[5] M. Geyer, F. Plenzig, J. Rauschnabel, M. Hanack, B. del Rey, Á. Sastre, T. Torres, *Synthesis* **1996**, 1139.

[6] R. A. Kipp, J. A. Simon, M. Beggs, H. E. Ensley, R. H. Schmehl, *J. Phys. Chem. A* **1998**, *102*, 5659.

[7] Representative data. **1**: Yield: 51 %; m.p. >300 °C; UV/Vis ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-4}$) = 573 (8.96), 555(sh), 532 (2.59), 309 (4.04), 275 (3.03) nm; FAB-MS (*m*-nitrobenzyl alcohol): calcd for $C_{24}BClF_{12}N_6$: *m*/*z*: 646 [M^+]. *cis* Isomer **2**: Yield: <1 %; m.p. >320 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 10.47$ ppm (s, 2H, arom); IR (KBr): $\tilde{\nu} = 2959$, 2926, 2857, 1732, 1534, 1483, 1262, 1221, 1165, 1107, 1019, 965, 801, 771, 745, 706, 660, 581, 419 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-4}$) = 690 (11.1), 658 (3.39), 632 (3.40), 602 (3.94), 443 (0.86), 320 (4.61), 275 (3.81) nm; HR-FAB-MS: calcd for $C_{42}H_3B_2Cl_2F_{16}N_{12}$: [$M^+$+H]: *m*/*z*: 1070.9911, found 1070.9927. TLC (silica), $R_f = 0.53$ (toluene/hexane, 1:1). *trans* Isomer **3**: Yield: <1 %; m.p. >320 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 10.49$ ppm (s, 2H, arom); IR (KBr): $\tilde{\nu} = 2924$, 2957, 2855, 1717, 1534, 1483, 1271, 1221, 1165, 1109, 1019, 992, 965, 704, 642, 592, 419 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-4}$) = 693 (6.43) , 662 (1.90), 636 (1.96), 605 (2.39), 448 (0.51), 320 (2.78), 281 (3.35) nm; HR-FAB-MS: calcd for $C_{42}H_3B_2Cl_2F_{16}N_{12}$: [$M^+$ + H]: *m*/*z*: 1070.9911, found 1070.9905. TLC (silica), $R_f = 0.43$ (toluene/hexane, 1:1).

[8] Crystal data for the SubPc **1**: 0.06 × 0.17 × 0.22 mm, monoclinic, $P2_1/c$, $a = 11.2997(11)$, $b = 10.6022(11)$, $c = 19.1563(19)$ Å, $\beta = 95.507(7)^\circ$, $V = 2284.4(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.880$ Mg m^{-3}, $2\theta_{max} = 52.7^\circ$, $\lambda = 0.71073$ Å, ω scans, 170(2) K, 20288 measured, 4664 independent reflections included in the refinement, Lorentzian but no absorption corrections performed ($\mu = 0.297$ mm^{-1}, min./max. transmission = 0.937/0.982), solved by direct methods (SHELXS-90), refined by using SHELXL-97, 397 parameters, no H atoms, $R = 0.0948$, $wR = 0.1055$ for all data refined against $|F^2|$, residual electron density max./min. 0.32/ – 0.31 e Å^{-3}. Crystal data for the *cis*-SubPc dimer · 2 CH_2Cl_2 **2**: 0.04 × 0.04 × 0.40 mm, monoclinic, $P2_1/c$, $a = 14.4237(13)$, $b = 31.630(3)$, $c = 10.2000(10)$ Å, $\beta = 101.354(3)^\circ$, $V = 4562.4(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.807$ Mg m^{-3}, $2\theta_{max} = 56.6^\circ$, $\lambda = 0.71073$ Å, ω scans, 91(2) K, 37305 measured, 6637 independent reflections included in the refinement, Lorentzian and absorption corrections (SADABS) performed ($\mu = 0.495$ mm^{-1}, min./max. transmission = 0.826/0.980), solved by direct methods (SHELXS-90), refined by using SHELXL-97, 743 parameters, H atoms constrained, $R = 0.1135$, $wR = 0.1586$ for all data refined against $|F^2|$, residual electron density max./min. 1.18/ – 0.85 e Å^{-3}. Crystal data for the *trans*-SubPc dimer · 3.25 CH_2Cl_2 **3**: 0.03 × 0.12 × 0.16 mm, triclinic, $P\bar{1}$, $a = 10.8638(11)$, $b = 13.4945(15)$, $c = 17.2990(18)$ Å, $\alpha = 107.608(4)$, $\beta = 91.300(5)$, $\gamma = 101.347(4)^\circ$, $V = 2360.8(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.805$ Mg m^{-3}, $2\theta_{max} = 50.7^\circ$, $\lambda = 0.71073$ Å, ω scans, 91(2) K, 22234 measured, 8623 independent reflections included in the refinement, Lorentzian but no absorption corrections performed ($\mu = 0.537$ mm^{-1}, min./max. transmission = 0.919/0.984), solved by direct methods (SHELXS-90), refined by using SHELXL-97, 743 parameters, H atoms constrained, $R = 0.1198$, $wR = 0.1937$ for all data refined against $|F^2|$, residual electron density max./min. 1.02/ – 0.95 eÅ^{-3}. CCDC-181314 (**1**), CCDC-181315 (**2**), and CCDC-181316 (**3**) contain the supplementary crystallographic data for this paper. These data can be can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

