Clarification of the Nature of the "First Chiral and Highly Lewis Acidic Silyl Cationic Catalyst". Concerning the Question of Siliconium Ions vs Silyl Cations[1]

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Received December 17, 1998. Revised Manuscript Received July 22, 1999

Abstract: Density functional theory (DFT)/IGLO NMR studies show that the "first chiral and highly Lewis acidic silyl cationic catalyst" (Jorgensen et al. *J. Am. Chem. Soc.* **1998**, *120*, 7637) is not a free tertiary alkylsilicenium ion or a somewhat coordinatively stabilized silyl cation but a de facto silylated acetonitrilium ion **4** which possesses some chirality and thus is capable of catalyzing reported reactions, however, with very low enantioselectivity. Attempts to find a minimum energy structure for the free silicenium ion **1** calculationally at the B3LYP/6-31G* level were unsuccessful and resulted instead in showing the stability of the derived intramolecularly silylated spirosilacyclopropylarenium ion **2** (a Cram-type aronium ion). In benzene solution a silylated benzenium ion **5** (Wheland intermediate) is obtained.

Introduction

In a recent paper, Jorgensen et al. reported[2] the preparation in the condensed phase of the first chiral tertiary alkylsilicenium ion **1**

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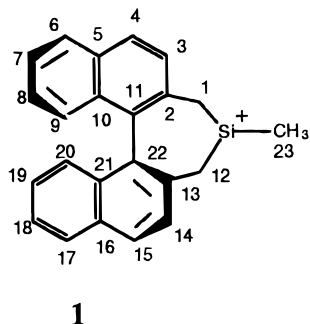
as its tetrakis(pentafluorophenyl)borate (TPFPB) as well as tetrakis(3,5-bistrifluoromethylphenyl)borate (TFPB) counterions and their use as a novel chiral Lewis acid catalyst. The ion prepared in acetonitrile solution was characterized as a nitrile-coordinated trialkylsilicenium ion **1**. However, the reported ^{29}Si NMR chemical shift in acetonitrile solution was 34.0 ppm for both counteranions, indicating lack of any significant trivalent, tricoordinate silicenium cation character, which would be expected to have a ^{29}Si NMR chemical shift in the range 300−350 ppm.[1] The chiral Lewis acid catalysis was claimed to be due to a small equilibrium concentration of a free trialkylsilicenium ion **1**.

Previously, Lambert et al. claimed to have obtained[3] triethylsilyl tetrakis(pentafluorophenyl)borate salt, $Et_3Si^+B(C_6F_5)_4{}^-$

from toluene solution. Our subsequent studies[1,4−6] have demonstrated that, contrary to claims,[3] the observed species is a triethylsilylated toluenium ion, a silylated arenium ion (cyclohexadienyl cation, Wheland intermediate, or σ-complex). Pauling,[7] Schleyer et al.,[8] and Olsson and Cremer[9] independently showed that the ion reported by Lambert et al. (including the X-ray structure) is indeed the triethylsilylated-toluenium ion. Cacace et al.[10] gave compelling evidence for the existence of such $[R_3Si - arene]^+$ σ complexes by the actual isolation of derived silylated neutral products from gas-phase radiolytic ion−molecule reactions and their FT-ICR mass spectrometric studies. It must be restated that the only bona fide persistent trivalent silicenium ion so far obtained is Lambert's trimesitylsilylium tetrakis(pentafluorophenyl)borate (TPFPB). This triarylsilicenium ion due to the steric crowding does not react with the counterion or solvent.[11]

Kira and Sakurai have demonstrated[12] that attempted generation of trialkylsilyl tetrakis(3,5-bistrifluoromethylphenyl)borates in solvents such as ethers, ketones, and nitriles possessing nonbonded electron pairs containing heteroatoms led to silylated onium ions. Olah et al. have showed the formation of silylated oxonium, carboxonium, and nitrilium ions.[1] Bahr and Boudjouk have investigated[13] the structure of a series of trialkylsilylated

