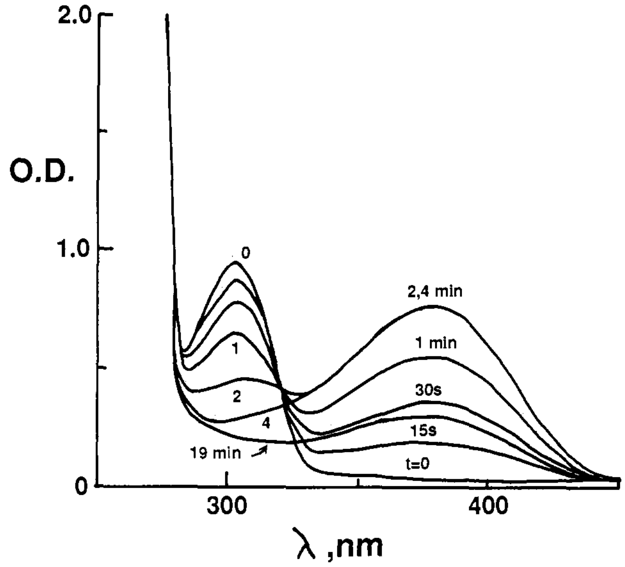
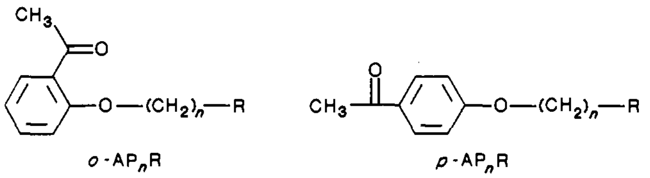


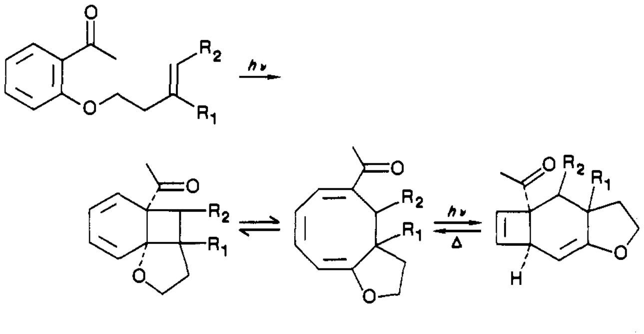
Figure 1. UV spectrum of 0.00024 M *o*-AP$_2$b in benzene as a function of time of 313-nm irradiation.

Chart I

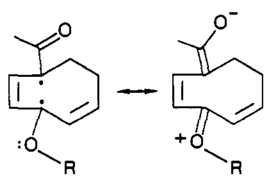


o-AP$_2$a	R, CH═CH$_2$	*p*-AP$_2$a, *p*-AP$_3$a
o-AP$_2$b	R, CMe═CH$_2$	*p*-AP$_2$b
o-AP$_2$c	R, CH═CH—Et	*p*-AP$_2$c
o-AP$_2$d	R, CH═CMe$_2$	*p*-AP$_3$d

Scheme I



same bond weakening presumably promotes the unusually rapid bicyclo[4.2.0]octa-2,4-diene to cycloöctatriene rearrangement.



In summary, intramolecular 2 + 2 cycloaddition of double bonds to the benzene ring of π,π^* triplet ketones leads in good chemical yield to bicyclo[4.2.0]octadiene and cycloöctatriene structures that can be interconverted cleanly. The carbonyl that facilitates the reaction by causing efficient intersystem crossing of the n,π^* singlet remains for further synthetic elaboration, such that the overall process appears to have considerable potential. In fact, we are now looking at the bimolecular counterpart and observe that the analogous cycloaddition indeed occurs.[14] We shall report on the regioselectivity as soon as a general pattern emerges.

Acknowledgment. This work was supported by NSF Grant CHE 85-06703. We thank Prof. Andrew Gilbert for informing us that he has observed similar photoreactions.

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[14] Irradiation of *p*-methoxyacetophenone in 1-hexene and GC collection produces a yellow compound with the characteristic NMR spectrum of a cycloöctatriene.

