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]

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Supplementary Material Available: Details of crystallographic data collection, tables of positional and thermal parameters, and tables of interatomic distances and angles for **3**$\cdot$(n-C_7H_{16}) (12 pages); listing of observed and calculated structure factors for **3**$\cdot$(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{^{1}H} NMR (81.02 MHz) (10% C_6D_6/THF, referenced to external 85% H_3PO_4) 8.4 ppm; ^{11}B{^{1}H} 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

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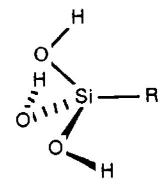
The facile equilibration of silyl isocyanides and silyl cyanides, which has been recognized for nearly three decades,[1,2] and the generally low equilibrium concentration of the isocyanide (0.15% in the case of trimethylsilyl isocyanide at 25 °C)[2,3] have discouraged comparative chemical reactivity 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. ^{1}H 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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calculations at the optimized geometry were done with a larger basis set of the form (13s9p1d/10s6p1d/5s1p)/[6s4p1d/5s3p1d/3s1p].[17] All of the calculations on **5** and **6** were done with basis set 1.

The calculated geometry for **3** has r(Si–C) = 1.872 Å, r(C–N) = 1.141 Å, r(Si–H) = 1.467 Å, and θ(HSiH) = 111.5° in good agreement with the experimental[18] values of r(Si–C) = 1.847 Å, r(C–N) = 1.158 Å, and r(Si–H) = 1.49 Å. For **4**, the geometry is not known, and we calculate r(Si–N) = 1.745 Å, r(N–C) = 1.165 Å, r(Si–H) = 1.466 Å, and θ(HSiH) = 111.0°. The cyano stretch in **3** is calculated to be at 2488 $\mathrm{cm^{-1}}$ (scaled, 2189 $\mathrm{cm^{-1}}$)[19] and in **4** at 2294 $\mathrm{cm^{-1}}$ (scaled, 2019 $\mathrm{cm^{-1}}$). The calculated splitting is somewhat larger than what is found experimentally in **1** and **2** and for $\mathrm{Me_3SiCN}$ and $\mathrm{Me_3SiNC}$.[1,3] The calculated intensity of the cyano stretch in **3** is 11 km/mol, almost 50 times less intense than the cyano stretch in **4**, 505 km/mol. At the SCF level, we predict that $\mathrm{SiH_3CN}$ is less stable than $\mathrm{SiH_3NC}$ by 1.5 kcal/mol.[20] However, this is reversed at the correlated level, and with MP-2 $\mathrm{SiH_3CN}$ is 7.8 kcal/mol more stable than $\mathrm{SiH_3NC}$.[20] This is in agreement with the experiment since $\mathrm{SiH_3NC}$ is not observed.[18] The CNDO results significantly underestimate the stability of the isocyanide.

The calculated value for ΔE for the silyl cyanide/isocyanide isomerization can be compared to the values for the methyl cyanide/isocyanide and hydrogen cyanide/isocyanide isomerizations. The SCF value for ΔE for $\mathrm{CH_3CN/NC}$ is 19.2 kcal/mol, and the correlated value is 22.7 kcal/mol;[21] the latter value is in good agreement with the experimental value of 23.7 ± 0.1 kcal/mol.[22] For HCN/NC, the SCF value for ΔE is 9.5 kcal/mol, and the correlated value is 14.6 kcal/mol.[23] As R in RCN forms a more ionic R–C bond, the value for ΔE is decreasing. The $\mathrm{CH_3}$ group (the most covalent character in the R–C bond) has the largest value for ΔE, 22.7 kcal/mol; the $\mathrm{SiH_3}$ group (the most ionic character in the R–C bond) has the lowest value for ΔE, 7.8 kcal/mol. The correlation correction increases with decreasing covalent character in the R–C bond with $\Delta E_{\mathrm{corr}} = 3.5$ kcal/mol for R = $\mathrm{CH_3}$, $\Delta E_{\mathrm{corr}} = 5.1$ kcal/mol for R = H, and $\Delta E_{\mathrm{corr}} = 9.3$ kcal/mol for R = $\mathrm{SiH_3}$.

Substitution of three hydroxyl groups for hydrogen leads to only small changes in geometry with r(Si–C) = 1.883 Å and r(C–N) = 1.141 Å for **5** and r(Si–N) = 1.752 Å and r(C–N) = 1.165 Å for **6**. The vibrational positions show an increase of ~60 $\mathrm{cm^{-1}}$ for the CN stretch for both isomers and are at 2547 $\mathrm{cm^{-1}}$ (2241 $\mathrm{cm^{-1}}$, scaled) for **5** and 2359 $\mathrm{cm^{-1}}$ (2076 $\mathrm{cm^{-1}}$, scaled) for **6**. The intensities of the cyano stretch exhibit the same type of difference as seen previously and are calculated to be 12 km/mol for **5** and 440 km/mol for **6**. Substitution of OH for H makes the two structures closer in energy. Again the isocyanide is predicted to be more stable at the SCF level with **5** being 5.2 kcal/mol less stable than **6**.[24] However, correlation reverses the energy difference, and **5** is 3.7 kcal/mol more stable at the MP-2 level.[24] This is in very good agreement with the experimental value of 2.6 ± 1.1 kcal/mol considering the difference in the oxygen substituents, hydrogen and *tert*-butyl. Comparison of ΔE for **5** and **6** with that for **3** and **4** clearly shows a significant substituent effect.

Acknowledgment. We are grateful to A. H. Janowicz for valuable discussions.

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Polyether Biosynthesis. 3. Origin of the Carbon Skeleton and Oxygen Atoms of Lenoremycin

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Polyether antibiotics are naturally occurring ionophores produced by a variety of actinomycete species.[1] Extensive investigations in several laboratories have established that these branched chain, polyoxygenated fatty acids are formed from simple acetate, propionate, and butyrate precursors[2] and have led to the formulation of a general stereochemical model of polyether antibiotic structure and biogenesis.[3] According to this model, the characteristic oxygenation pattern of each polyether can be accounted for by a cascade of ring closures from a postulated polyepoxide intermediate. Indirect support for the polyepoxide theory has come from the determination of the origin of the oxygen atoms of monensin A (**1**),[4,5] as illustrated in Scheme I. Completely consistent results have also been reported for the polyether antibiotics lasalocid[6] and maduramycin.[7]

Lenoremycin (**2**)[8] and the closely related metabolites dianemycin,[9] leuseramycin,[10] and moyukamycin[11] are pentacyclic ethers containing a second tetrahydropyran–tetrahydrofuran spiroketal in place of the more commonly occurring pair of tetrahydrofuran rings typical of monensin. We have previously pointed out that the polyepoxide model can be extended to include the dianemycin class of polyethers by postulating the intermediacy of the appropriate diepoxy triketone **3** in place of the triepoxy diketone precursor **4** of monensin[3] (Scheme II). To test this model, we have now established the origins of the carbon skeleton and oxygen atoms of lenoremycin.

Previous work by Seto has established the acetate and propionate origins of dianemycin and led to a preliminary assignment of the ^{13}C NMR spectrum of lenoremycin.[9b] We have confirmed and extended these ^{13}C NMR assignments, including a number of small but important corrections, by a straightforward com-

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