[9] HyperChem Pro software package, Hypercube, Inc. Gainesville, FL, USA, **1997**.

[10] N. Kobayashi, T. Ishizaki, K. Ishii, H. Konami, *J. Am. Chem. Soc.* **1999**, *121*, 9096.

[11] a) A. Tajiri, J. Winkler, *Z. Naturforsch.* **1983**, *38a*, 1263; b) A. Kaito, T. Nozawa, T. Yamamoto, M. Hatano, Y. Orii, *Chem. Phys. Lett.* **1977**, *52*, 154.

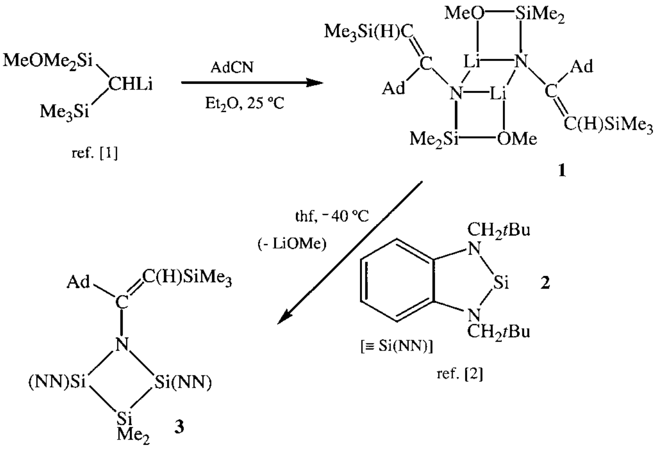
[12] Similar spectra have been reported for a planar dinuclear phthalocyanine that shares a common benzene ring (N. Kobayashi, T. Fukuda, D. Lelièvre, *Inorg. Chem.* **2000**, *39*, 3632).

Synthesis and Structure of an Azatrisilacyclobutane and Its Precursor, a Novel Lithium Enamide Having a Tricyclic $(LiNSiO)_2$ Skeleton[**]

Floria Antolini, Barbara Gehrhus,* Peter B. Hitchcock, and Michael F. Lappert*

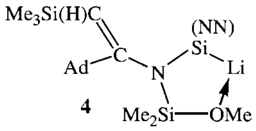
We report results that have a bearing on two diverse but related and currently topical areas of organometallic chemistry. The first concerns insertion of an α-hydrogen-free nitrile into an Li–C bond, and specifically of 1-adamantyl cyanide (AdCN) into the chiral bis(silyl)methyl compound Li[CH(SiMe$_2$OMe)(SiMe$_3$)][1] to yield the lithium enamide **1**. The second deals with the insertion of the thermally stable bis(amino)silylene Si[(NCH$_2$*t*Bu)$_2$C$_6$H$_4$-1,2] (Si(NN)) **2**[2] into an Li–N bond, and particularly of Si(NN) into **1** to afford the azatrisilacyclobutane **3**, in which a transient insertion product **4** is a plausible intermediate.

The reactions and conditions leading to the new colorless crystalline compounds **1** and **3** are summarized in Scheme 1.



Scheme 1. Synthesis of **3** via **1**.

The yields (**1**, 64 %; **3**, 50 %) of X-ray quality crystalline materials were not optimized. Each of **1** and **3** revealed the parent molecular ion in the EI mass spectra and gave satisfactory microanalyses and multinuclear NMR spectra.



