

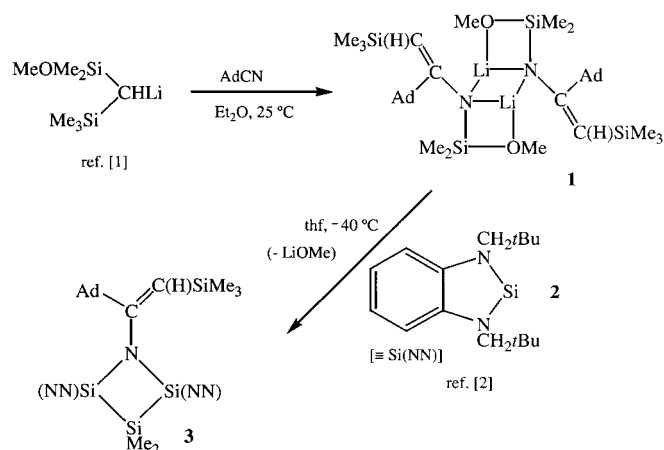
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- [7] Representative data. **1**: Yield: 51%; m.p. > 300 °C; UV/Vis (CHCl₃): λ_{max} ($\epsilon \times 10^{-4}$) = 573 (8.96), 555(sh), 532 (2.59), 309 (4.04), 275 (3.03) nm; FAB-MS (*m*-nitrobenzyl alcohol): calcd for C₂₄BClF₁₂N₆: *m/z*: 646 [*M*⁺]. *cis* Isomer **2**: Yield: < 1%; m.p. > 320 °C; ¹H NMR (300 MHz, CDCl₃): δ = 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 (CHCl₃): λ_{max} ($\epsilon \times 10^{-4}$) = 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 C₄₂H₃B₂Cl₂F₁₆N₁₂: [*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, CDCl₃): δ = 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 (CHCl₃): λ_{max} ($\epsilon \times 10^{-4}$) = 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 C₄₂H₃B₂Cl₂F₁₆N₁₂: [*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, *P*₂₁/*c*, *a* = 11.2997(11), *b* = 10.6022(11), *c* = 19.1563(19) Å, β = 95.507(7)°, *V* = 2284.4(4) Å³, *Z* = 4, ρ_{calcd} = 1.880 Mg m⁻³, $2\theta_{\text{max}}$ = 52.7°, λ = 0.71073 Å, ω scans, 170(2) K, 20288 measured, 4664 independent reflections included in the refinement, Lorentzian but no absorption corrections performed (μ = 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 CH₂Cl₂ **2**: 0.04 × 0.04 × 0.40 mm, monoclinic, *P*₂₁/*c*, *a* = 14.4237(13), *b* = 31.630(3), *c* = 10.2000(10) Å, β = 101.354(3)°, *V* = 4562.4(7) Å³, *Z* = 4, ρ_{calcd} = 1.807 Mg m⁻³, $2\theta_{\text{max}}$ = 56.6°, λ = 0.71073 Å, ω scans, 91(2) K, 37305 measured, 6637 independent reflections included in the refinement, Lorentzian and absorption corrections (SADABS) performed (μ = 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 CH₂Cl₂ **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, α = 107.608(4), β = 91.300(5), γ = 101.347(4)°, *V* = 2360.8(4) Å³, *Z* = 2, ρ_{calcd} = 1.805 Mg m⁻³, $2\theta_{\text{max}}$ = 50.7°, λ = 0.71073 Å, ω scans, 91(2) K, 22234 measured, 8623 independent reflections included in the refinement, Lorentzian but no absorption corrections performed (μ = 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 e Å⁻³. CCDC-181314 (**1**), CCDC-181315 (**2**), and CCDC-181316 (**3**) contain 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 Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).
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Synthesis and Structure of an Azatrisilacyclobutane and Its Precursor, a Novel Lithium Enamide Having a Tricyclic (LiNSiO)₂ Skeleton**

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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(SiMe₂OMe)(SiMe₃)]^[1] to yield the lithium enamide **1**. The second deals with the insertion of the thermally stable bis(amino)silylene Si[(NCH₂tBu)₂C₆H₄-1,2] (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.

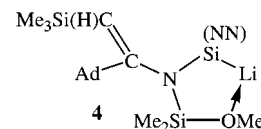
The reactions and conditions leading to the new colorless crystalline compounds **1** and **3** are summarized in Scheme 1.



