in the coordination sphere of the copper appears to be sufficient to prevent formation of a higher order cyanocuprate.

We have previously shown that the tris(trimethylsilyl)methylalumininate $[\text{Li}(\text{thf})_2\text{AlH}_3\text{C}(\text{SiMe}_3)_3]_2$ reacts with aldehydes or ketones to give alkoxyaluminates that are analogues of presumed intermediates in reactions of carbonyl compounds with aluminium hydride reducing agents.³² We surmised that from the reactions of lithium cyanocuprates containing very bulky tri(organosilyl)methyl groups with alkyl halides or enones it might be possible to isolate and structurally characterise similar intermediates that would throw light on the efficacy of cyanocuprates in organic synthesis. However, under the conditions described in the Experimental section, compound **1d** failed to react with iodomethane, chlorotrimethylsilane, and the enones 3-butene-2-one and 2-cyclohexen-1-one. It seems that the $(\text{Me}_3\text{Si})_3\text{C}$ group attached to copper is so large that the reactions normally observed for cyanocuprates are inhibited.

Experimental

Air and moisture were excluded as far as possible from all reactions by use of Schlenk techniques, flame-dried glassware and Ar as blanket gas. NMR spectra, in C_6D_6 for **1d** and **1e** and in $\text{thf}-d_8$ for **3**, were recorded at 300.1 (^1H), 75.4 (^{13}C), 194.5 (^7Li), 50.7 (^{15}N) and 99.4 MHz (^{29}Si); chemical shifts are relative to SiMe_4 (H, C and Si), aqueous LiCl or MeNO_2 .

Syntheses

[Li(thf)₂NCCu{C(SiMe₃)₃}]₂ (1d). A solution of $\text{Li}(\text{thf})_2\text{C}(\text{SiMe}_3)_3$ ³³ (1.50 g, 3.93 mmol) in thf (40 cm^3) was added to a stirred suspension of CuCN (0.35 g, 3.93 mmol) in thf (30 cm^3) at -78°C . The mixture was allowed to warm to room temperature to give a colourless solution and solvent was removed under vacuum. The pale yellow glassy residue was extracted with toluene (40 cm^3). The extract was filtered to remove a small amount of suspended solid then concentrated to ca. 20 cm^3 and kept at -30°C to give colourless crystals of **1d** (1.20 g, 65%), suitable for X-ray diffraction analysis. Found: C, 48.12; H, 9.28; N, 2.69. $\text{C}_{38}\text{H}_{86}\text{Cu}_2\text{Li}_2\text{N}_2\text{O}_4\text{Si}_6$ requires C, 48.31; H, 9.20; N, 2.97%. δ_{H} 0.54 (27 H, s, SiMe_3), 1.39 (8 H, m, thf) and 3.51 (8 H, m, thf). δ_{C} 5.2 ($^1J_{\text{SiC}} = 39.8$ Hz, CSi_3), 8.0 ($^1J_{\text{SiC}} = 49.1$ Hz, SiMe_3), 25.3 (thf), 68.6 (thf) and 154.4 (CN). $\delta_{\text{Si}} -8.2$. δ_{Li} 1.62 ($\Delta\nu_{1/2} = 2$ Hz). ν_{CN} 2123 cm^{-1} .

[Li(thf)₂NCCu{C(SiMe₃)₂(SiMe₂NMe₂)}]₂ (1e). A solution of the lithium reagent,¹⁶ made at -78°C from $(\text{Me}_3\text{Si})_2(\text{Me}_2\text{NMe}_2\text{Si})\text{CCl}$ (1.85 g, 6.3 mmol) in thf (50 cm^3) and Li^nBu (7.8 mmol) in hexane (3 cm^3), was added dropwise with stirring to a suspension of CuCN (0.56 g, 6.3 mmol) in thf (20 cm^3) at -78°C . The mixture was allowed to warm to room temperature and the solution was then filtered. The solvent was removed

Table 2 Summary of crystallographic data for compounds **1d**, **1e** and **3**

	1d	1e	3
Chemical formula	C ₃₈ H ₈₆ Cu ₂ Li ₂ N ₂ O ₄ Si ₆	C ₄₀ H ₉₂ Cu ₂ Li ₂ N ₄ O ₄ Si ₆	C ₃₀ H ₇₀ Cu ₂ Li ₂ N ₂ O ₆ Si ₆
Formula weight	944.6	1002.7	864.38
<i>T</i> /K	173(2)	173(2)	239(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)	<i>C</i> 2/ <i>c</i> (no. 15)
<i>a</i> /Å	13.452(8)	13.344(6)	29.916(9)
<i>b</i> /Å	17.080(11)	13.797(12)	9.4377(19)
<i>c</i> /Å	18.748(13)	16.934(12)	17.892(4)
<i>a</i> °	82.91(5)	103.59(7)	90
<i>β</i> °	73.53(5)	94.01(5)	109.06(2)
<i>γ</i> °	84.41(5)	106.63(6)	90
<i>U</i> /Å ³	4090(5)	2872(3)	4775(2)
<i>Z</i>	3	2	4
<i>μ</i> /mm ⁻¹	0.95	0.90	1.08
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.075, 0.160	0.066, 0.166	0.053, 0.127
all data	0.154, 0.200	0.101, 0.191	0.084, 0.145
Measured/independent reflections	9978/9978	7019/7019	4275/4199
Reflections with <i>I</i> > 2σ(<i>I</i>)	5492	4889	<i>R</i> (int) 0.0357 2999