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The crystalline lithium enamide **1** is a centrosymmetric dimer (Figure 1).[3] It has a rhomboidal, planar $(LiN)_2$ core (the endocyclic angles at the Li atoms are wider than those at the N

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[*] Dr. B. Gehrhus, Prof. M. F. Lappert, Dr. F. Antolini,
Dr. P. B. Hitchcock
School of Chemistry, Physics and Environmental Science
University of Sussex
Brighton, BN1 9QJ (UK)
Fax: (+44) 1273-677-196
E-mail: B.Gehrhus@sussex.ac.uk, M.F.Lappert@sussex.ac.uk

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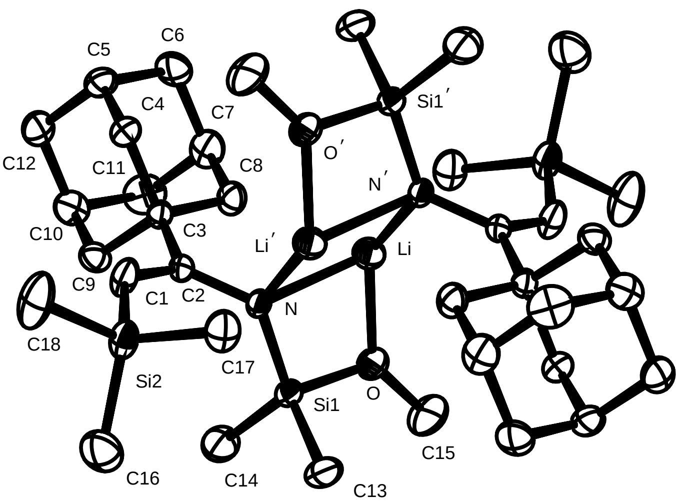


Figure 1. Molecular structure of **1** with selected bond lengths [Å] and angles [°]: Li-N 2.179(3), Li-N′ 1.977(3), N-C2 1.401(2), C2-C1 1.353(2), Li-O 1.917(3); Li-N-Li′ 75.86(14), N-Li-N′ 104.14(14).

atoms), which is the center of a fused tricyclic ladder structure. The outer planar four-membered LiNSiO rings have endocyclic angles ranging from 77.4(1)° at Li to 99.5(1)° at Si. As a result of the intramolecular coordination of the OMe group to Li, the Li–N bond is slightly longer than the Li–N′ bond (2.179(3) and 1.977(3) Å, respectively). The Li–O distance of 1.917(3) Å is appropriate for a donor–acceptor bond (cf., 1.933(3) Å in [Li{μ-N(SiMe$_3$)C(Ph)=C(H)SiMe$_3$}(thf)]$_2$.[4] The other geometric parameters are unexceptional (cf., ref. [3]). The hydrogen atom and the adamantyl groups are arranged in a cisoid fashion about each C=C bond; that is, **1** is the *Z* isomer.

The molecular structure of the azatrisilacyclobutane **3** is shown in Figure 2.[3] At its core is a puckered Si$_3$N ring which is folded by 18.4° on the N1–SiMe$_2$ vector; the silylene moieties point slightly towards each other, and the neopentyl groups at the nitrogen atoms are *cis*-orientated, away from the center of the molecule. Likewise, the bulky SiMe$_3$ and adamantyl substituents on the C=C fragment connected to the almost planar N1 (sum of angles 357.75°) point away from the molecule to give exclusively the *E* isomer of **3**, in contrast to **1**.

The Si1–Si3 (2.3578(9) Å) and Si2–Si3 (2.3592(8) Å) distances in the Si$_3$N ring are at the lower end of values reported for comparable tetrasilacycles (2.363–2.445 Å).[5] The endocyclic Si–N bond lengths are slightly longer than those within the silylene moiety. The internal angles of the Si$_3$N ring range from 75.39(3)° at the central silicon atom Si3 to 110.46(9)° at the N atom. The transannular Si···Si distance of 2.884 Å is much longer than the 2.511 Å of the sterically hindered (tBu$_2$Si)$_3$.[6] This can be compared to related Si$_3$N ring derivatives (R$_2$Si)$_3$NC$_6$H$_{11}$ (R = *i*Pr or *t*Bu; no experimental data were given; Table 1).[7] The bonding parameters of crystalline **3** are also in good agreement with the calculated values for the parent (H$_2$Si)$_3$NH (Si1···Si1′ 2.87, Si1–Si2 2.354, Si1–N 1.742 Å, and Si1-N-Si1′ 111.1°).[8, 9] No structural information is available for the azatrisilacyclobutanes (Me$_2$Si)$_3$NM(N$_3$)[CH(SiMe$_3$)$_2$]$_2$ (M = Ge and Sn), which were obtained by treatment of M[CH(SiMe$_3$)$_2$]$_2$ with N$_3$(SiMe$_2$)$_3$N$_3$.[10, 11] Only a few other X-ray-characterized compounds with Si$_3$X (X ≠ Si) ring structures have been described (Cambridge data base); X = C,[12–15] X = N,[7] X = Ge,[5, 16] X = O,[17, 18] and X = Te.[19]

