Notes

Structural Diversity in Organolithium, -sodium, and -potassium Cyanocuprates

Colin Eaborn, Michael S. Hill,* Peter B. Hitchcock, and J. David Smith

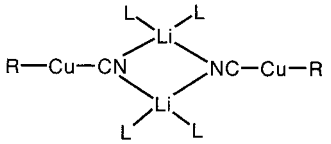
School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, BN1 9QJ, U.K.

Received August 28, 2000

Summary: An unprecedented series of "lower order" alkali metal (Li, Na, K) cyanocuprates containing the bulky ($(Me_2PhSi)_3C$) ligand has been synthesized. Both monomeric and dimeric forms of the lithium derivative have been characterized; the tetrameric potassium compound provides a striking example of molecular self-assembly driven by K−π-aryl interactions.

Introduction

"Lower order" lithium cyanocuprates, RCuCNLi, are important in organic chemistry as regioselective alkylating reagents.[1] The recent determination of the structures of the dimeric molecules **1** and **2**[2,3] has advanced understanding of their nature and mode of reaction.[4] Although the constitution of these compounds has not been as controversial as that of their "higher order" counterparts, $R_2CuCNLi_2$,[5,6] these solid state structures may not necessarily be those of the reactive species in solution. Cryoscopic and electrospray mass spectrometric data in THF for a number of "lower order" systems indicate the presence of monomeric as well as dimeric and higher oligomeric forms.[7,8]



1 R = Ar = 2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$; L=THF
2 R = *t*-Bu; L = OEt_2

Our earlier work on compounds containing the very bulky alkyl ligands $(Me_3Si)_3C$ and $(Me_2PhSi)_3C$ provided the first structurally authenticated example of a dialkylcuprate (a Gilman reagent), namely, $[Li(THF)_4]^+$-$[Cu\{C(SiMe_3)_3\}_2]^-$.[9] The reports on **1** and **2** prompted us to examine the structures of analogous compounds, **3**−**6**, containing the $(Me_2PhSi)_3C$ ligand. We present the first X-ray evidence for the existence of both monomeric and dimeric forms of the same lithium cyanocuprate, viz., **3** and **4**, and the first examples of sodium and potassium derivatives, **5** and **6**, of this type. Related work on such heavier alkali metal organocuprates is restricted to a single report of sodium Gilman reagents, R_2CuNa (R = butyl or pentyl), prepared from RNa and a variety of Cu(I) starting materials.[10]

$[(Me_2PhSi)_3CCuCNLi(THF)_3]$
3

$[(Me_2PhSi)_3CCuCNM(THF)_2]_2$
4 M = Li, 5 M = Na

$[(Me_2PhSi)_3CCuCNK]_4$
6

Results and Discussion

Compounds **3**−**6** were synthesized by addition of a THF solution of $(Me_2PhSi)_3CM$ (M = Li, Na, or K) to a slurry of CuCN in THF at −78 °C and were characterized by NMR and IR spectroscopy. In no case was a "higher order" cuprate (i.e., a compound of the form $R_2CuCNLi_2$) obtained from reactions of CuCN with 2 equiv of $(Me_2PhSi)_3CM$, presumably for steric reasons. In the case of the lithium reagent **3**, removal of THF from the reaction mixture produced a colorless glass that, upon standing in contact with hexane, gave large air- and light-sensitive crystals. Although the crystals were suitable for X-ray study, the very long *c* axis of the unit cell led to peak overlap and a consequent high *R* factor in the refinement.[11] This precludes detailed discussion

---

* Corresponding author. E-mail: m.s.hill@sussex.ac.uk. Fax: (+44) 1273-677196.

[1] Krause, N.; Gerold, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 187.

[2] Hwang, C.-S.; Power, P. P. *J. Am. Chem. Soc.* **1998**, *120*, 6409.

[3] Boche, G.; Bosold, F.; Marsch, M.; Harms, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1684.

[4] Krause, N. *Angew. Chem., Int. Ed.* **1999**, *38*, 79, and references therein.

[5] (a) Lipshutz, B. H.; James, B. *J. Org. Chem.* **1994**, *59*, 7585. (b) Snyder, J. P.; Bertz, S. H. *J. Org. Chem.* **1995**, *60*, 4312. (c) Bertz, S. H.; Miao, G.; Eriksson, M. *Chem. Commun.* **1996**, 815. (d) Bertz, S. H.; Nilsson, K.; Davidsson, Ö.; Snyder, J. P. *Angew. Chem., Int. Ed.* **1998**, *37*, 314.

