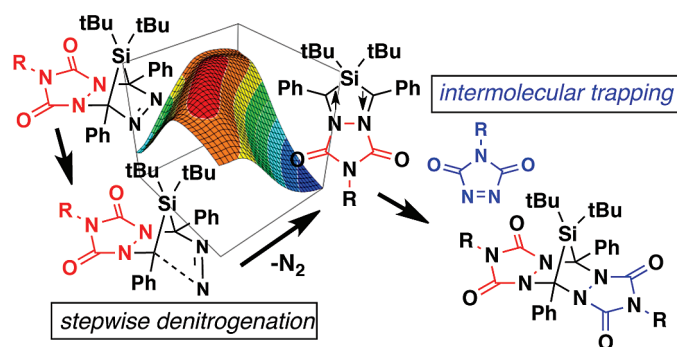# Generation and Intermolecular Trapping of 1,2-Diaza-4-silacyclopentane-3,5-diyls in the Denitrogenation of 2,3,5,6-Tetraaza-7-silabicyclo[2.2.1]hept-2-ene: An Experimental and Computational Study

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In our previous computational study, we found that silicon and nitrogen atoms have a notable effect on the reactivity of 1,2-diaza-4-silacyclopentane-3,5-diyls. Thus, the singlet state of the diradical was calculated to be much more stable than the corresponding ring-closing product, i.e., 2,3-diaza-5-silabicyclo[2.1.0]pentane, and the triplet state of the diradical. In the present study, derivatives of the diradical were generated experimentally in the denitrogenation of precursor azoalkanes, i.e., 2,3,5,6-tetraaza-7-silabicyclo[2.2.1]hept-2-enes, which can be prepared by cycloaddition of a diazasilole with 4-phenyl-1,2,4-triazole-3,5-dione (PTAD) or 4-methyl-1,2,4-triazole-3,5-dione (MTAD). The diradicals were trapped intermolecularly to afford polycyclic compounds. The computational studies (UB3LYP/6-31G*) of the denitrogenation of a model azoalkane suggested that stepwise denitrogenation with an activation energy of ca. 22 kcal/mol is the thermodynamically favored pathway for generation of the singlet diradical 1,2-diaza-4-silacyclopentane-3,5-diyl derivative via a 1,4-diazenyldiradical intermediate. The low activation energy of the denitrogenation reaction was consistent with the experimental observation that the azoalkane was labile under the preparation conditions used in this study.

Introduction

Diradicals are defined as molecules in which two electrons occupy two degenerate or nearly degenerate molecular orbitals.[1] Thus, there are two spin-multiplicities—singlet ↑↓ and triplet ↑↑ states. The reactivity and properties of the singlet states are significantly different from those of the triplet states.[2] In localized diradicals (Scheme 1),[3] for example, the singlet states are intermediates in processes that involve homolytic bond cleavage and formation. Thus, localized singlet diradicals are *intramoleculary* reactive and very short-lived.[4] By contrast, the triplet states are connected to the singlet states via the spin-forbidden intersystem-crossing

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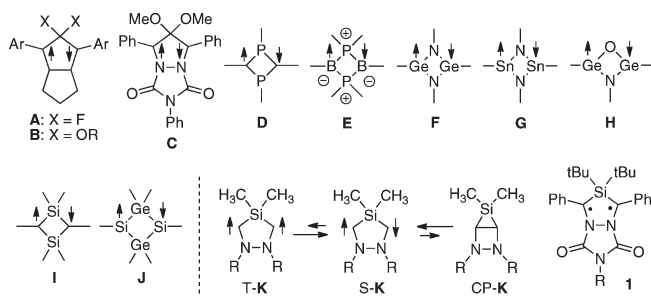
SCHEME 1. **Chemistry of Localized Singlet and Triplet Diradicals**
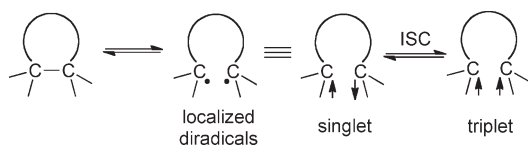
process (ISC). Thus, the lifetime of localized triplet diradicals is long enough for conformational change and intermolecular reactivity.[5] The structure and reactivity of triplet diradicals have been thoroughly investigated because these species can be detected using conventional spectroscopic analyses, including ESR measurements.[2,6−8]