The pathway leading to the lithium compound **1** (first step in Scheme 1) is likely to be similar to that described for the conversion of Li[CH(SiMe$_3$)$_2$] and *t*BuCN into the η^3-1-azaallyllithium compound **I**.[4, 20] The substitution of an SiMe$_3$ group in Li[CH(SiMe$_3$)$_2$] by SiMe$_2$OMe introduces an element of asymmetry and also an available intramolecular donor site; hence, there are a number of new features. The first is that the formation of **1** involves selective 1,3-migration from C to N of the SiMe$_2$OMe (rather than the SiMe$_3$) group; the second is the preference for the enamidolithium tautomer in **1** (cf., **I**). Both are attributed to the presence in **1** of the strong MeO →Li bond. For comparison, reference is made to

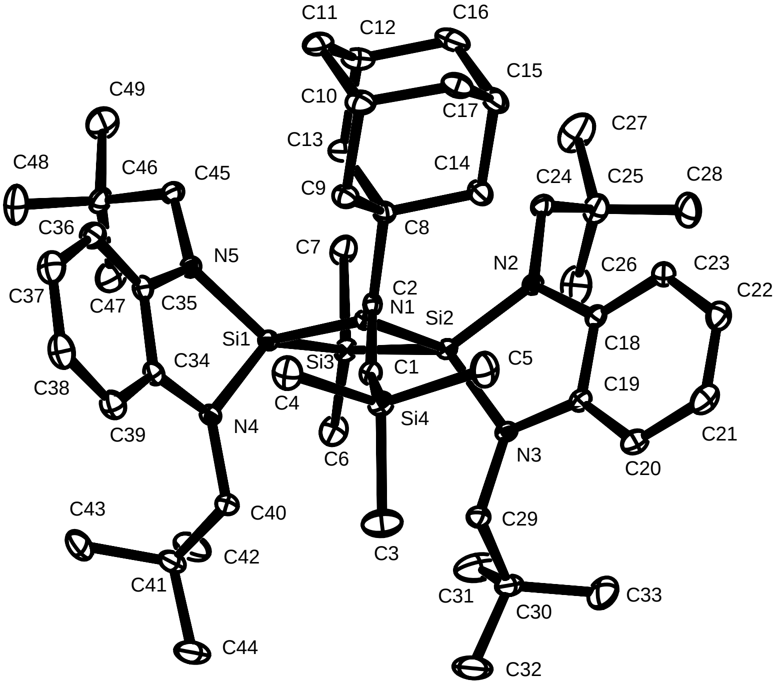
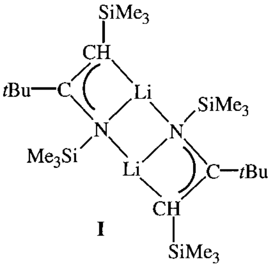


Figure 2. Molecular structure of **3** with selected bond lengths [Å] and angles [°]: Si1-N1 1.7576(18), Si1-Si3 2.3578(9), Si2-Si3 2.3592(8), Si1-N5 1.733(2), Si1-N4 1.746(2), Si2-N1 1.753(2), Si2-N3 1.745(2), N1-C2 1.459(3), C1-C2 1.352(3); N5-Si1-N4 90.56(9), N2-Si2-N3 91.03(9), N1-Si1-Si3 85.39(6), N1-Si2-Si3 85.44(6), Si1-Si3-Si2 75.39(3), Si2-N1-Si1 110.46(9).