[6] For solid-state structures of "higher-order" cyanocuprates see ref 3 and: Kronenburg, C. M. P.; Jastrzebski, J. T. B. H.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1998**, *120*, 9688.

[7] Gerold, A.; Jastrzebski, J. T. B. H.; Kronenburg, C. M. P.; Krause, N.; van Koten, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 755.

[8] Lipshutz, B. H.; Keith, J.; Buzard, D. J. *Organometallics* **1999**, *18*, 1571.

[9] Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Organomet. Chem.* **1984**, *263*, C23.

[10] Bertz, S. H.; Gibson, C. P.; Dabbagh, G. *Organometallics* **1988**, *7*, 227.

[11] Details of crystal data and structure refinement for **3** are available as Supporting Information.

10.1021/om000748q CCC: $19.00

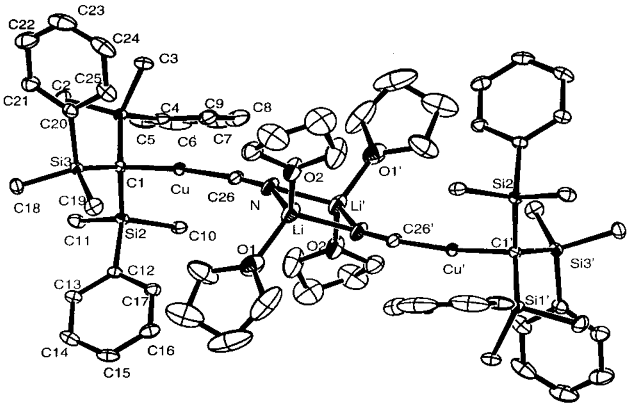


Figure 1. Molecular structure of **4** (30% probability ellipsoids). H atoms omitted for clarity. Selected bond lengths [Å] and angles [deg]: Cu−C1 1.933(3), Cu−C26 1.851(4), N−C26 1.151(5), Li−N 2.059(10), Li−N′ 2.062(9), Li−O1 1.912(11), Li−O2 1.899(9): C1−Cu−C26 173.68(16), Cu−C26−N 174.9(4), N−Li−N′ 97.1(4), Li−N−Li′ 82.9(4), O1−Li−O2 109.1(5), Li−N−C26 138.4(5), Li′−N−C26 136.0(4).

of bond lengths and angles, but the molecular connectivity is unambiguous. Within the asymmetric unit there are two independent noninteracting monomers with the formula [$(Me_2PhSi)_3CCuCNLi(THF)_3$]. Whereas in the dimers **1** and **2** the coordination at Li is completed by N−Li−N bridges, in **3** it is completed by coordination of a third molecule of THF. Compound **3** is the first example of a monomeric “lower order” cyanocuprate.

In an attempt to obtain crystals suitable for the collection of an improved data set, a sample of **3** was recrystallized from toluene. This resulted in the loss of a molecule of THF and dimerization to form **4**. The molecule of solvent could also be removed from **3** by storage for 5−6 h under dynamic vacuum (10^{-3} mmHg). Like that of the sterically hindered aryl derivative **1**, the structure of **4** (Figure 1) comprises discrete centrosymmetric dimers, but there are no Cu(d^{10})···Cu(d^{10}) contacts such as those observed in the less bulky *t*Bu analogue, **2**.[3] The C1−Cu−CN angle [173.68(16)°] is a little narrower than that in **1** [175.6(2)°] but greater than those in **2** [168.0(3)° and 170.0(3)°]. The Cu−C26−N angle at the cyanide carbon of **4** is also slightly more bent [174.9(4)°] than that in **1** [179.3(5)°]. The Cu−C1 distance in **4** [1.933(3) Å] is shorter than that in the linear anion of the dialkyl cuprate $[Li(THF)_4]^+$-$[Cu\{C(SiMe_3)_3\}_2]^-$ [2.027(7) Å][9] and marginally shorter than that in **2** [1.969(7) Å], where the Cu is effectively three-coordinate. The Cu−C26 distance to the cyanide carbon is 1.851(4) Å, shorter than that in **2** [1.878(8) Å] but essentially identical to that in **1** [1.858(5) Å].