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.

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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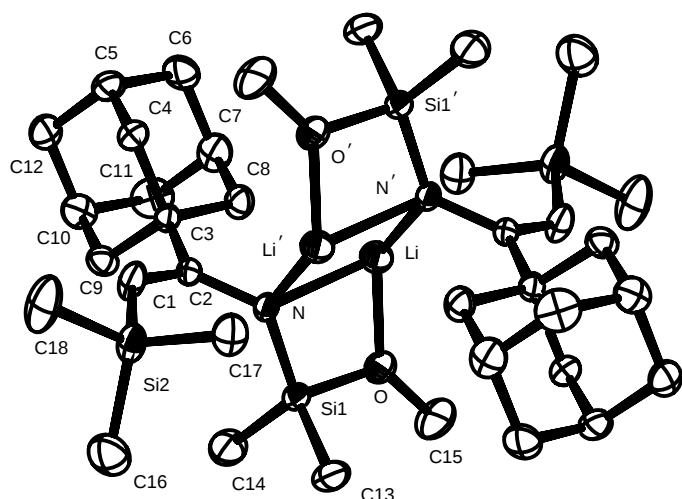


Figure 1. Molecular structure of **1** with selected bond lengths [Å] and angles [°]: Li–N 2.179(3), Li–N' 1.977(3), N–C2 1.401(2), C2–C1 1.353(2), Li–O 1.917(3); Li–N–Li' 75.86(14), N–Li–N' 104.14(14).

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(SiMe₃)C(Ph)=C(H)SiMe₃}(thf)₂]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 Si₃N ring which is folded by 18.4° on the N1–SiMe₂ 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 SiMe₃ 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 Si₃N 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 Si₃N 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 (*t*Bu₂Si)₃.^[6] This can be compared to related Si₃N ring derivatives (R₂Si)₃NC₆H₁₁ (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 (H₂Si)₃NH (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 (Me₂Si)₃NM(N₃)[CH(SiMe₃)₂]₂ (M = Ge and Sn), which were obtained by treatment of M[CH(SiMe₃)₂]₂ with N₃(SiMe₃)₃N₃.^[10, 11] Only a few other X-ray-characterized compounds with Si₃X (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(SiMe₃)₂] and *t*BuCN into the η³-1-azaallyllithium compound **1**.^[4, 20] The substitution of an SiMe₃ group in Li[CH(SiMe₃)₂] by SiMe₂OMe 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 SiMe₂OMe (rather than the SiMe₃) group; the second is the preference for the enamidolithium tautomer in **1** (cf., **1**). Both are attributed to the presence in **1** of the strong MeO → Li bond. For comparison, reference is made to

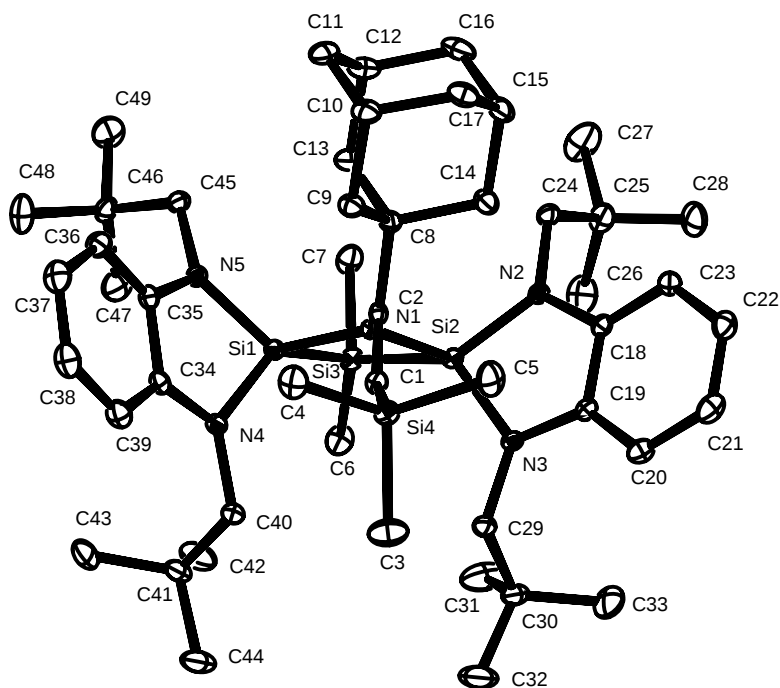
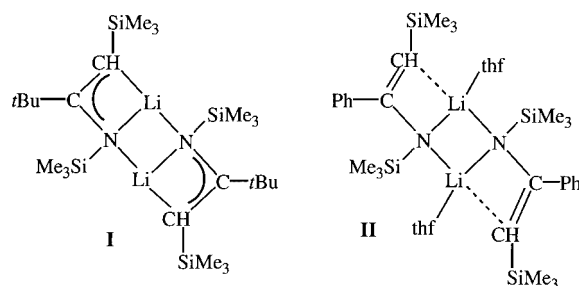