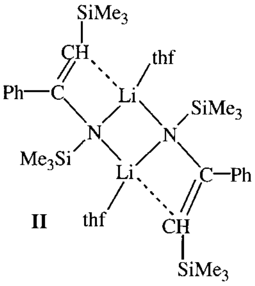
Table 1. Selected bond lengths [Å] and angles [°] for **3** and related azatrisilacyclobutanes (R$_2$Si)$_3$NC$_6$H$_{11}$.[7]

$\overline{\mathrm{NSi_aSi_bSi_c}}$	R = *i*Pr	R = *t*Bu	**3**
Si$_a$–Si$_b$	2.362(2)	2.365(2)	2.3592(8)
Si$_b$–Si$_c$	2.377(2)	2.393(2)	2.3578(9)
Si$_a$–N	1.757(4)	1.758(2)	1.7534(18)
Si$_c$–N	1.757(4)	1.768(3)	1.7576(18)
Si$_a$-N-Si$_c$	109.5(2)	109.5(2)	110.46(9)
N-Si$_a$-Si$_b$	88.2(1)	88.2(2)	85.44(6)
N-Si$_c$-Si$_b$	87.7(1)	87.7(1)	85.39(6)
Si$_a$-Si$_b$-Si$_c$	74.5(1)	74.5(1)	75.39(3)

the similar situation in **II**,[4] which has additional thf ligands. Finally, steric reasons are probably the origin of stereospecific formation of **1** as the *Z* isomer.

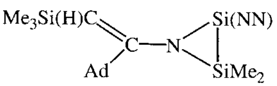


I



II

We recently examined the facile reactions between the silylene Si(NN) (**2**) and various alkali metal alkyls, a silyl, and amides that contain Li–C, Li–Si, or M–N (M = Li, Na, K) bonds. In general, **2** was readily inserted into the appropriate M–X bond to give the metal silyl M[Si(NN)X],[21, 22] except for X = N(SiMe$_3$)$_2$, for which M[Si(NN)N(SiMe$_3$)$_2$] was the transient intermediate along the pathway to the metal amide M[N(SiMe$_3$){Si(NN)SiMe$_3$}] (M = Li, Na, K).[21] Hence, we anticipated that the reaction between the lithium enamide **1** and Si(NN) would lead to the insertion product **4**. We suggest that **4** was indeed formed, but that it readily extruded LiOMe to generate the azadisilacyclopropane **5**, which in turn underwent insertion of a further molecule of Si(NN) to give the stable azatrisilacyclobutane **3**. A structure related to **5** is **III**, obtained from Si(NN) and AdN$_3$,[23] and facile insertion of Si(NN) into the Si–C bond of an oxacyclopropane or azacyclopropene is well documented.[23, 24] A remaining problem is to account for the *Z*-**1** to *E*-**3** change. As for the case of **3**, the *E* stereochemistry is clearly preferred for steric reasons, while the *Z* arrangement is attributed to **1** having reacted in solution as the η^3-1-azaallyllithium tautomer; such behavior is amply precedented.[4]



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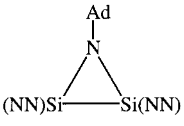

III

In conclusion, we have synthesized two novel compounds **1** and **3**, established their structures, and provided suggestions relating to plausible intermediates. These results contribute to the current interest in metal 1-azaallyls[25] and stable bis(amino)silylenes.[26, 27]

Experimental Section

1: AdCN (0.44 g, 2.74 mmol) was added in small portions to a solution of Li[CH(SiMe$_2$OMe)(SiMe$_3$)] (0.5 g, 2.74 mmol) in diethyl ether (60 mL) at ambient temperature. The mixture was stirred for 12 h. The volatile materials were removed in vacuo, and the residual solid was extracted into hot toluene. After filtration and concentration, the solution was set aside at ambient temperature to yield colorless crystals of **1** (0.6 g, 64 %). Elemental analysis (%) calcd for $C_{36}H_{68}Li_2N_2O_2Si_4$: C 62.7, H 4.06, N 9.97; found: C 60.7, H 4.03, N 9.76. M.p. 130 °C (decomp.). ^{1}H NMR (C$_6$D$_5$CD$_3$, 500.13 MHz, 348 K): $\delta = 0.17$ (s, 15 H, SiMe$_3$ and SiMe$_2$), 1.63, 1.75 and 1.95 (br s, 16 H, AdCN), 3.20 (s, 3 H, MeO), 4.49 (s, 1 H, CH allylic); ^{13}C NMR (C$_6$D$_5$CD$_3$, 125.76 MHz, 348 K): $\delta = 1.45$ (SiMe$_3$), 20.94 (SiMe$_2$), 29.76 (CH, AdCN), 37.58 (CH$_2$, AdCN), 49.49 (MeO), 97.56 (CH allyl), 179.42 (CN); ^{7}Li NMR (C$_6$D$_5$CD$_3$, 298 K): $\delta = -1.88$; ^{29}Si NMR (C$_6$D$_5$CD$_3$, 99.36 MHz, 298 K): $\delta = -13.38, -9.35$; EI-MS: *m*/*z* (%): 687 (10) [M_2]$^+$, 337 (25) [$M - \mathrm{Li}$]$^+$.