A "Clustered Cluster" with a "Pinwheel" Ligand Array. Synthesis and Structure of a Trinuclear Cupracarborane

Han Chyul Kang, Youngkyu Do,† Carolyn B. Knobler, and
M. Frederick Hawthorne*

Department of Chemistry and Biochemistry
University of California, Los Angeles
Los Angeles, California 90024

Received April 30, 1987

Recent applications of [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ (**1**)[1] in synthetic metallacarborane chemistry have resulted in novel polynuclear metallacarboranes containing M-H-B bridge bonds (M = metal). Examples include [$(C_2H_5)_2Al_2(\mu\text{-H})_2(C_2B_9H_9)(C_2B_9H_{11})$],[2] [$M_2Cu_2(\mu\text{-CO})_4(CO)_2(\mu\text{-H})_2(C_2B_9H_{10})_2$]$^{2-}$ (M = Mo, W),[3] and [$(PPh_3)_2Cu_2(\mu\text{-H})_2C_2B_9H_9$] (**2**).[4] The structural diversity observed in these metallacarboranes stems from the intrinsic dualism in the electron-donor properties of **1**. As an example, the homodinuclear formal d^{10} copper(I) complex **2** demonstrates two diverse bonding modes: an icosahedral *closo*-Cu^{I}C$_2$B$_9$ cage and a copper–copper interaction supported by Cu-H-B bridge bonds. Reported herein are the synthesis and structural characterization of a "clustered cluster",[3] [$Cu_3(\mu\text{-H})_3(C_2B_9H_9L)_3\cdot(n\text{-}C_7H_{16})$] [**3**·($n$-$C_7H_{16}$), L = methyl isonicotinate], containing *nido*-Cu^{I}C$_2$B$_9$ cages as well as Cu(I)–Cu(I) and Cu-H-B interactions.

The anaerobic reaction of **1** with 1 molar equiv of anhydrous CuCl produced glittering metallic copper and an intense blue coloration, indicating that an undesirable redox reaction had occurred.[5] In contrast to this observation, a "charge-compensated" carborane anion, [*nido*-9-($NC_5H_4CO_2CH_3$)-7,8-$C_2B_9H_{10}$]$^-$ (**4**), generated by deprotonation of the oxidative coupling[6] product[7] of [*nido*-7,8-$C_2B_9H_{12}$]$^-$ with a Lewis base, methyl isonicotinate ($NC_5H_4CO_2CH_3$), reacted with an equimolar amount of anhydrous CuCl in THF to give a novel tricopper "clustered cluster" **3** as outlined in eq 1–3. A deep bluish purple solution of Na·**4**

$$\mathrm{K}[nido\text{-}7,8\text{-}C_2B_9H_{12}] + NC_5H_4CO_2CH_3 + 2FeCl_3 \xrightarrow{\text{benzene}} [nido\text{-}9\text{-}(NC_5H_4CO_2CH_3)\text{-}7,8\text{-}C_2B_9H_{11}] + 2FeCl_2 + HCl + KCl \quad (1)$$

$$[nido\text{-}9\text{-}(NC_5H_4CO_2CH_3)\text{-}7,8\text{-}C_2B_9H_{11}] + NaH \xrightarrow{\text{THF}} Na[nido\text{-}9\text{-}(NC_5H_4CO_2CH_3)\text{-}7,8\text{-}C_2B_9H_{10}] + H_2 \quad (2)$$

$$3CuCl + 3Na[nido\text{-}9\text{-}(NC_5H_4CO_2CH_3)\text{-}7,8\text{-}C_2B_9H_{10}] \xrightarrow{\text{THF}} [Cu_3(\mu\text{-H})_3(C_2B_9H_9NC_5H_4CO_2CH_3)_3] + 3NaCl \quad (3)$$

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† Present address: Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul, Korea.

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[5] An intense blue coloration is a typical indication of the formation of [$Cu(C_2B_9H_{11})_2$]$^{2-}$: (a) Reference 1. (b) Warren, L. F., Jr.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 4823.

