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Ab initio/IGLO ^{29}Si NMR studies of trisubstituted silicenium and silylated arenium ions. Comparison with experimental data of claimed ions [1][†]

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Summary – *Ab initio*/IGLO (individual gauge for localized orbital) ^{29}Si NMR studies of trisubstituted silicenium and their related arenium ions have been carried out. Comparison of the obtained results with the reported experimental data indicate that to date no free long-lived trisubstituted silicenium cations have been observed in solution. The reported results in π-donor arene solvents clearly indicate the formation of silylated Wheland intermediates (arenium ions), whereas in previously discussed heteroatom n-donor solvents (such as ethers or nitriles) the related silylated onium (such as oxonium or nitrilium) ions are formed. At the same time due to the high electrophilicity of trivalent silicon and its affinity for oxygen, halogen, etc, counter ions, such as perchlorate or fluoroantimonates, are also unsuitable for the observation of long-lived trisubstituted silyl cations.

^{29}Si NMR / trisubstituted silicenium ion / silylated arenium ion

Introduction

Over the years there have been many attempts to obtain and spectroscopically characterize long-lived trivalent, tricoordinate silicenium (also called silylenium, silylium, etc) cations in the condensed phase [2]. In spite of their prevalence in the gas phase as high abundance fragments in the mass spectra of organosilicon compounds [3] and their possible involvement as short-lived, reactive intermediates in solution reactions, the observation of long-lived, stable silicenium cations in the condensed state remains elusive [4]. Our previous studies [5] have demonstrated that, contrary to claims by Lambert *et al* [6], trisubstituted silyl perchlorates are covalent compounds. Kira and Sakurai have demonstrated [7] that the attempted generation of trialkylsilyl tetrakis(3,5-bistrifluoromethylphenyl)borates in solvents such as ethers, ketones and nitriles possessing a non-bonded electron pair and containing heteroatoms led to silylated onium ions. Bahr and Boudjouk have investigated [8] the structure of a series of trialkylsilylated nitrilium ions with tetrakis(3,5-bistrifluoromethylphenyl)borate anion. Reed, Bau and coworkers [9a] have characterized the crystal structure of triisopropylsilyl acetonitrilium ion with a pentabromocarborane anion ($Br_5CB_9H_5^-$) and isolated zwitterionic, $i\mathrm{Pr}_3\mathrm{Si}(\mathrm{Br}_5\mathrm{CB}_9\mathrm{H}_5)$, from deuterated toluene solution. Considering the X-ray diffraction analysis the zwitterion must be considered as a 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 bromonium ion character. Reed *et al* recently [9b] isolated the stable salt of $\mathrm{Bu}^t_3\mathrm{Si(OH_2)}^+$. The CP-MAS ^{29}Si NMR resonance of $\mathrm{Bu}^t_3\mathrm{Si(OH_2)}^+$ appears at δ 46.7 in accordance with the onium ion character of the ion. The Si-O distance (1.779 Å) in the crystal structure of $\mathrm{Bu}^t_3\mathrm{Si(OH_2)}^+$ is only 0.1 Å longer than a typical Si-OH bond, again in good accord with the onium ion character.

Lambert and Zhang reported [10] the preparation of trisubstituted silicenium cations using tetrakis(pentafluorophenyl)borate as a weakly nucleophilic anion [11] in solvents such as benzene and toluene. However, the reported ^{29}Si NMR chemical shifts were in the range of δ^{29}Si 82 to 112 indicating the absence of any significant trivalent, tricoordinate silicenium cation character. Recently, Lambert *et al* have obtained [12] the crystal structure of the claimed triethylsilyl tetrakis(pentafluorophenyl)borate. They prepared it from toluene solution (inexplicably stated as a non-nucleophilic solvent) and characterized it as a free non-planar triethylsilicenium ion with a non-coordinating anion and only distant weak toluene coordination. The report attracted substantial attention [13] as the first isolation of a triply bonded stable silicenium cation salt. The claim of a *de facto* long-lived

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[†] Dedicated to Professor Raymond Calas

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Table I. Selected bond lengths (Å)and angles (°).

parameters	**1**	**1** (expt)[a]	**2**	**3**	**4**	**6**	**7**	**12**	toluene (expt)[b]
Si-C4	2.197	2.19	2.292	2.140	2.214	2.127	2.129	2.239	
C3-C4	1.424	1.43	1.415	1.430	1.420	1.437	1.448	1.422	1.373
C2-C3	1.370	1.39	1.377	1.367	1.375	1.381	1.371	1.375	1.382
C1-C2	1.403	1.38	1.393	1.405	1.394	1.393	1.402	1.394	1.387
C3-C4-C5	117.2	117.	118.6	116.9	118.4	117.3	117.7	118.2	119.5
R-Si-Rc	113.8	113.8	114.5	113.4	114.0	112.2	111.3	113.4	
Si-C4-C1	110.3	104	106.7	111.1	107.6	109.2	105.6	107.2	
H-C4-C1	157.9	168.7	163.1	155.5	160.9	155.1	156.5	160.3	

[a] X-ray data from ref 31 ; [b] ref 22 ; [c] average of three C-Si-C bond angles.

triethylsilicenium cation was, however, questioned by Olah *et al* [14], Pauling [15], Schleyer *et al* [16], and Olsson and Cremer [17].