Experimental studies of localized singlet 1,3-diradicals recently became possible after it was discovered that appropriate substituents at the C(2) position make the singlet energetically more stable than the triplet.[9] For example, singlet 1,3-diradicals **A**−**C** in five-membered ring systems were found to have lifetimes of up to 10 ms.[10] By taking advantage of the kinetic stability of four-membered ring-systems and the unique properties of heteroatoms, singlet diradicals **D**−**H** were isolated, and their structures were determined by X-ray crystallography.[11] Computational calculations predicted that the singlet diradicals **I** and **J**[12] would

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be isolable. In a very recent computational study, we found a notable cooperative effect of nitrogen and silicon atoms in the energetic stabilization of the singlet state of a 1,2-diaza-4-silacyclopentane-3,5-diyl S-**K**, which was calculated to be more stable than the ring-closing molecule CP-**K** and the triplet state T-**K**.[13] These calculations suggest that the singlet diradical S-**K** is long-lived enough to be intercepted in bimolecular reactions. In the present study, the generation and intermolecular trapping reaction of the 1,2-diaza-4-silacyclopentane-3,5-diyl derivative **1** was experimentally investigated in the denitrogenation reaction of the corresponding azoalkane. Indeed, the diradical species was found to be trapped intermolecularly by 4-phenyl-1,2,4-triazole-3,5-dione (PTAD) and 4-methyl-1,2,4-triazole-3,5-dione (MTAD) to give polycyclic compounds. The mechanism of the thermal denitrogenation process was also investigated at the (U)B3LYP/6-31G(d) level of theory.

A: X = F
B: X = OR
C
D
E
F
G
H

I
J
T-K
S-K
CP-K
1

Results and Discussion

The denitrogenation of cyclic azoalkanes may be the best way to cleanly generate diradical species. Our reaction scheme for the synthesis of the promising azo compound **AZ**, which was the precursor of the diradical **1**, is shown in Scheme 2. Thus, the synthesis of the 1,2,4-diazasilole **2** was begun with the denitrogenation reaction of the commercially available tetrazine **3** with silylene, which was generated by thermolysis of the silirane **4**. Thus, an equimolar mixture of the tetrazine **3** and silirane **4** was heated for 2 days at 125 °C

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SCHEME 2. Generation of 1,2-Diaza-4-silacyclopentane-3,5-diyls 1 from Azoalkane AZ
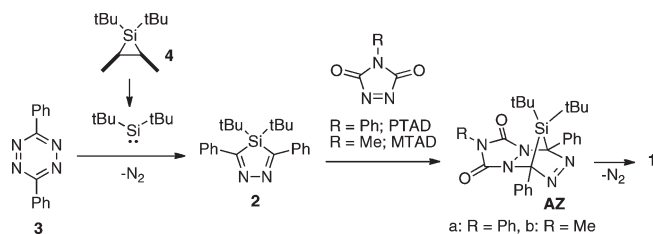

in dry benzene in a sealed tube. After the products of the thermolysate were purified, the diazasilole **2** was obtained as a yellow powder in 27% yield. The freshly prepared diazasilole (1 equiv) was mixed with PTAD (3 equiv) in benzene-d_6 and sealed. The reaction was monitored using ^{1}H NMR spectroscopy. At a reaction temperature of approximately 60 °C, the signals corresponding to the diazasilole **2** decreased and new signals were observed. After 4 h at 60 °C, compound **2** was completely consumed with concomitant product formation. After removal of the solvent under reduced pressure, the products were subjected to silica gel column chromatography. The polycyclic compound **5a** was isolated in 53% yield (Scheme 3).