3: A solution of **2** (0.41 g, 1.51 mmol) in THF (25 mL) was added dropwise to a cooled (−40 °C) solution of **1** (0.26 g, 0.76 mmol) in THF (20 mL). The reaction mixture was allowed to warm to ambient temperature and stirred for 12 h. The volatile substances were removed in vacuo. The residue was crystallized from pentane/Et$_2$O at 15 °C to give white crystals of **3** (0.32 g, 50 %). Elemental analysis (%) calcd for $C_{49}H_{83}N_5Si_4$: C 68.9, H 9.79, N 7.58; found: C 68.2, H 9.56, N 8.19. M.p. 270–275 °C. ^{1}H NMR (C$_6$D$_6$, 300.13 MHz): $\delta = 0.16$ (s, 9 H, SiMe$_3$), 0.63 and 0.80 (s, 6 H, SiMe$_2$, diastereotopic), 1.00 and 1.07 (s, 36 H, *t*Bu), 1.24 (s, 6 H, CH$_2$ Ad), 1.60–1.68 (q, 6 H, CH$_2$, Ad), 1.88 (s, 3 H, CH, Ad), 3.25, 3.28, 3.39, 3.42, 3.59, 3.63 (two overlapping signals), and 3.66 (2 AB type, 8 H, CH$_2$), 4.77 (s, 1 H, =CH), 6.69–6.86 (m, 8 H, phenyl); ^{13}C NMR (C$_6$D$_6$, 75.47 MHz): $\delta = -0.94$ and 2.00 (SiMe$_2$, diastereotopic), 2.70 (SiMe$_3$), 29.51 (CH$_2$, Ad), 29.54 and 29.60 (C*Me$_3$*) 35.04 and 35.29 (*C*Me$_3$), 36.97 and 41.36 (CH$_2$, Ad), 53.46 and 55.06 (CH$_2$, SiN$_2$), 109.98, 111.22, 116.88, 117.71, 138.28 and 140.08 (phenyl), 120.01 (=CH), 165.58 (=CN); ^{29}Si NMR (C$_6$D$_6$, 99.36 MHz): $\delta = -28.86$ (SiMe$_2$), −19.95 (SiN$_2$), −13.05 (SiMe$_3$); EI-MS: *m*/*z* (%): 853 (100) [*M*]$^+$.

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[1] T. F. Bates, S. A. Dandekar, J. L. Longlet, K. A. Wood, R. D. Thomas, *J. Organomet. Chem.* **2000**, *595*, 87.

[2] B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. Heinicke, R. Boese, D. Bläser, *J. Organomet. Chem.* **1996**, *521*, 211.

[3] Crystallographic data for **1**: [{Li(Me$_2$OMe)SiNC(Ad)CHSiMe$_3$}$_2$], $M_r = 687.16$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.4839(3)$, $b = 11.3455(3)$, $c = 11.5638(3)$ Å, $\alpha = 112.266(2)$, $\beta = 95.250(2)$, $\gamma = 112.675(2)°$, $V = 1020.53(5)$ Å^3, $Z = 1$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $\mu = 0.18$ mm^{-1}. Data were collected at 173(2) K on a KappaCCD diffractometer; 4766 independent reflections ($R_{int} = 0.049$), 4317 reflections with $I > 2\sigma(I)$, refined using SHELXL-97,[28] $R1 = 0.050$ and $wR2$ (all data) = 0.132. CCDC-176979 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). Crystallographic data for **3**: [{Me$_3$SiC(H)C(Ad)N}{Si(NCH$_2$-Bu^t)$_2$C$_6$H$_4$}$_2${SiMe$_2$}], $M_r = 854.56$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.6544(3)$, $b = 23.1542(4)$, $c = 21.3560(6)$ Å, $\beta = 96.083(1)°$, $V = 5238.7(2)$ Å^3, $Z = 4$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $\mu = 0.15$ mm^{-1}. Data were collected at 173(2) K on a KappaCCD diffractometer; 9183 independent reflections ($R_{int} = 0.052$), 7188 reflections with $I > 2\sigma(I)$, refined using SHELXL-97,[28] $R1 = 0.049$ and $wR2$ (all data) = 0.126. CCDC-176609 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[4] P. B. Hitchcock, M. F. Lappert, M. Layh, D.-S. Liu, R. Sablong, T. Shun, *J. Chem. Soc. Dalton Trans.* **2000**, 2301.