The ready conversion of **3** into **4** suggests that these solid state species are probably also present in THF/toluene solutions. It is noteworthy that cryoscopic and electrospray mass spectral results indicate that similar species are present in solutions of less hindered cyanocuprates, e.g., ArCuCNLi (Ar = Ph or 2-thienyl).[7,8]

The colorless sodium compound **5** was crystallized from toluene. The ^{1}H NMR integral ratios in C_6D_6 and microanalytical data indicate a composition with two molecules of THF per sodium analogous to that of **4**. The ν(CN) stretching vibration, which is known to be sensitive to the cyanide bonding environment,[12,13] lies at 2127 cm^{-1}, close to the values observed for **4** (2126 cm^{-1}) and the dimeric aryl **1** (2123 cm^{-1}),[2] indicating a similar dimeric structure. In contrast, the tetrameric arrangement adopted by the analogous potassium derivative **6** (see below), in which the cyanide nitrogen is four-coordinate, gives ν(CN) 2112 cm^{-1}.

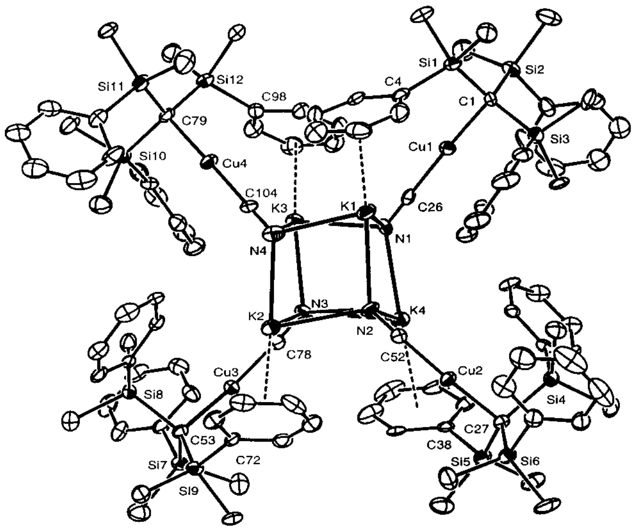


Figure 2. Molecular structure of **6** (30% probability ellipsoids). H atoms and toluene molecules are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Cu1−C1 1.948(11), Cu1−C26 1.883(13), Cu2−C27 1.958(10), Cu2−C52 1.866(12), Cu3−C53 1.918(11), Cu3−C78 1.853(12), Cu4−C79 1.949(10), Cu4−C104 1.856(12), K1−N1 3.183(11), K1−N2 2.806(10), K1−N4 2.842(12), K2−N2 2.834(10), K2−N3 3.351(11), K2−N4 2.774(10), K3−N1 2.848(10), K3−N3 2.754(10), K3−N4 3.399(11), K4−N1 2.764(10), K4−N2 3.112(10), K4−N3 2.806(10): C1−Cu1−C26 175.7(5), C27−Cu2−C52 174.3(5), C53−Cu3−C78 175.0(5), C79−Cu4−C104 178.4(5), N1−K1−N2 77.5(3), N1−K1−N4 77.3(3), N2−K1−N4 78.3(3), N2−K2−N3 79.8(3), N2−K2−N4 79.0(3), N3−K2−N4 73.1(3), N1−K3−N3 76.0(3), N1−K3−N4 73.7(3), N3−K3−N4 72.6(3), N1−K4−N2 79.3(3), N1−K4−N3 76.6(3), N2−K4−N3 84.5(3).

Colorless crystals of the potassium compound **6** suitable for an X-ray study were grown from toluene solution containing a few drops of THF and were shown to comprise THF-free tetramers with no imposed crystallographic symmetry (Figure 2).[11] In the central distorted K_4N_4 cube each potassium atom is bound to three cyanide nitrogens and further coordinated by η^6- and η^2- (to the *ortho* and *meta* carbon atoms of the ring) π-aryl interactions with two phenyl groups of a single adjacent $(Me_2PhSi)_3C$ ligand. Although there is significant variation in individual bond lengths, the K−C(ring) distances of all the η^6- and η^2-coordinated phenyl groups are typical of those documented for a wide range of organometallic derivatives.[14] The η^6-interactions range from 3.085(13) (K1−C7) to 3.527(12) Å (K3−C103) with individual values determined by the conformation of the molecule as a whole. The η^2-K−C(ring) distances are typically ca. 3.3 Å. There is substantial deviation from ideal cubic geometry within the K_4N_4 cube. The N−K−N

---

[12] Nakamoto, K. In *Infrared Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986.