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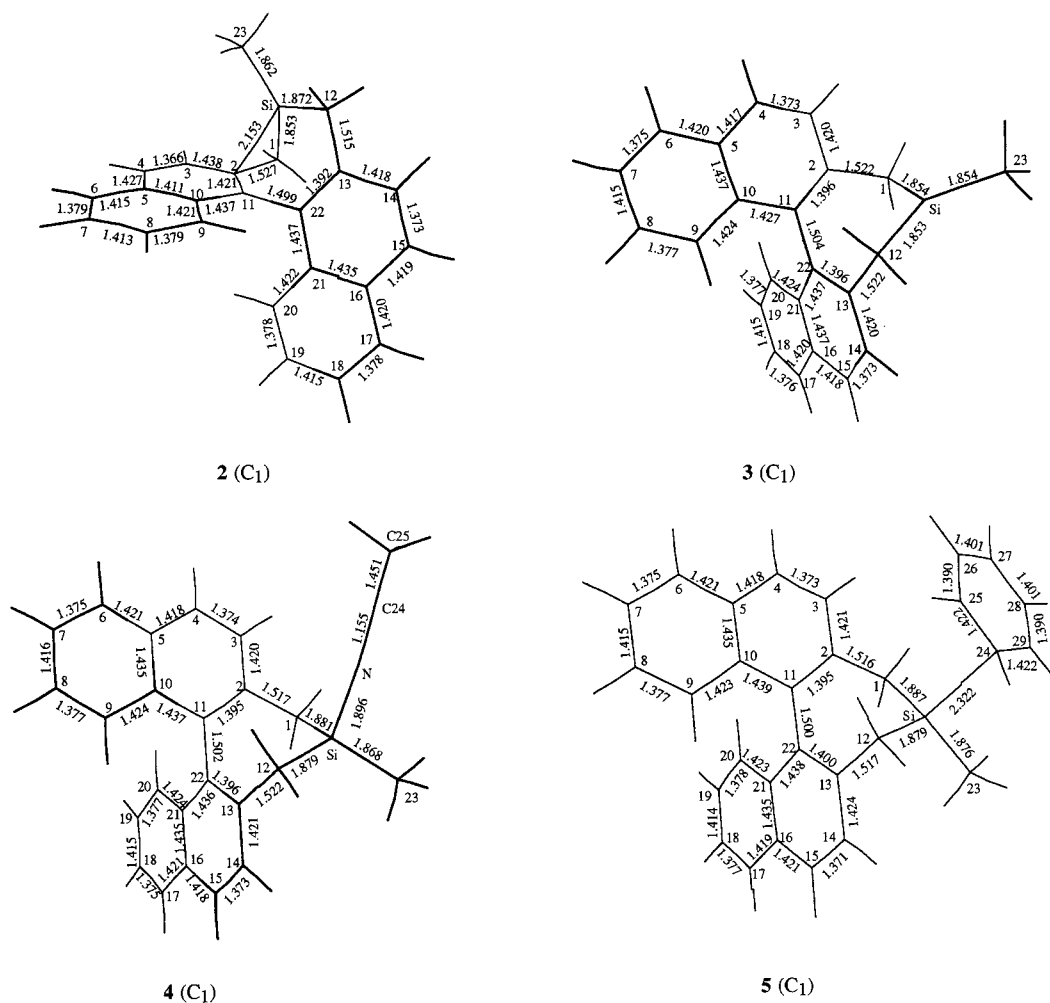(12) Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114,* 6697.

Figure 1. B3LYP/6-31G* optimized structures of **2**, **3** (**3** was optimized by constraining the both Si−C1−C2 and Si−C12−C13 angles to 109.5°), **4**, and **5**.

nitrilium ions with tetrakis(3,5-bistrifluoromethylphenyl)borate anion. Reed, Bau, and co-workers,[14a] in addition to crystal structure characterization of the triisopropylsilyl acetonitrilium ion with a pentabromocarborane anion ($Br_5CB_9H_5^-$), have isolated zwitterionic, $^iPr_3Si(Br_5CB_9H_5)$, from deuterated toluene solution. The zwitterion based on the X-ray diffraction analysis must be considered of silylated bromonium ion. The average C−Si−C bond angle was found to be 115.8(2.0)°. The Si−Br distance is only 0.2 Å longer than a normal Si−Br single bond in accordance with the silabromonium ion nature. The ^{29}Si NMR chemical shift of 97.9 ppm also reaffirms the silylated bromonium ion nature and not that of a persistent silicenium ion.

We report now density functional theory (DFT)/IGLO NMR studies and their comparison with experimental results which clearly show that ion **1** reported by Jorgensen et al.[2] is indeed a silanitrilium ion. Furthermore, the true chiral Lewis acid catalyst cannot be a free silicenium ion **1** but a silaarenium ion Cram-type aronium ion **2**.[14b] In benzene solution the ion exists as a benzenium ion **5**.