SCHEME 3. Formation of Polycyclic Adducts 5 in the Denitrogenation of Azoalkanes AZ
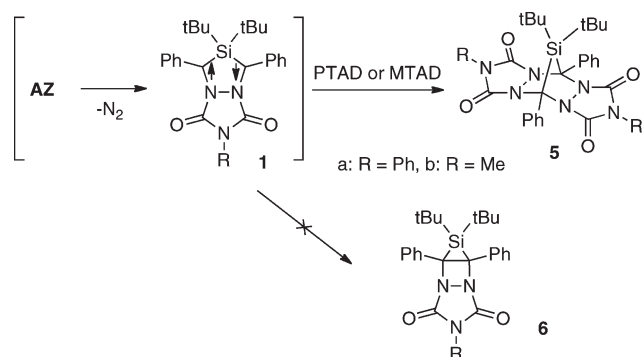
The ring-closed compound **6a** was not detected, even in trace amounts. As a result of the reaction of the diazasilole with MTAD (3 equiv), the corresponding adduct **5b** was obtained in 90% yield. The structures of **5a,b** were determined unequivocally by spectroscopic analyses, including ^{1}H, ^{13}C NMR, HRMS, and elemental analysis (see the Experimental Section). The formation of the compounds **5a,b** strongly suggests that 1,2-diaza-4-silacyclopentane-3,5-diyls **1a,b** were generated from the azoalkanes **AZa,b**, which formed during the cycloaddition reaction of the diazasilole **2** with either PTAD or MTAD. Trace amounts of the azoalkanes **AZ** were not detected during the Diels–Alder (DA) cycloaddition reaction of **2** with PTAD or MTAD. These results suggest that the denitrogenation of **AZ** is faster than the DA reaction of **2**. When the DA reaction with MTAD was performed in the presence of 10 equiv of vinylene carbonate or cyclopentadiene, the compound **5b** was obtained in 86% yield. We could not detect trapping products other than **5b**. When the DA reaction was conducted under oxygen atmosphere (O$_2$), the PTAD adduct **5a** was obtained in 58% yield. Thus, we propose that the singlet state of the

SCHEME 4. Computational Study of the Denitrogenation of a Model Azoalkane 7
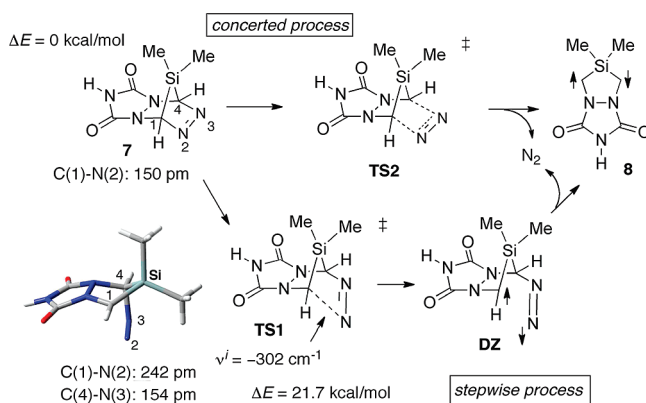
diradical **1** is trapped by PTAD to afford **5**. It is well-known that triplet diradicals are trapped by molecular oxygen at the diffusion rate constant, and the singlet of compound **8** has been calculated to be much more stable than the triplet state with a large singlet–triplet energy gap of $\Delta E_{ST} = E_S - E_T = -9.3$ kcal/mol (Scheme 4).[13] To understand the experimental observations and determine the mechanism of the denitrogenation reaction, we decided to compute the denitrogenation of the model azoalkane **7** (Scheme 4), in which the phenyl groups were replaced by hydrogen atoms and a methyl group was used in place of the *tert*-butyl group on the silicon atom.
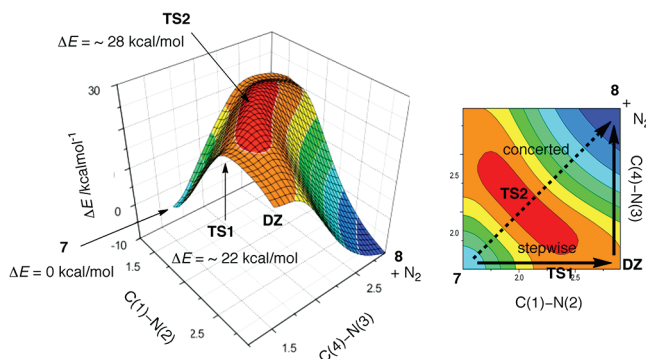

FIGURE 1. Potential energy surface for the C(1)−N(2) and C(4)−N(3) bond-breaking during the denitrogenation of azoalkane **7**.