[13] For the use of IR spectroscopy as a diagnostic tool in cyanocuprate chemistry see: Huang, H.; Alvarez, K.; Lui, Q.; Barnhart, T. M.; Snyder, J. P.; Penner-Hahn, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 8808.

[14] Smith, J. D. *Adv. Organomet. Chem.* **1998**, *43*, 267.

angles range from 74.6(3)° to 84.5(3)° and the K−N−K angles from 93.6(3)° to 107.6(3)° with displacements of the potassium atoms to maximize π-phenyl interactions. These displacements are also apparent from the K−N bond lengths; individual KN_3 subunits consist of two shorter K−N bonds [in the range 2.754(10)−2.849(10) Å, similar to K−N distances in related compounds][15] and one longer K−N interaction [in the range 3.112(10)−3.399(10) Å]. This longer bond is in each case approximately *trans* to the strongly interacting η^6-phenyl ring. Of the shorter K−N interactions, those opposite the η^2-coordinated phenyl group are lengthened in a similar fashion, reflecting the importance of intramolecular arene solvation in controlling the self-assembly of the tetramer and excluding THF from the potassium coordination sphere. There appear to be no other reports of simple K_4N_4 cubane structures,[16] but similar K−π-aryl interactions have been observed in a number of cage-type oligomers,[17] for example the primary phosphanide [(2,6-dimesitylphenyl)P(H)K]$_4$ and the thiolate [$(KSCPh_3)_6$(toluene)$_2$].[18,19] The four C−Cu−C−N linkages in **6** act as spacer units between the central K_4N_4 cube and the peripheral ligands and are only slightly distorted from linearity [average C−Cu−C 176.1(10)°; average N−C−Cu 176.4(11)°] by the strong K−phenyl interactions.

The NMR spectra of **6** recorded in THF-d_8 provide no evidence for restricted rotation about the Cu−CSi_3 bond, indicating that the K−π-aryl interactions do not persist in this donor solvent. Preliminary variable-temperature NMR studies of **6** in toluene-d_8 indicate that the tetrameric cage is disrupted when the temperature is raised to 348 K and that isomeric species, possibly toluene-solvated lower oligomers, form on subsequent cooling. Studies of this behavior, the reactions of **3**−**6**, and the chemistry of other $(R_3Si)_3C$-containing cyanocuprate derivatives are planned. The heavier alkali metal organocuprates may show important differences from the lithium compounds in reactivity and selectivity.

Experimental Section

Air and moisture were excluded as far as possible by the use of flame-dried glassware and Ar blanket gas. Solvents were purified by distillation from an appropriate drying agent (toluene and THF from potassium, hexane from Na/K alloy). NMR spectra were recorded at 300.13 (^{1}H), 125.8 (^{13}C), 99.4 (^{29}Si), 194.5 (^{7}Li), and 132.3 MHz (^{23}Na) in C_6D_6 unless otherwise stated; intensities of the quaternary and ^{29}Si signals were enhanced by polarization transfer. $(Me_2PhSi)_3CLi(THF)$, $(Me_2PhSi)_3CNa$, and $(Me_2PhSi)_3CK$ were synthesized as described previously.[20−22]

[$(Me_2PhSi)_3CCuCNLi(THF)_3$], 3. A solution of $(Me_2PhSi)_3CLi(THF)$ (2.16 g, 4.35 mmol) in THF (20 mL) was added dropwise to a slurry of CuCN (0.40 g, 4.47 mmol) in THF (25 mL) at −78 °C. The solution was protected from light and allowed to warm to room temperature during 16 h. The pale yellow turbid solution was filtered, and the solvent removed to leave a sticky glass. This glass was covered with hexane (20 mL) and set aside for 48 h to give **3** as large colorless, air-, moisture-, and light-sensitive crystals. Yield: 1.94 g, 61%, mp softens >90 °C, 150 °C (decomp). Anal. Calcd for $C_{38}H_{57}CuLiNO_3Si_3$: C, 62.41; H, 7.80; N, 1.92. Found: C, 62.34; H, 7.81; N, 1.92. ^{1}H NMR: δ 0.57 (s, 18H, $SiMe_2$), 1.42 (br m, 12H, THF), 3.64 (br m, 12H, THF), 7.20 (m, 9H, *m*, *p*-C_6H_5), 7.89 (m, 6H, *o*-C_6H_5). ^{13}C{^{1}H} NMR: δ 2.7 (CSi_3), 6.5 ($SiMe_2$, $^1J_{SiC}$ = 50.8 Hz.), 25.5 (THF), 68.8 (THF), 127.2 (*p*-C_6H_5), 127.4 (*m*-C_6H_5), 135.1 (*o*-C_6H_5), 147.5 (*i*-C_6H_5), CN not observed. ^{29}Si NMR: δ −9.6. ^{7}Li NMR: δ −0.75. IR (Nujol): 2126 cm^{-1} (C≡N).