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[7] Spectroscopic data for [*nido*-9-($NC_5H_4CO_2CH_3$)-7,8-$C_2B_9H_{11}$]: IR spectrum (KBr): 3116 (w), 2561 (s), 2529 (s), 1731 (s), 1434 (s), 1325 (w), 1288 (s), 1244 (w), 1118 (m), 1026 (w), 959 (w), 868 (w), 830 (w), 766 (w), 687 (w) cm^{-1}. Chemical shifts upfield of the reference are designated as negative. ^{11}B{^{1}H} NMR (160.463 MHz) (THF, referenced to external BF$_3$·OEt$_2$ in C$_6$D$_6$): 1.3, –5.6, –16.6, –17.7, –20.2, –22.0, –27.7, –30.5, –37.7 ppm. ^{1}H NMR (200.133 MHz) (CD$_2$Cl$_2$, referenced to residual solvent protons = 5.32 ppm): 9.0 (d, NC$_5$H$_4$), 8.2 (d, NC$_5$H$_4$), 4.1 (s, CH$_3$), 2.9 (s, carborane CH), 2.2 (s, carborane CH), –2.7 (br, B–H–B) ppm.

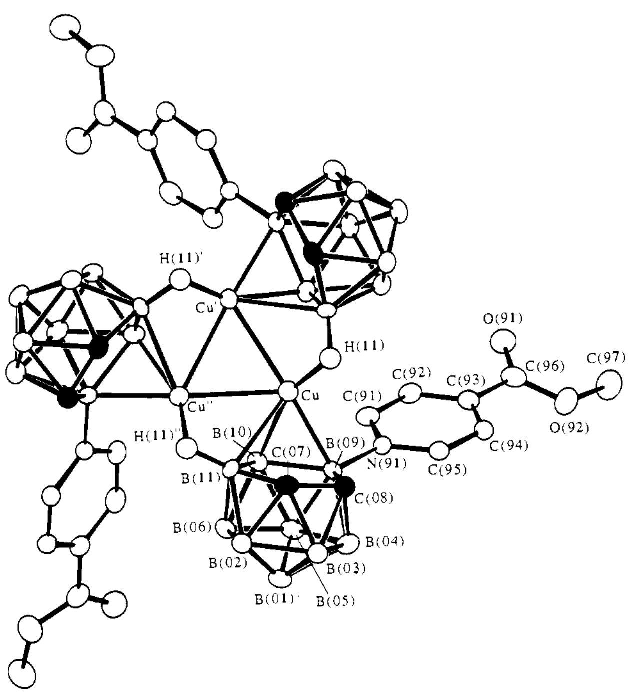

Figure 1. Structure of $[Cu_3(\mu\text{-}H)_3(C_2B_9H_9NC_5H_4CO_2CH_3)_3]$ showing the atom labeling scheme. All hydrogen atoms except the bridging hydrides have been omitted for clarity. Selected values of interatomic distances (Å): Cu–Cu′, 2.519 (2); Cu–H(11), 1.608; Cu–C(7), 2.634 (9); Cu–C(8), 2.635 (9); Cu–B(9), 2.265 (8); Cu–B(10), 2.116 (8); Cu–B(11), 2.307 (8); Cu″-B(11), 2.120 (8); B(11)–H(11)″, 1.214; N(91)–B(9), 1.552(9). Selected interatomic angles (deg): Cu–Cu′–Cu″, 60; Cu″–H(11)″–B(11), 96.37; Cu″–Cu–B(11), 51.89 (20); Cu′–Cu–H(11), 85.81; Cu–B(9)–N(91), 104.72 (44); Cu–B(11)–H(11)″, 105.94.

(1 mmol) in THF was allowed to react anaerobically with 1 mmol of CuCl at ambient temperature for 20 h, developing an intensely red reaction mixture. Filtration produced a filtrate which was repeatedly treated with *n*-heptane until the precipitation of an unidentified orange-yellow solid ceased. Removal of this solid followed by further treatment of the filtrate with *n*-heptane afforded red crystalline **3**·(n-C_7H_{16}), the nature of which was established by single-crystal X-ray analysis[8] as well as other means.[9]

The crystal structure of the racemic system consists of well-separated neutral trinuclear cupracarborane clusters and disordered *n*-heptane solvate molecules. The structure of one enantiomeric from of **3** is displayed in Figure 1. The metallacarborane cluster **3** contains three $[CuC_2B_9H_{10}NC_5H_4CO_2CH_3]$ units which are linked by both Cu–H–B and Cu–Cu interactions about a crystallographic 3-fold axis such that a "pinwheel" structure results. Each of the elements associated with the three Cu–H–B bridge bonds taken separately form three equilateral triangles, the interplanar distances of which are 0.549 Å (between the Cu_3 and the B_3 plane) and 1.050 Å (between the Cu_3 and the H_3 plane).