[5] H. Suzuki, K. Okabe, R. Kato, N. Sato, Y. Fukuda, H. Watanabe, M. Goto, *Organometallics* **1993**, *12*, 4833.

[6] A. Schäfer, M. Weidenbruch, K. Peters, H. G. von Schnering, *Angew. Chem.* **1984**, *96*, 311; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 302.

[7] M. Goto, *Kagaku Gijutsu Kenkyusho Hokoku* **1991**, *86*, 127.

[8] R. S. Grev, H. F. Schaefer III, *J. Am. Chem. Soc.* **1987**, *109*, 6577.

[9] C. Liang, L. C. Allen, *J. Am. Chem. Soc.* **1991**, *113*, 1878.

[10] T. Ohtaki, W. Ando, *Chem. Lett.* **1994**, 1061.

[11] T. Ohtaki, Y. Kabe, W. Ando, *Heteroat. Chem.* **1994**, *5*, 313.

[12] M. Weidenbruch, J. Hamann, K. Peters, H. G. von Schnering, H. Marsmann, *J. Organomet. Chem.* **1992**, *441*, 185.

[13] M. Weidenbruch, J. Hamann, S. Pohl, W. Saak, *Chem. Ber.* **1992**, *125*, 1043.

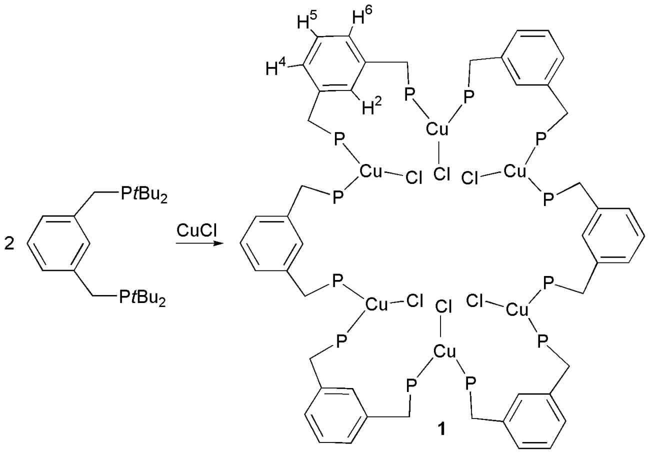
[14] D. Bravo-Zhivotovskii, Y. Apeloig, Y. Ovchinnikov, V. Igonin, Y. T. Struchkov, *J. Organomet. Chem.* **1993**, *446*, 123.
[15] Y. Apeloig, D. Bravo-Zhivotovskii, M. Bendikov, D. Danovich, M. Botoshansky, T. Vakul'skaya, M. Voronkov, R. Samoilova, M. Zdravkova, V. Igonin, V. Shklover, Yu. T. Struchkov, *J. Am. Chem. Soc.* **1999**, *121*, 8118.
[16] H. Suzuki, Y. Fukuda, N. Sato, H. Ohmori, M. Goto, H. Watanabe, *Chem. Lett.* **1991**, 853.
[17] H. Watanabe, E. Tabei, M. Goto, Y. Nagai, *J. Chem. Soc. Chem. Commun.* **1987**, 522.
[18] M. Unno, H. Masuda, H. Matsumoto, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2449.
[19] M. Weidenbruch, A. Grybat, W. Saak, E. M. Peters, K. Peters, *Monatsh. Chem.* **1999**, *130*, 157.
[20] P. B. Hitchcock, M. F. Lappert, D.-S. Liu, *J. Chem. Soc. Chem. Commun.* **1994**, 2637.
[21] B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. C. Slootweg, *Chem. Commun.* **2000**, 1427.
[22] X. Cai, B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. C. Slootweg, *J. Organomet. Chem.* **2002**, *643–644*, 272; X. Cai, B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. C. Slootweg, *J. Organomet. Chem.* **2002**, *651*, 149.
[23] B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1048.
[24] B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Organometallics* **1997**, *16*, 4861.
[25] C. F. Caro, M. F. Lappert, P. G. Merle, *Coord. Chem. Rev.* **2001**, *219–221*, 605.
[26] M. Haaf, T. A. Schmedake, R. West, *Acc. Chem. Res.* **2000**, *33*, 704.
[27] B. Gehrhus, M. F. Lappert, *J. Organomet. Chem.* **2001**, *617–618*, 209.
[28] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen (Germany), **1997**.