[$(Me_2PhSi)_3CCuCNLi(THF)_2$]$_2$, 4. A sample of **3** was recrystallized from toluene at −35 °C to give colorless crystals giving spectral data essentially identical to those of **3** except for a reduction in the integral value ascribed to signals for THF in the ^{1}H NMR spectrum. Subsequent crystallographic analysis showed the product to be **4**, mp 155−158 °C (dec). Anal. Calcd for $C_{68}H_{98}Cu_2Li_2N_2O_4Si_6$: C, 61.96; H, 7.44; N, 2.13. Found: C, 62.00; H, 7.56; N, 1.98.

[$(Me_2PhSi)_3CCuCNNa(THF)_2$]$_2$, 5. This was synthesized similarly from $(Me_2PhSi)_2CNa$ (0.47 g, 1.07 mmol) and CuCN (0.10 g, 1.12 mmol). Crystallization from toluene at −35 °C yielded **5** as colorless microcrystals. Yield: 0.31 g, 42%, mp 135−138 °C (dec). Anal. Calcd for $C_{68}H_{98}Cu_2Na_2N_2O_4Si_6$: C, 60.55; H, 7.27; N, 2.08. Found: C, 60.31; H, 6.99; N, 1.99. ^{1}H NMR: δ 0.32 (s, 18H, $SiMe_2$), 1.09 (br m, 8H, THF), 3.12 (br m, 18H, THF), 6.92 (m, 9H, *m*, *p*-C_6H_5), 7.63 (m, 6H, *o*-C_6H_5). ^{13}C{^{1}H}: δ 6.4 ($SiMe_2$), 25.6 (THF), 68.2 (THF), 127.3 (*p*-C_6H_5), 127.7 (*m*-C_6H_5), 135.1 (*o*-C_6H_5), 148.1 (*i*-C_6H_5), CN not observed. ^{29}Si NMR: δ −9.6. ^{23}Na NMR: δ −7.1 ($\Delta\nu_{1/2} \approx 1.2$ kHz). IR (Nujol): 2127 cm^{-1} (C≡N).

[$(Me_2PhSi)_3CCuCNK$]$_4$, 6. This was synthesized similarly from $(Me_2PhSi)_3CK$ (0.59 g, 1.29 mmol) and CuCN (0.12 g, 1.34 mmol). Crystallization by slow cooling of a hot (60 °C) toluene solution containing a few drops of THF afforded large colorless blocks of **6** as a bis(toluene) solvate. The occluded solvent was easily removed under dynamic vacuum (10^{-3} mmHg). Yield: 0.30 g, 43%, mp 138−140 °C. Anal. (for unsolvated product) Calcd for $C_{26}H_{33}CuKNSi_3$: C, 57.15; H, 6.09; N, 2.56. Found: C, 57.06; H, 6.30; N, 2.19. ^{1}H NMR (THF-d_8): δ 0.08 (s, 18H, $SiMe_2$), 7.06 (m, 9H, *m*, *p*-C_6H_5), 7.58 (m, 6H, *o*-C_6H_5). ^{13}C{^{1}H} NMR (THF-d_8): δ 1.9 (CSi_3, $^1J_{SiC}$ = 39.2 Hz.), 6.3 ($SiMe_2$), 127.1 (*p*-C_6H_5), 127.3 (*m*-C_6H_5), 135.4 (*o*-C_6H_5), 147.8 (*i*-C_6H_5), CN not observed. ^{29}Si NMR (THF-d_8): δ −10.9. IR (Nujol): 2112 cm^{-1} (C≡N).