In general, denitrogenation of azoalkanes proceeds via one of two possible mechanisms[14]—*stepwise* versus *concerted* (Scheme 4). First, to obtain information on the mechanism, a three-dimensional (3-D) potential energy surface (PES) for the two C−N bonds that are broken, i.e., C(1)−N(2) and C(4)−N(3), was calculated at the UB3LYP/6-31G(d) theoretical level (Figure 1). Apparently, the shape of the 3-D plot is consistent with the energetically preferred, stepwise denitrogenation mechanism that proceeds via the diazenyl diradical **DZ**. Thus, the stepwise pathway via **TS1** ($\Delta E = \sim 22$ kcal/mol) was calculated to be the energetically

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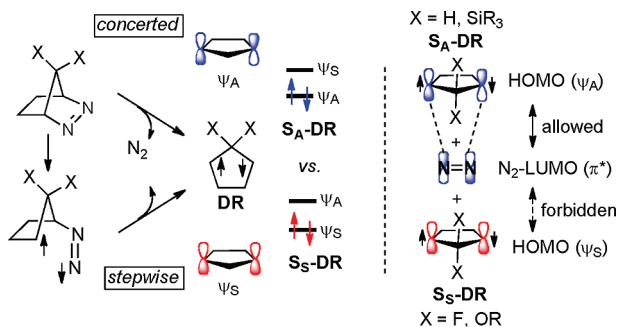
FIGURE 2. Substituent effects on the electronic configuration of the lowest singlet state of cyclopentane-1,3-diyls **DR** and the denitrogenation mechanism of the azoalkanes, diazabicyclo[2.2.1]hept-2-enes.

FIGURE 3. Orbital interaction diagram of the high-lying 2p AOs with the low-lying Si−C σ^*, depicting the electronic configuration of the lowest singlet state of the diradical **8** and the relative energy level of the symmetric NBMO (ψ_S) and the antisymmetric NBMO (ψ_A).

favored process by ca. 6 kcal/mol compared with the concerted process, which proceeds via the transition state **TS2** ($\Delta E = \sim 28$ kcal/mol). Actually, the transition state **TS1**, $\Delta E = 21.7$ kcal/mol including zero-point-energy correction, was optimized with an imaginary frequency of 302 cm^{-1} at the same level of theory. The bond lengths of the two C−N bonds were calculated to be 242 and 154 pm, respectively. The concerted transition state **TS2** was not located at the same level of theory. Thus, optimization of **TS2** ultimately produced the structure of the transition state **TS1**. The diazenyl diradical **DZ** was also labile at the same level of theory to afford molecular nitrogen and the singlet diradical **8**. This result means that the activation energy of the second C−N bond cleavage is a process without barriers. The question then becomes why the stepwise denitrogenation process is energetically favored.

We recently reported that the mechanism for the denitrogenation of bicyclic azoalkanes, e.g., diazabicyclo[2.2.1]-hept-2-enes, is largely dependent upon the electronic configuration of the lowest singlet state of the diradicals **DR** in the denitrogenation reaction, i.e., **S$_S$-DR** versus **S$_A$-DR**, where electronic configuration is determined by the substituent X (Figure 2).[15] When the two electrons selectively occupy the symmetric, nonbonded molecular orbital (NBMO, ψ_S, X = F, OR), concerted denitrogenation is a symmetry-forbidden process, since the phases of the diyl-HOMO (ψ_S) and the N$_2$-LUMO (π^*) do not match. Thus, the stepwise denitrogenation reaction was the energetically favored process. By contrast, concerted denitrogenation is the energetically favored mechanism for azoalkanes (X = H, SiR$_3$), since the two electrons selectively occupy the antisymmetric NBMO (ψ_A) of the resulting diradical **S$_A$-DR**. Thus, the phases of the diyl-HOMO (ψ_A) and the N$_2$-LUMO (π^*) match. To understand the energetic preference of the stepwise denitrogenation of the azoalkane **AZ** (Scheme 4 and Figure 1), the electronic configuration of the lowest singlet state of the diradical **8** was calculated using the complete active space multiconfiguration SCF (CASSCF) method. As shown in Figure 3, the symmetric NBMO (ψ_S), i.e., diyl-HOMO, was at a lower energy than the antisymmetric NBMO (ψ_A), i.e., diyl-LUMO. At the CASSCF(2,2)/6-31G(d) level of theory, 74% of the two electrons are calculated to selectively occupy
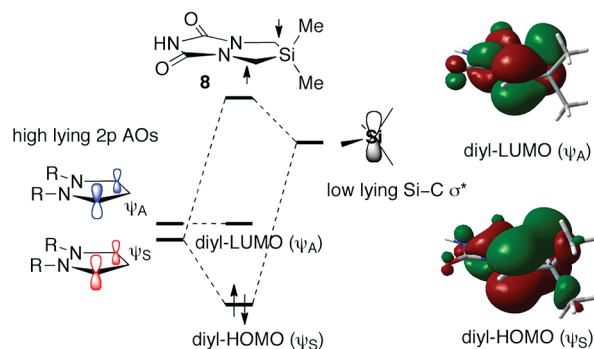
the bonding ψ_S orbital. This result indicates that the diradical is weakly π-single bonded between the two radical sites. The electronic configuration of the lowest singlet state of the diradical **8** can be explained by examining the orbital interaction between the high-lying, symmetric NBMO (ψ_S) and the low-lying Si−C σ^* orbital,[16] which energetically stabilizes the ψ_S (Figure 3). These computational results clearly suggest that the concerted denitrogenation reaction is a symmetry-forbidden process. Thus, stepwise denitrogenation was calculated to be the energetically favored process (Scheme 4 and Figure 1).