Compound **3** contains the ubiquitous triangular geometry of trinuclear complexes, but represents the first example of a discrete equilateral metallic core of Cu(I) with a relatively short copper–copper distance of 2.519 (2) Å. Several trinuclear complexes containing a scalene or isosceles Cu_3 triangle have been previously reported.[10,11] The edge distances range from 2.749 to 3.610 Å[10,11] although one exceptionally short copper–copper distance of 2.546 Å is associated with $[(CuI)_3(Ph_2PCH_2PPh_2)_2]$.[10b] The triangular Cu_3 core has also been observed in polynuclear raft systems where neighboring copper atoms are disposed in such a fashion as to give relatively short edge distances (~2.62 Å).[12] The relatively short interatomic Cu(I)–Cu(I) separations in **3** can be described in terms of a metal–metal interaction since the requirements of the bridging ligand set[13] of **4** are likely to be minimal as observed in **2**.[4]

The polyhedral frameworks of the CuC_2B_9 cages in **3** adopt nido geometry, which is a common structural pattern observed in the electron-rich late transition metal metallacarboranes.[14,15] In **3**, the lower B_5 plane is nearly planar (±0.001 Å) while the upper C_2B_3 plane is slightly distorted with folding parameters[14] θ and ϕ of 1.6° and 2.0°, respectively. The copper atom slips toward the B_3 unit of the upper C_2B_3 plane with the value of 0.59 Å for the slipping parameter Δ,[14] resulting in η^3-borallylic ligation of **4** to the metal atom. This feature is reflected in a Cu–C/Cu–B distance ratio (1.18). These values for Δ and the distance ratio fall into the range observed in slipped metallacarboranes rather than closo icosahedral metallacarboranes.[4] The nido geometry for the CuC_2B_9 cages in **3** is in marked contrast to the closo CuC_2B_9 geometry in **2** and [*closo*-3-(PPh_3)-3,1,2-$CuC_2B_9H_{11}]^-$.[4]

In **3**, the methyl isonicotinate rings exhibit unhindered rotation in solution as low as 198 K as observed by variable-temperature ^1H FT NMR spectroscopy. Sterically, the methyl isonicotinate group can be regarded as an "innocent" substituent. Electronically, the methyl isonicotinate substituent apparently interacts with the C_2B_9 cage[16] and supports the formation and stabilization of a triangular d^{10} Cu_3 core in **3**. Additional evidence related to this electronic interaction comes from the isolation and X-ray analysis of a methyl isonicotinate substituted analogue of [*closo*-3-(PPh_3)-3,1,2-$CuC_2B_9H_{11}]^-$, [*closo*-3-(PPh_3)-4-$(NC_5H_4CO_2CH_3)$-3,1,2-$CuC_2B_9H_{10}$] (**5**).[17] In this neutral cupracarborane the degree of metal atom displacement falls into the intermediate region between the closo geometry seen in [*closo*-3-(PPh_3)-3,1,2-$CuC_2B_9H_{11}]^-$ and the nido geometry expected and observed in **3**, indicating that the substituent is not electronically innocent. It is interesting to note that the formation of **5** from **3** can be inferred from ^{31}P NMR spectra. When a THF solution of **3** and an excess of triphenylphosphine was stirred at

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(8) (a) A low-temperature X-ray diffraction study has been carried out since single-crystal X-ray analysis performed at 298 K revealed a severely disordered solvate molecule. Diffraction data were collected at 128 K on a Picker FACS-1 diffractometer modified by Professor C. E. Strouse of this department, using Mo Kα radiation, to a maximum 2θ of 50°. Data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by conventional heavy-atom techniques. (b) Crystallographic data for **3**·(n-C_7H_{16}): a = 17.280 (4) Å, c = 28.630 (7) Å, V = 7457 Å^3; rhombohedral space group, $R\bar{3}$; unique data ($I > 3\sigma(I)$), 2309; R (R_w), 6.5% (10.6%). All calculations were performed on the DEC VAX 750 of the J. D. McCullough Crystallography Laboratory using the UCLA crystallographic package.