Figure 2. Molecular structure of **3** with selected bond lengths [Å] and angles [°]: Si1–N1 1.7576(18), Si1–Si3 2.3578(9), Si2–Si3 2.3592(8), Si1–N5 1.733(2), Si1–N4 1.746(2), Si2–N1 1.753(2), Si2–N3 1.745(2), N1–C2 1.459(3), C1–C2 1.352(3); N5–Si1–N4 90.56(9), N2–Si2–N3 91.03(9), N1–Si1–Si3 85.39(6),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

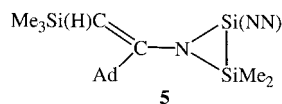
Table 1. Selected bond lengths [Å] and angles [°] for **3** and related azatrisilacyclobutanes (R₂Si)₃NC₆H₁₁.^[7]

NSi _a Si _b Si _c	R = <i>i</i> Pr	R = <i>t</i> 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)

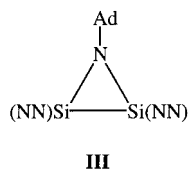
the similar situation in **II**,^[4] which has additional thf ligands. Finally, steric reasons are probably the origin of stereospecific formation of **1** as the *Z* isomer.



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(SiMe₃)₂, for which M[Si(NN)N(SiMe₃)₂] was the transient intermediate along the pathway to the metal amide M[N(SiMe₃)₂Si(NN)SiMe₃] (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 azadisilacyclobutane **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 AdN₃,^[23] and facile insertion of Si(NN) into the Si–C bond of an oxacyclobutane or azacyclobutene 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]

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(SiMe₂OMe)(SiMe₃)] (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 C₃₆H₆₈Li₂N₂O₂Si₄: C 62.7, H 4.06, N 9.97; found: C 60.7, H 4.03, N 9.76. M.p. 130 °C (decomp.). ¹H NMR (C₆D₅CD₃, 500.13 MHz, 348 K): δ = 0.17 (s, 15H, SiMe₃ and SiMe₂), 1.63, 1.75 and 1.95 (brs, 16H, AdCN), 3.20 (s, 3H, MeO), 4.49 (s, 1H, CH allylic);

¹³C NMR (C₆D₅CD₃, 125.76 MHz, 348 K): δ = 1.45 (SiMe₃), 20.94 (SiMe₂), 29.76 (CH, AdCN), 37.58 (CH₂, AdCN), 49.49 (MeO), 97.56 (CH allyl), 179.42 (CN); ⁷Li NMR (C₆D₅CD₃, 298 K): δ = –1.88; ²⁹Si NMR (C₆D₅CD₃, 99.36 MHz, 298 K): δ = –13.38, –9.35; EI-MS: *m/z* (%): 687 (10) [M]⁺, 337 (25) [M – 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/Et₂O at 15 °C to give white crystals of **3** (0.32 g, 50 %). Elemental analysis (%) calcd for C₄₉H₈₃N₅Si₄: C 68.9, H 9.79, N 7.58; found: C 68.2, H 9.56, N 8.19. M.p. 270–275 °C. ¹H NMR (C₆D₆, 300.13 MHz): δ = 0.16 (s, 9H, SiMe₃), 0.63 and 0.80 (s, 6H, SiMe₂, diastereotopic), 1.00 and 1.07 (s, 36H, tBu), 1.24 (s, 6H, CH₂ Ad), 1.60–1.68 (q, 6H, CH₂, Ad), 1.88 (s, 3H, CH, Ad), 3.25, 3.28, 3.39, 3.42, 3.59, 3.63 (two overlapping signals), and 3.66 (2 AB type, 8H, CH₂), 4.77 (s, 1H, =CH), 6.69–6.86 (m, 8H, phenyl); ¹³C NMR (C₆D₆, 75.47 MHz): δ = –0.94 and 2.00 (SiMe₂, diastereotopic), 2.70 (SiMe₃), 29.51 (CH₂, Ad), 29.54 and 29.60 (CMe₃) 35.04 and 35.29 (CMe₃), 36.97 and 41.36 (CH₂, Ad), 53.46 and 55.06 (CH₂, SiN₂), 109.98, 111.22, 116.88, 117.71, 138.28 and 140.08 (phenyl), 120.01 (=CH), 165.58 (=CN); ²⁹Si NMR (C₆D₆, 99.36 MHz): δ = –28.86 (SiMe₂), –19.95 (SiN₂), –13.05 (SiMe₃); EI-MS: *m/z* (%): 853 (100) [M]⁺.