As clearly indicated in Figure 1, the model azoalkane **7** loses molecular nitrogen in a stepwise manner with an activation energy of 21.7 kcal/mol to give the 1,2-diaza-4-silacyclopentane-3,5-diyl **8** (Scheme 4). The computational results strongly suggest that the singlet diradicals **1a,b** are generated in a stepwise manner during the denitrogenation of **AZ**. The activation energy of the denitrogenation of **AZ** should be significantly lower than that of the compound **7**, since the radical moiety is well stabilized by the phenyl group. Thus, it would be reasonable that we could not detect the azoalkane **AZ** during thermolysis of the diazasilole with either PTAD or MTAD at 60 °C (Scheme 2).

As mentioned in the trapping experiments of the diradical **1** with vinylene carbonate and cyclopentadiene, we could not obtain trace amounts of the trapping adduct. The cycloaddition reaction of **1** with vinylene carbonate is a symmetry-forbidden process, since the diyl-HOMO (LUMO) does not match the alkene-LUMO (HOMO). Thus, it would be understandable that the diradical **1** cannot be trapped by vinylene carbonate. Alternatively, the cycloaddition reaction with cyclopentadiene is a symmetry-allowed process; thus, it would be possible to trap **1** by cyclopentadiene. However, trace amounts of the adduct were not detected. The experimental results clearly indicate that the trapping process is faster by MTAD than by cyclopentadiene.

Conclusions

As predicted in our previous computational study, the 1,2-diaza-4-silacyclopentane-3,5-diyl species was *intramolecularly* unreactive, but reacted *intermolecularly* to give the

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adduct **5**. The mechanism of denitrogenation of the precursor azoalkane was also investigated by computations at the UB3LYP/6-31G(d) theoretical level. Stepwise denitrogenation via the diazenyl diradical was the energetically favored process compared with concerted denitrogenation. We found that the electronic configuration of the lowest singlet state of the 1,2-diaza-4-silacyclopentane-3,5-diyl plays an important role in controlling the mechanism of the denitrogenation reaction. Thus, the two spins of the singlet diradicals **1** and **8** selectively occupy the symmetric NBMO, as shown by the CASSCF calculations. The results of the present study indicate that singlet diradicals, which were previously considered intermediates only of *intramolecular* reactions, can be applied for *intermolecular* reactions.

Computational Methods

Structures were optimized at the B3LYP/6-31G(d)[17,18] level of theory. The computations for the singlet state of diradicals were optimized using the UB3LYP/6-31G(d) with a broken-symmetry method (initial guess $<S^2> = 1.00$). The azoalkane was analyzed at the restricted B3LYP/6-31G(d) theoretical level. The geometries of stationary points and transition states were all located, and vibrational analyses were performed with the Gaussian 03 suite of programs.[19] The optimized geometries and their electronic energies are available in the Supporting Information. The occupation number in the symmetric NBMO (ψ_S) of the singlet diradical **8** was calculated at the CASSCF[20]-(2,2)/6-31G(d)//UB3LYP/6-31G(d) theoretical levels.