(9) IR spectrum (KBr): 3119 (w), 2951 (w), 2557 (s), 2440 (w), 2368 (w), 1733 (s), 1434 (s), 1327 (m), 1294 (s), 1113 (s), 1087 (m), 956 (w), 868 (w), 763 (w), 693 (w), 502 (w), 450 (w) cm^{-1}. Chemical shifts upfield of the reference are designated as negative. $^{11}B\{^1H\}$ NMR (160.463 MHz) in THF, referenced to external $BF_3 \cdot OEt_2$ in C_6D_6: −6.0, −12.6 −19.7, −26.7, −30.7, −34.6 ppm. ^1H NMR (200.133 MHz) in CD_2Cl_2 (referenced to residual solvent protons = 5.32 ppm): 8.7 (m, NC_5H_4), 8.1 (d, NC_5H_4), 4.0 (s, CH_3), 2.8 (s, carborane CH), 2.0 (s, carborane CH) ppm.

(10) Scalene triangular Cu_3 core: (a) Rao, Ch. P.; Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1986**, *25*, 428. (b) Ho, D. M.; Bau, R. *Inorg. Chem.* **1983**, *22*, 4079. (c) Nardin, G.; Randaccio, L.; Zangrando, E. *J. Chem. Soc. Dalton Trans.* **1975**, 2566. (d) Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *J. Organomet. Chem.* **1973**, *60*, C39.

(11) Isosceles triangular Cu_3 core: (a) Bresciani, N.; Marsich, N.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1974**, *10*, L5. (b) Tiethof, J. A.; Stalick, J. K.; Corfield, P. W. R.; Meek, D. W. *J. Chem. Soc., Chem. Commun.* **1972**, 1141.

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(16) A deep bluish purple coloration of Na[*nido*-9-$(NC_5H_4CO_2CH_3)$-7,8-$C_2B_9H_{10}$] in THF as compared to a colorless solution of Na_2[*nido*-7,8-$C_2B_9H_{11}$] in THF can be considered to be a consequence of a carborane anion-to-ligand charge-transfer excitation.

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ambient temperature under an argon atmosphere, the ^{31}P NMR spectrum of the resulting mixture displayed a signal corresponding to that of **5**,[18] in addition of the resonance for the free triphenylphosphine. This interconversion was further substantiated by the ^{11}B NMR of the reaction mixture.[18]

Acknowledgment. We gratefully acknowledge the support of this work by the Office of Naval Research. We also thank Dr. A. Varadarajan for useful discussions.

Supplementary Material Available: Details of crystallographic data collection, tables of positional and thermal parameters, and tables of interatomic distances and angles for **3**·(n-C_7H_{16}) (12 pages); listing of observed and calculated structure factors for **3**·(n-C_7H_6) (12 pages). Ordering information is given on any current masthead page.

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[18] NMR data for [*closo*-3-(PPh_3)-4-($NC_5H_4CO_2CH_3$)-3,1,2-$CuC_2B_9H_{10}$]: $^{31}P\{^1H\}$ NMR (81.02 MHz) (10% C_6D_6/THF, referenced to external 85% H_3PO_4) 8.4 ppm; $^{11}B\{^1H\}$ NMR (160.463 MHz) (THF): −6.7, −16.0, −17.2, −19.5, −22.3, −26.4, −34.7 ppm.

Studies of the Chemistry of Tri(*tert*-butoxy)silyl Isocyanide. Ab Initio Calculations of Silyl Cyanide/Isocyanide Energies

Walter R. Hertler,* David A. Dixon,* Ellen W. Matthews,
Fredric Davidson, and Fulton G. Kitson

Contribution No. 4406
Central Research and Development Department
E. I. Du Pont de Nemours & Co., Inc.
Experimental Station, Wilmington, Delaware 19898

Received June 15, 1987

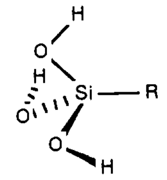
The facile equilibration of silyl isocyanides and silyl cyanides, which has been recognized for nearly three decades,[1,2] and the generally low equilibrium concentration of the isocyanide (0.15% in the case of trimethylsilyl isocyanide at 25 °C)[2,3] have discouraged comparative chemical reactivity studies of these species.[4] CNDO calculations[5] predict silyl cyanide to be ~55 kcal/mol more stable than silyl isocyanide. We have found that tri(*tert*-butoxy)silyl cyanide (**1**) and -isocyanide (**2**)[6] at room temperature equilibrate only very slowly with a half-life of about 3 months. Thus, for the first time a system is available for the independent study of the chemistry of silyl cyanides and isocyanides without interference from equilibration. We also present high level ab initio calculations on silyl cyanide (**3**) and isocyanide (**4**) and on a conformer of $(OH)_3SiCN$ (**5**) and $(OH)_3SiNC$ (**6**).