Results and Discussion

DFT[15] calculations of assumed ion **1** were carried out with

the Gaussian-98 series of programs.[16] The structure **1** was fully optimized at the B3LYP[17]/6-31G* level.[18] The minimum energy structure was found to be of C_1 symmetry **2**, an intramolecularly silylated arenium ion which can be considered as a silanaphthalenium ion (analogue of Cram's phenonium ions).[14b] Selected optimized parameters are shown in Figure 1. The calculated critical Si−C2 bond distance of **2** is 2.153 Å is even shorter than the experimentally obtained as well as calculated Si−C bond distance in *p*-triethylsilyltoluenium ion.[3−6] Attempts to find a minimum for the free silicenium ion **1** (close to C_2 symmetrical) failed because of rearrangement to form the more stable silylated arenium ion **2**. High electrophilicity of trivalent silicon for the π-donor aromatic naphthyl group in **1** is responsible for the inability to stabilize the free silicenium ion

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Table 1. IGLO Calculated ^{29}Si and ^{13}C NMR Chemical Shifts[a]

2	Si = 52.9, C1 = 21.6, C2 = 96.9, C3 = 135.1, C4 = 140.5, C5 = 139.0, C6 = 131.9, C7 = 141.3, C8 = 134.9, C9 = 133.0, C10 = 132.1, C11 = 160.9, C12 = 14.1, C13 = 131.9, C14 = 129.5, C15 = 140.8, C16 = 132.8, C17 = 134.3, C18 = 133.7, C19 = 135.9, C20 = 126.8, C21 = 132.7, C22 = 129.8, C23 = −4.3
3	Si = 334.4, C1 = 24.3, C2 = 122.3, C3 = 129.8, C4 = 138.9, C5 = 134.5, C6 = 133.4, C7 = 134.9, C8 = 135.2, C9 = 129.2, C10 = 134.7, C11 = 136.2, C12 = 24.9, C13 = 122.4, C14 = 129.9, C15 = 138.9, C16 = 134.5, C17 = 133.4, C18 = 134.9, C19 = 135.2, C20 = 129.2, C21 = 134.7, C22 = 136.2, C23 = 5.2
4	Si = 44.2, C1 = 16.8, C2 = 129.2, C3 = 129.5, C4 = 136.9, C5 = 133.0, C6 = 132.9, C7 = 133.6, C8 = 134.4, C9 = 129.5, C10 = 134.7, C11 = 135.7, C12 = 16.6, C13 = 126.2, C14 = 130.1, C15 = 138.0, C16 = 133.7, C17 = 133.4, C18 = 133.7, C19 = 134.3, C20 = 129.0, C21 = 134.3, C22 = 135.5, C23 = −4.0, C24 = 144.0, C25 = 6.1
5	Si = 70.4, C1 = 12.3, C2 = 129.3, C3 = 130.2, C4 = 136.8, C5 = 132.6, C6 = 133.0, C7 = 133.7, C8 = 134.4, C9 = 129.1, C10 = 134.9, C11 = 135.0, C12 = 21.5, C13 = 122.8, C14 = 130.5, C15 = 138.1, C16 = 134.2, C17 = 132.9, C18 = 134.8, C19 = 134.2, C20 = 129.6, C21 = 133.8, C22 = 139.1, C23 = 0.4, C24 = 95.9, C25 = 160.7, C26 = 133.2, C27 = 156.9, C28 = 132.2, C29 = 159.7

[a] For numbering scheme see Figure 1.

center. The ^{29}Si and ^{13}C NMR chemical shift of the arenium ion **2** using B3LYP/6-31G* geometries were calculated by IGLO (individual gauge for localized orbital) method.[19] The calculated ^{29}Si NMR shift is 52.9 ppm, and the calculated ^{13}C NMR chemical shift of the methyl carbon (CH$_3$, C23) is −4.3 ppm (Table 1).

For comparison we have also optimized the trivalent silicenium ion **3** at the B3LYP/6-31G* level by constraining the both Si−C1−C2 and Si−C12−C13 angles to 109.5°. The Si−C2 bond distance in **3** is 2.764 Å. **3** was found to be 13.0 kcal/mol less stable than **2** at the B3LYP/6-31G*//B3LYP/6-31G* level. The calculated ^{29}Si chemical shift of **3** is 334.4 ppm (Table 1). Clearly the almost 300 ppm difference between that calculated and experimentally observed by Jorgensen[2] clearly exclude the observation of a free long-lived tertiary alkylsilicenium ion **1** (vide supra). The calculated ^{13}C NMR chemical shift of the methyl carbon (CH$_3$, C23) 5.2 ppm (Table 1) for **3** is also considerably different from the reported shift of −4.2 ppm.[2]