Crystallography. Crystallographic data for **4** at 173(2) K: ($C_{68}H_{98}Cu_2Li_2N_2O_4Si_6$, M_r = 1316.98) crystal dimensions 0.2 × 0.1 × 0.05 mm^3; triclinic, space group $P\bar{1}$(No. 2), a = 11.3889(5), b = 11.7975(7), c = 15.8328(7) Å, α = 99.652(3)°, β = 91.493(3)°, γ = 114.319(3)°, V = 1900.4(2) Å^3, Z = 1, ρ_{calcd} = 1.15 Mg m^{-3}. Data were collected on a Kappa CCD area detector, λ(Mo Kα) = 0.71073 Å. Of 19 453 reflections measured ($4.29° < \theta < 25.02°$), 6642 were independent (R_{int} = 0.078). The structure was solved by direct methods (SHELXS-97)[23] and refined for 173 parameters against F^2 (SHELXL-97).[24] The non-hydrogen atoms were refined anisotropically,

---

(15) For example: (a) Al-Juaid, S. S.; Eaborn, C.; El-Hamruni, S.; Farook, A.; Hitchcock, P. B.; Hopman, M.; Smith, J. D.; Clegg, W.; Izod, K.; O'Shaughnessy, P. *J. Chem. Soc., Dalton Trans.* **1999**, 3267. (b) Andrews, P. C.; Kennedy, A. R.; Mulvey, R. E.; Raston, C. L.; Roberts, B. A.; Rowlings, R. B. *Angew. Chem., Int. Ed.* **2000**, *39*, 1960. (c) Kennedy, A. R.; Mulvey, R. E.; Raston, C. L.; Roberts, B. A.; Rowlings, R. B. *Chem. Commun.* **1999**, 353. (d) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Organomet. Chem.* **1996**, *488*, 241.

(16) Search of Cambridge Structural Database, The United Kingdom Chemical Database Service: Fletcher, D. A.; McMeeking, R. F.; Parkin, D. *Chem. Inf. Comput. Sci.* **1996**, *36*, 746. A K_4N_4 cage has recently been reported as part of a K_6N_6 oligomer in [$KNPh_3$]$_6$: Chitsaz, S.; Neumuller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 9.

(17) Haiduc, I.; Edelmann, F. T. *Supramolecular Organometallic Chemistry*; Wiley-VCH: Weinheim, 1999.

(18) Rabe, G. W.; Kheradmandan, S.; Yap, G. P. A. *Inorg. Chem.*, **1998**, *37*, 6541.

(19) Chadwick, S.; Englich, U.; Ruhlandt-Senge, K. *Organometallics* **1997**, *16*, 5792.

(20) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1390.

(21) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Izod, K.; Mallien, M.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1268.

(22) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Jaggar, A. J.; Smith, J. D. *Organometallics* **1994**, *13*, 753.

and the hydrogen atoms were included with isotropic temperature factors; wR2 = 0.138, R1 = 0.053 [for 4717 reflectionswith $I > 2\sigma(I)$], GOF = 1.02. Crystallographic data for **6** at 173(2) K: ($C_{104}H_{132}Cu_4K_4N_4Si_{12}\cdot 2C_7H_8$, $M_r = 2370.0$) crystal dimensions $0.35 \times 0.35 \times 0.08$ mm^3; triclinic, space group $P\bar{1}$- (No. 2), $a = 17.454(5)$, $b = 17.695(5)$, $c = 21.311(5)$ Å, $\alpha = 92.55(2)°$, $\beta = 97.59(2)°$, $\gamma = 105.07(2)°$, $V = 6278(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.25$ Mg m^{-3}. Data were collected on an Enraf-Nonius CAD4 diffractometer, λ(Mo Kα) = 0.71073 Å; 17 430 independent reflections were measured ($2° < \theta < 23°$). The structure was solved by direct methods (SHELXS-97)[23] and refined for 1185 parameters against F^2 (SHELXL-97).[24] There are two poorly defined molecules of toluene, for which the C atoms were refined isotropically with the C_6 rings as rigid bodies and the methyl groups coplanar. Other non-H atoms were anisotropic. wR2 = 0.206, R1 = 0.091 [for 8122 reflections with $I > 2\sigma(I)$], GOF = 1.04.

Acknowledgment. We thank the Engineering and Physical Sciences Research Council (UK) for financial support.

Supporting Information Available: Details of crystal data and structure refinement for **3**, **4**, and **6** including thermal ellipsoid plots of **3a** and **3b**, atom coordinates, equivalent isotropic displacement factors, bond lengths and angles, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000748Q

---

[23] Sheldrick, G. M. *SHELXS-97*, Program for the Solution of Crystal Structures; Göttingen, 1997.

[24] Sheldrick, G. M. *SHELXl-97*, Program for the Refinement of Crystal Structures; Göttingen, 1997.