As prepared, mixtures of **1** and **2** contain 1–4% of **2**, depending upon the distillation conditions. Heating at reflux (bp, 232 °C) increases the **2** content to 6–7%. ^{13}C NMR analysis[7] showed the presence of 6.5% of **2**, which then permitted the estimation of IR extinction coefficients for the –CN and –NC stretching vibrations.[8] The facile separation of **1** and **2** by GC permitted characterization by mass spectroscopy which showed nearly identical fragmentation patterns for the two isomers.

In contrast to the potent silylating agent,[9] trimethylsilyl cyanide, a solution of **1** and **2** (6% **2**) reacts only slowly with methanol during several days at 25 °C. Acetic acid is far more reactive than is methanol, but in both cases little, if any, of **1** reacts before **2** is consumed.

Similarly, ethylenebis(triphenylphosphine)platinum[10] coordinates only the isocyanide **2** as evidenced by the disappearance of the 2103-cm^{-1} IR band and the appearance of new bands at 2015 and 1915 cm^{-1}. The 2198-cm^{-1} band of **1** is unchanged. The degenerate cyanide-exchange reaction which occurs rapidly in CD_3CN solutions of tetraethylammonium cyanide (TEACN) and either trimethylsilyl cyanide or triisopropylsilyl cyanide (as evidenced by a single time-averaged CN resonance in each ^{13}C NMR spectrum) does not occur on the NMR time scale in a solution of TEACN and a mixture of **1** and **2**. That the reaction does occur on a slower time scale, however, was demonstrated by an NMR experiment with [^{15}N]-TEACN. We attribute the retardation of the cyanide exchange to steric hindrance by the *tert*-butyl groups in the transition state leading to a pentaccordinate dicyanotrialkoxy siliconate. Because the thermal equilibration of **2**-enriched samples of **1** at 25 °C is too slow to be used for determination of the equilibrium composition, equilibration with TEACN was used to determine that the equilibrium composition at 25 °C is 1.1% **2** and 98.9% **1**. From the temperature–equilibrium constant data, $\Delta G = 2.7 \pm 1.1$ kcal/mol, $\Delta H = 2.6 \pm 1.1$ kcal/mol, and $\Delta S = 0 \pm 0.6$ eu. The value of ΔH is somewhat lower than the value of 4.0 ± 0.04 kcal/mol found for the pair Me_3SiCN and Me_3SiNC.[3]

Geometries were gradient optimized[11-13] at the ab initio level in C_{3v} symmetry for **3**, **4**, **5**, and **6**. The last two compounds were optimized in the following conformation in order to mimic the type of conformation expected when an alkyl group is substituted for hydrogen and to avoid hydrogen bonding. At the optimized geometries, the force fields were calculated analytically[14] as were the infrared intensities and MP-2 correlation corrections.[15] The geometry optimizations of **3** and **4** were done with a polarized double-ζ basis set (basis set 1) of the form (11s7p1d/9s5p1d/4s1p)/[6s4p1d/3s2p1d/2s1p] in the order Si/C, N/H.[16] Final



5 : R = CN

6 : R = NC

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[7] ^{13}C NMR ($CDCl_3$, 75.6 MHz, δ ppm downfield from tetramethylsilane) for **1**: 125.2 (CN), 75.89 (quat C), 31.16 (Me); for **2**: 180.8, 75.44, 30.92. ^{29}Si NMR (59.7 MHz) for **1**: −104.9; for **2**: −93.2. ^1H NMR (300 MHz) for **1**: 1.325; for **2**: 1.311.

[8] The IR extinction coefficients (L·mol^{-1}·cm^{-1}) for the CN stretch of **1** (2198 cm^{-1}) and **2** (2103 cm^{-1}) are 124 and 900 in CCl_4, 132 and 1132 in 1-chloronaphthalene, and 180 and 1545 in THF, respectively.

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