from the filtrate under vacuum to leave a brown solid. This was extracted with hexane, and the extract was filtered and concentrated to *ca.* 12 cm³, then kept at 5 °C to give colourless crystals of **1e** (1.3 g, 41 %) mp 145–151 °C). Found: C, 47.86; H, 9.28; N, 5.51. C₄₀H₉₂Cu₂Li₂N₄O₄Si₆ requires C, 47.87; H, 9.18; N, 5.58%. δ_H 0.47, 0.48 (24 H, SiMe₂ and SiMe₃), 1.4, (8 H, m, thf), 2.7 (6 H, s, NMe₂) and 3.5 (8 H, m, thf). δ_C 5.9 (¹*J*_{SiC} = 54.2 Hz, SiMe₂), 6.6 (¹*J*_{SiC} = 39.8 Hz, CSi₃), 7.9 (¹*J*_{SiC} = 48.9 Hz, SiMe₃), 25.4 (thf), 39.9 (NMe₂), 68.6 (thf) and 154.4 (CN). δ_{Li} 0.88. δ_N -378. δ_{Si} -9.7 (SiMe₃) and 1.3 (SiMe₂). ν_{CN} 2122 cm⁻¹.

[Li(th f)NCCu{C(SiMe₃)(SiMe₂OMe)₂}]₂ (3**).** A solution of [LiC(SiMe₃)(SiMe₂OMe)₂]¹⁷ (0.90 g, 1.74 mmol) in thf (20 cm³) was added to a stirred slurry of CuCN (0.31 g, 3.49 mmol) in thf (20 cm³) at -78 °C and the brown solution was allowed to warm to room temperature. The solvent was removed to give a brown glass that was washed with hexane (2 × 20 cm³). The residue was then dissolved in toluene (10 cm³) and the solution kept at -30 °C to give **3** as colourless needles (0.91 g, 61%), suitable for an X-ray diffraction study. Found: C, 41.60; H, 7.94; N, 3.29. C₃₀H₇₀Cu₂Li₂N₂O₆Si₆ requires C, 41.68; H, 8.18; N, 3.24%. δ_H 0.09 (9 H, s, SiMe₃), 0.11, 0.12 (6 H, s, SiMe₂) and 3.36 (6 H, s, OMe). δ_C 4.9, 5.1 (SiMe₂), 7.1 (SiMe₃), 9.0 (¹*J*_{CSiO} 50.0 Hz, ¹*J*_{CSiMe} = 39.7 Hz, CSi₃), 49.8 (OMe) and 147.5 (CN). δ_{Si} -10.0 (SiMe₃), 9.5 (SiMe₂). δ_{Li} 0.94 (Δν_{1/2} = 1 Hz). ν_{CN} 2140 cm⁻¹.

Attempted reactions of [Li(th f)₂NCCu{C(SiMe₃)₃}]₂ (**1d**)

With MeI. A solution of iodomethane (0.20 g, 1.41 mmol) in thf (5 cm³) was added to a solution of **1d** (0.50 g, 0.53 mmol) in thf (20 cm³) at -78 °C. The colourless solution was allowed to warm to room temperature and volatile compounds were removed. The pale yellow solid residue was shown by ¹H NMR to be unchanged **1d**.

With Me₃SiCl. There was no reaction when Me₃SiCl (0.20 g, 1.84 mmol) was added to a solution of **1d** (0.50 g, 0.53 mmol) under similar conditions.

With 3-buten-2-one. 3-Buten-2-one (0.10 g, 7.1 mmol) in thf (5 cm³) was added to a solution of **1d** (0.50 g, 0.53 mmol) in thf (15 cm³) at -78 °C. Volatile material was removed to leave a colourless glass that was shown to be unchanged **1d**. In an NMR scale reaction the ¹H, ¹³C and ⁷Li spectra of a solution containing **1d** and an equimolar quantity of 3-buten-2-one in C₆D₅CD₃ were recorded over the temperature range 203 to 348 K. No reaction was observed.

With 2-cyclohexen-1-one. No reaction was detected when **1d** (0.50 g, 0.53 mmol) was treated with 2-cyclohexen-1-one (0.15 g, 1.56 mmol) in thf (20 cm³).

With (Me₃Si)₃CLi(th f)₂. A solution of (Me₃Si)₃CLi(thf)₂ (0.65 g, 1.69 mmol) in thf (20 cm³) was added to a solution of **1d** (0.80 g, 0.85 mmol) in thf (25 cm³) at -78 °C. The colourless solution was allowed to warm to room temperature and the solvent was removed under vacuum to leave a colourless glass. This was dissolved in toluene (15 cm³) and the solution was kept at -30 °C for 2 days to give colourless crystals that were judged to be a mixture of LiC(SiMe₃)₃(thf)₂ and **1d** by mechanical separation of individual crystals and measurement of unit cell parameters by X-ray diffraction studies.

With MeLi. A solution of MeLi (0.66 cm³, 1.6 M in Et₂O) was added to a solution of **1d** in thf (20 cm³) at -78 °C. The mixture was allowed to warm to room temperature and the solvent was removed to give a colourless glass that was extracted with toluene (20 cm³). The solvent was removed from the extract and the residue identified as unchanged **1d** by ¹H NMR and IR spectroscopy.

Crystallography

Data were collected on an Enraf Nonius CAD4 diffractometer; the structures were solved by direct methods (SHELXS 86) and refined by full matrix least squares (SHELXL 97).³⁴ All non-hydrogen atoms were anisotropic and hydrogen atom positions were included in riding mode. More details are given in Table 2. An attempt to collect data from **3** at 173 K resulted in the loss of the crystal, possibly through a destructive phase transition.

CCDC reference numbers 188683–188685.

See <http://www.rsc.org/suppdata/dt/b2/b206176g/> for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the EPSRC for financial support and the Government of Libya for the award of a scholarship to S. M. El-H.

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