Synthesis, Spectroscopy, and Solid-State Structural Characterization of the Hexanuclear Copper Macrocycle [$Cu_6Cl_6(\mu$-PCHP$)_6$]**

Elizabeth D. Blue, T. Brent Gunnoe,* and
Neil R. Brooks

The study of late-transition-metal complexes with electron counts of d^8–d^{10} has been of significant interest as a result of their interesting photophysical and photoredox chemistry.[1–7] Extensive study of d^{10} systems has allowed an increased understanding of, and control over, photophysical properties, and it has been suggested that the rich luminescent behavior of many closed-shell systems arises from weak metal–metal interactions.[1–3, 5, 8, 9] Increasing interest in the preparation and study of late-transition-metal polynuclear systems stems, in part, from possible applications as therapeutic agents (e.g., photocleavage of DNA), photovoltaics, photocatalysts, and tunable chemical sensors.[2, 10–12] One challenge to both the study and the understanding of the properties of late-transition-metal polynuclear complexes is the controlled preparation of new structural motifs. Tetranuclear copper cubanes have been the focus of some attention for Group 11 transition metals,[4] and other polynuclear copper complexes with variable structural patterns are of interest and have been reported.[13–19] Closely related to work reported herein are penta- and tetranuclear copper macrocycles and recently reported high nuclearity gold systems.[12, 20–22] We now report the synthesis and characterization (including solid-state X-ray diffraction analysis) of a novel hexanuclear copper macrocycle of the type [$Cu_6Cl_6(\mu$-PCHP$)_6$] (PCHP = 1,3-$(CH_2PtBu_2)_2C_6H_4$).

The reaction of CuCl with the bisphosphane 1,3-$(CH_2PtBu_2)_2C_6H_4$ (PCHP) in a 1:2 stoichiometry yields the hexanuclear complex $Cu_6Cl_6(\mu$-PCHP$)_6$ (**1**; Scheme 1). Similar to reactions of aryl Cu^I compounds with bis(diphenylphosphanyl)methane in which metal:ligand stoichiometry is important, slow addition of the CuCl to a solution (CH_2Cl_2) of the PCHP ligand is important to the success of the reaction.[23] Complex **1** is a macrocycle that incorporates 48 atoms into the large ring structure (if the aryl moieties are each counted as contributing 3 atoms to the macrocycle) and in which each copper atom is bound by phosphorus atoms from two different PCHP ligands. Complex **1** was characterized by elemental analysis, X-ray crystallography, cyclic voltammetry experiments, as well as UV/Vis, ^1H, ^{13}C, and ^{31}P NMR spectroscopy.



Scheme 1. Preparation of the macrocycle $Cu_6Cl_6(\mu$-PCHP$)_6$ (**1**; P = $PtBu_2$).

Broad resonances in the ^1H NMR spectrum of **1** at room temperature in CD_2Cl_2 reveal a fluxional process. At −10 °C sharp resonances are observed with a singlet at $\delta = 8.68$ ppm (aromatic H2), doublets at $\delta = 8.25$ and 7.04 ppm (aromatic H4 and H6), a triplet at $\delta = 7.13$ ppm (aromatic H5), multiplets at approximately $\delta = 3.0$ ppm corresponding to the methylene protons, and four phosphane *t*Bu resonances between $\delta = 1.0$ and 1.8 ppm. The aromatic C2–H2 bonds

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[*] Prof. T. B. Gunnoe, E. D. Blue
Department of Chemistry
North Carolina State University
Campus Box 8204, Raleigh, NC 27695-8204 (USA)
Fax: (+1) 919-515-8909
E-mail: brent_gunnoe@ncsu.edu

Dr. N. R. Brooks
X-ray Crystallographic Laboratory, Department of Chemistry
University of Minnesota, Minneapolis, MN 55455 (USA)

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