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- [3] Crystallographic data for **1**: [[Li(Me₂OMe)SiNC(Ad)CHSiMe₃]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, α = 112.266(2), β = 95.250(2), γ = 112.675(2)°, *V* = 1020.53(5) Å³, *Z* = 1, λ (MoK α) = 0.71073 Å, μ = 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* > 2σ(*I*), refined using SHELXL-97,^[28] *R*1 = 0.050 and *wR*2 (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/contents/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**: [[Me₃SiC(H)C(Ad)N][Si(NCH₂–Bu)₂C₆H₄]₂SiMe₃], *M_r* = 854.56, monoclinic, space group *P*₂/*c* (no. 14), *a* = 10.6544(3), *b* = 23.1542(4), *c* = 21.3560(6) Å, β = 96.083(1)°, *V* = 5238.7(2) Å³, *Z* = 4, λ (MoK α) = 0.71073 Å, μ = 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* > 2σ(*I*), refined using SHELXL-97,^[28] *R*1 = 0.049 and *wR*2 (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/contents/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).
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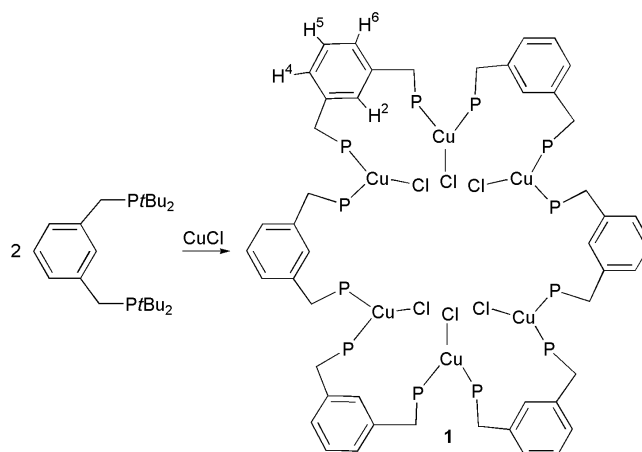
Synthesis, Spectroscopy, and Solid-State Structural Characterization of the Hexanuclear Copper Macrocycle $[\text{Cu}_6\text{Cl}_6(\mu\text{-PCHP})_6]^{**}$

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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 $[\text{Cu}_6\text{Cl}_6(\mu\text{-PCHP})_6]$ (PCHP = 1,3- $(\text{CH}_2\text{PrBu}_2)_2\text{C}_6\text{H}_4$).

The reaction of CuCl with the bisphosphane 1,3- $(\text{CH}_2\text{PrBu}_2)_2\text{C}_6\text{H}_4$ (PCHP) in a 1:2 stoichiometry yields the hexanuclear complex $\text{Cu}_6\text{Cl}_6(\mu\text{-PCHP})_6$ (**1**; Scheme 1). Sim-



Scheme 1. Preparation of the macrocycle $\text{Cu}_6\text{Cl}_6(\mu\text{-PCHP})_6$ (**1**; P = PrBu_2).

ilar 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.

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 $t\text{Bu}$ resonances between $\delta = 1.0$ and 1.8 ppm. The aromatic C2–H2 bonds

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