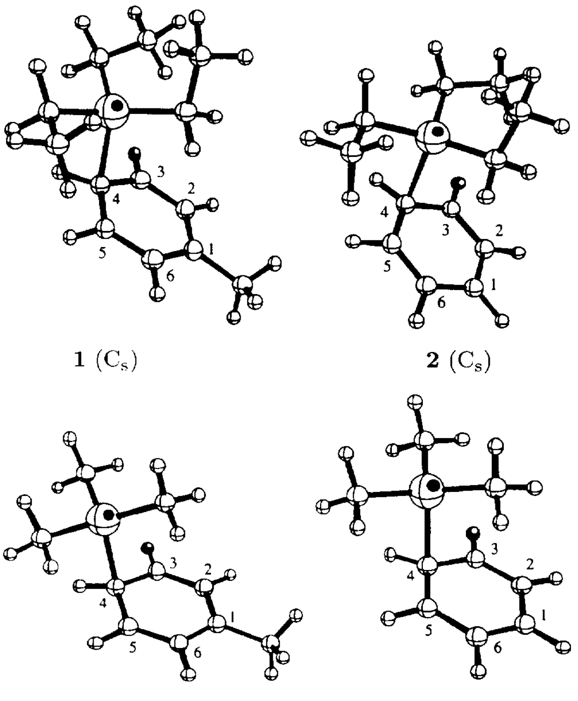
We report now detailed results of comprehensive *ab initio*/IGLO NMR studies and comparison with experimental work which clearly show that the reported crystal structure is not that of trivalent silicenium cation with distant toluene coordination, but of a *p*-(triethylsilyl)toluenium ion, a silylated cyclohexadienyl cation (Wheland intermediate or σ-complex). Related studies led to similar conclusions on related trialkylsilyl and (*tris*silyl)silyl systems [10].

Results and discussion

Electrophilic Friedel-Crafts-type trialkylsilylation of aromatics usually fails, as the reaction is reversible. Previously, we have achieved electrophilic trialkylsilylation (albeit in poor to moderate yields) of benzene, toluene [18] and ferrocene [19] under typical Friedel-Crafts reaction conditions in the presence of strongly hindered amines (Hünig bases). The presence of a hindered proton acceptor base was necessary to obtain the trialkylsilylated aromatic products. Recent studies by Cacace *et al* have also shown the facile trimethylsilylation of toluene in the gas phase [20].

We have reproduced Lambert's reported results by reacting triethylsilane with trityl tetrakis(pentafluorophenyl)borate in toluene and related aromatic solvents. Solutions with two phases were obtained with the silicon complex remaining in the bottom dark red colored layer. The "toluene-d_8" solution showed a ^{29}Si NMR chemical shift of 83.2 ppm (reported 81.8 ppm [10]). When the toluene solution was treated with tenfold excess of dry, freshly distilled (over sodium hydride) diisopropylethylamine, the product mixture obtained showed the presence 7% *p*- and *m*-(triethylsilyl)toluene-d_7 (2:1 ratio, respectively). The product identity was confirmed by comparison with authentic samples. The preferential formation of *p*-(triethylsilyl)toluene indicates σ-bonding interaction of silicon with the *para* position of toluene (where the maximum electron density is located) leading to *p*-triethylsilylated toluenium ion. Deprotonation of the arenium ion by the hindered base provides the silylated toluene. The formation of the *meta* product is attributed to *meta* silylated arenium ion in solution. These results are also in accordance with the reported gas phase studies of Cacace *et al* [20]. Similar results were also obtained with *m*-xylene and mesitylene giving the corresponding triethylsilylated aromatics.