The purported ion **1** was prepared in acetonitrile solution leading to a silanitrilium ion.[20] We have therefore optimized the silylacetonitrilium ion **4** at the B3LYP/6-31G* level (Figure 1). The Si−N bond distance is 1.896 Å, indicating strong Si−N bonding. IGLO calculated ^{29}Si NMR chemical shifts of **4** is 44.2 ppm compared with the experimentally observed value of 34.0 in acetonitrile solution. The calculated ^{13}C NMR chemical shift of the methyl carbon (CH$_3$, C23) is −4.0 ppm (Table 1) is also close the reported shift of −4.2 ppm.[2] Expectedly, the formation of **4** from **3** and acetonitrile was calculated to be exothermic by 47.2 kcal/mol at the B3LYP/6-31G*//B3LYP/6-31G* level.

Jorgensen et al. reported[2] the ^{29}Si NMR chemical shift of the purported ion **1** in C$_6$D$_6$ at δ^{29}Si 83.6. We have now investigated the corresponding Wheland intermediate **5** structure at the B3LYP/6-31G* level and found it to be a stable minimum. The calculated ^{29}Si NMR chemical shift of **5** was found to be δ^{29}Si 70.4, similar to what was experimentally observed.[2]

Conclusions

In conclusion, our DFT/IGLO NMR studies show that the reported[2] catalyst **1** with tetrakis(pentafluorophenyl)borate as anion obtained from acetonitrile solution is a de facto *N*-silanitrilium and not a free trialkylsilicenium ion. Attempts to find a minimum energy structure at the DFT B3LYP/6-31G* level corresponding to the free silicenium ion **1** itself were unsuccessful and resulted instead in the intramolecularly silylated arenium ion (Cram-type phenonium ion)[14b] **2**. If ion **1**

would be formed under persistent ion conditions, high electrophilicity of trivalent silicon for the neighboring π-donor aromatic naphthyl group in **1** would result in its intramolecular delocalization into a silaphenonium ion. As we pointed out previouly, incipient trialkylsilicenium cations, which are more reactive electrophiles than their carbocation analogues in the condensed phase, inevitably react with electron donor nucleophilic solvents (including aromatics, ethers, nitriles, etc.) or anions, as well as undergoing intramolecular silylation with neighboring π-aryl substituents as in **2**, as shown in the present case. Consequently no credence can be given to the statement in ref 2. "The optimal solvent is a perfectly nonnucleophilic solvent. Benzene and toluene have emerged as good candidates, although toluene has been shown to coordinate to the TMS cation.... The focus was therefore turned to CH$_3$CN as the solvent." Clearly benzene and toluene are good π donors and therefore readily react with any silyl cations. In fact, benzene solvent forms the corresponding Wheland intermediate **5**. Acetonitrile is a good n-donor base and is readily N-silylated to form silanitrilium ions. In neither case is it possible to consider the existence of a persistent tertiary alkylsilicenium ion. Further internal silylation of neighboring electron-donor groups (including aryl rings) also prevents the possibility of obtaining long-lived trivalent silyl cations, as do interactions with counterions, except in sterically extremely crowded situations.

It is regrettable that for a decade numerous claims were made for the isolation of long-lived silicenium ions in the condensed phase and with the exception of Lambert's crowded trimesitylsilicenium ion[11] all turned out to be incorrect. It is hoped that the question of persistent unencumbered trivalent alkylsilicenium ions in the condensed state can be put to rest until one finds yet unknown truely extremely low nucleophilicity systems for their study. No such systems, however, have yet been reported.

Calculational Methods, Basis Set, and Geometry

DFT[15] calculations were performed with the GAUSSIAN-94[16] package of programs. Optimized geometries were obtained at the B3LYP[17]/6-31G* level.[18] Energies were obtained at the B3LYP/6-31G*//B3LYP/6-31G* level. NMR calculations were performed according to the reported method using IGLO programs[19] at the IGLO II″ levels using B3LYP/6-31G* geometries. Huzinaga[21] Gaussian lobes were used as follows: basis II″: Si, 11s7p2d contracted to [5111111, 211111, 11], d exponent = 1.4 and 0.35; C, N: 7s3p contracted to [4111,21], H, 3s contracted to [21]. ^{29}Si and ^{13}C NMR chemical shifts were referenced to TMS (calculated absolute shift, i.e., σ(Si) = 368.9 and σ(C) = 217.6).

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