Experimental Section

Synthesis of 4,4-Di-*tert*-butyl-3,5-diphenyl-4*H*-1,2,4-diazasilole (2). 2,3-*cis*-Dimethyl-1,1-di-*tert*-butylsilacyclopropane (**4**)[21] (991 mg, 5.0 mmol) and commercially available 3,6-diphenyl-1,2,4,5-tetradine (**3**) (1.0 g, 4.25 mmol) were dissolved in dry benzene (15 mL) under nitrogen atmosphere. After the mixture was degassed, the reaction tube was sealed and heated to 125 °C. After 2 days at 125 °C, the mixture was cooled to room temperature, and the thermolysate was subjected to silica gel column chromatography (EtOAc/*n*-hexane = 5/95). The diazasilole **2** was isolated as a yellow solid in 27% yield (403 mg, 1.15 mmol): ^{1}H NMR (CDCl$_3$) δ 7.99 (m, 4 H), 7.45 (m, 6 H), 1.20 (s, 18 H); ^{13}C NMR (CDCl$_3$) δ 177.6 (s), 137.0 (s), 130.5 (d), 129.6 (d), 128.6 (d), 29.0 (q), 19.5 (s); IR (KBr) ν 2969, 2953, 2937, 2859, 1476, 1472, 1459, 1435, 1367, 763, 694 cm^{-1}; HRMS (EI) calcd for C$_{22}$H$_{28}$N$_2$Si 348.2023, found 348.2024. Anal. Calcd for C$_{22}$H$_{28}$N$_2$Si: C, 75.81; H, 8.10; N, 8.04. Found: C, 75.58; H, 7.99; N, 8.11.

Diels−Alder Reaction of 2 with PTAD. A degassed suspension of **2** (5 mg, 0.014 mmol) and the commercially available PTAD (7.5 mg, 0.042 mmol) was heated in dry benzene-*d$_6$* at 60 °C for 7 h; the reaction was monitored by ^{1}H NMR. After the reaction mixture was cooled to room temperature, the products were subjected to silica gel column chromatography (EtOAc/*n*-hexane = 10/90) to separate the products. The PTAD-adduct **5a** was obtained as a white powder (5 mg, 7.46 × 10^{-3} mmol) in 53% yield: ^{1}H NMR (CDCl$_3$) δ7.97 (d, *J* = 7.29 Hz, 4 H), 7.5−7.2 (m, 16 H), 1.26 (s, 18 H); ^{13}C NMR (CDCl$_3$) δ152.5, 130.7, 129.9, 128.8, 128.5, 128.2, 127.9, 126.4, 125.9, 82.3, 30.6, 23.1; IR (KBr) ν 1793, 1745, 1502, 1396, 1151, 1023, 786, 758, 690, 569, cm^{-1}; HRMS (EI) calcd for C$_{38}$H$_{38}$N$_6$O$_4$Si 670.2726, found 670.2731. Anal. Calcd for C$_{38}$H$_{38}$N$_6$O$_4$Si: C, 68.04; H, 5.71; N, 12.53. Found: C, 67.87; H, 5.42; N, 12.46.

Diels−Alder Reaction of 2 with MTAD. A degassed suspension of **2** (34.4 mg, 0.098 mmol) and commercially available MTAD (30.5 mg, 0.269 mmol) was heated in dry benzene-*d$_6$* at 50 °C for 24 h; the reaction was monitored by ^{1}H NMR. After being cooled to room temperature, the products were subjected to silica gel column chromatography (EtOAc/*n*-hexane = 20/80) for separation. The MTAD adduct **5b** was obtained as a white powder (48 mg, 0.088 mmol) in 90% yield: ^{1}H NMR (CDCl$_3$) δ 7.86−7.85 (d, *J* = 7.56 Hz, 4 H), 7.43−7.40 (t, *J* = 7.56 Hz, 4 H), 7.35−7.32(t, *J* = 7.39 Hz, 2 H), 3.01 (s, 6 H), 1.17 (s, 18 H); ^{13}C NMR (CDCl$_3$) δ 153.5 (s), 129.9 (s), 128.1 (d), 127.8 (d), 126.2 (d), 81.2 (s), 30.5 (q), 25.6 (q), 22.9 (s); IR (KBr) ν 1796, 1740, 1498, 1448, 1391, 1281, 1149, 1037, 935, 889, 815, 768, 697, 681, 634, 590, 508, 499 cm^{-1}; HRMS (EI) calcd for C$_{28}$H$_{34}$N$_6$O$_4$Si 546.2411, found 546.2396. Anal. Calcd for C$_{28}$H$_{34}$N$_6$O$_4$Si: C, 61.52; H, 6.27; N, 15.37. Found: C, 61.54; H, 6.32; N, 15.31.

Note Added after ASAP Publication. This paper was published on the Friday, February 12, 2010, with errors in the abstract graphic. The corrected version was reposted on February 18, 2010.

Supporting Information Available: Complete ref 19, computational details, and copies of ^{1}H and ^{13}C NMR spectra of compounds **2** and **5a,b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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