To ascertain the formation of a carbocationic Wheland intermediate from the triethylsilyl species and toluene *ab initio* theoretical studies were carried out. We have calculated the geometries of *p*-(triethylsilyl)toluenium ion **1**, (triethylsilyl)benzenium ion **2**, *p*-(trimethylsilyl)toluenium ion **3** and (trimethylsilyl)benzenium ion **4** using the Gaussian-92 series of programs [21]. Ions **1-4** were fully optimized at the standard HF/6-31G* level (fig 1). The selected parameters are listed in table I. The calculated bond lengths and bond angles of **1** (which pertain to idealized gas phase) agree remarkably well with the experimental crystal structure data reported by Lambert [12] indicating that the experimental results in fact correspond to a true arenium ion (σ-complex). Compared to toluene itself [22], the σ-complexed toluene in the crystal structure is clearly deformed (table I) as the angle H-C4-

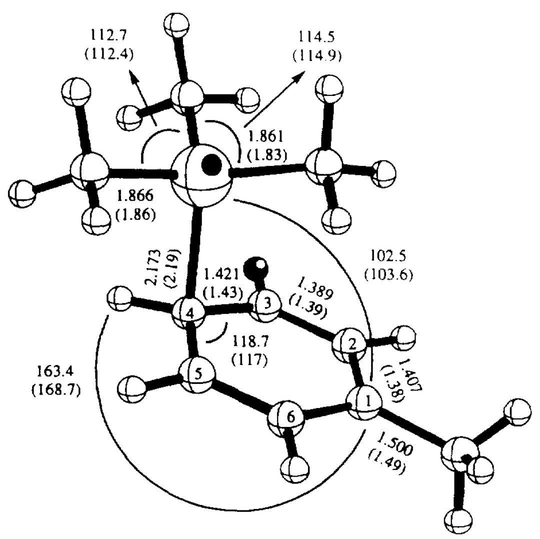


1 (C_s) **2** (C_s)

3 (C_s) **4** (C_s)

Fig 1. HF/6-31G* optimized structures of **1-4** (see table I for parameters).

C1 is 166.4° and the dihedral angle of C5-C4-C3-C2 is 3°. The Si-C4 bond length of 2.18 Å (experiment) and 2.197 Å (theoretical) in the Wheland complex compared to a normal Si-C covalent bond distance of 1.85 Å can be rationalized by contributing β-silicon hyperconjugation rendering the silicon atom somewhat electron deficient (*ie* limited siliconium cation character) with the positive charge, however, predominantly residing in the arenium ion. We have calculated bond orders [23a] of Si-C4 and C3-C4 of **1** at the HF/6-31G*//HF/6-31G* level using the SPARTAN program [23b]. The calculated bond orders of Si-C4 and C3-C4 are 0.5 and 1.3, respectively, indicate silicon hyperconjugation [24]. Because of such hyperconjugative interaction the structure cannot be directly compared to arenium ions such as trispyrrolidinobenzenium (a relatively poor model due to predominant charge delocalization on the nitrogen) [25] or even the heptamethylbenzenium ions [26] for which X-ray crystal structures are reported. Schleyer *et al* [16] and Cremer *et al* [17] also independently calculated the model compound **3** at the HF/6-31G* level and the results are in accord with our calculations. However, Lambert *et al* [27] and Reed *et al* [28] criticized the quality of HF/6-31G* optimized geometry of **3**. Notably, the calculated bond angle of Si-C4-C1 of p-(trimethylsilyl)toluenium ion **3** is 111°, which is deviated by 7° from experimental value found in p-(triethylsilyl)toluenium ion **1**. We have now fully optimized the structure **3** at the correlated level of MP2/6-31G* (fig 2). The agreement between the MP2/6-31G* calculated and experimental geometries is even better. The calculated bond angle Si-C4-C1 of **3** is 102.5° is very close to experimental value of 103.6°. Both calculated and experimental structures show that the hydrogen attached to C4 is out of the plane of the toluene molecule. Thus, calculated H-C4-C1 is 163.4°, which agrees with experimental value of 168.7°. The experimental angle of C4-X-C1 (where X is the middle point C3 and C5) is 176.8°. It is also close to calculated value of 174.1° indicating the distortion of toluene. Similarly, experimental and calculated C3-C4-H angles are 118.4° and 116.4°, respectively, again suggesting distortion of toluene.



3 (C_s)

Fig 2. MP2/6-31G* optimized structures of **3** (experimental value).

We have also calculated the ^{29}Si NMR chemical shifts of the arenium ions **1-4** using Schindler and Kutzelnigg's IGLO (individual gauge for localized orbital) method [29] at the II' level [30] using HF/6-31G* geometries. Previously, we have demonstrated that IGLO can predict very accurately the ^{29}Si NMR chemical shifts of silicon compounds [1]. The calculated ^{29}Si shift of 82.1 ppm for p-(triethylsilyl)toluenium ion **1** agrees with the reported shift of 81.8 ppm and our presently reported shift of 83.2 ppm in solution (table II). The calculated ^{29}Si shift of p-(triethylsilyl)benzenium ion **2** is 104.6 ppm. The experimental value of **2** is 92.3 ppm. These comparisons clearly show that the obtained crystallographic data pertain to an arenium σ-complex and not, as claimed, to a distorted free silicenium cation [12]. The observation of ^{29}Si chemical shift 92.3 ppm for **2** and 81.8 ppm for **1** by Lambert [12] reflects lesser π-basicity of benzene. We have also calculated ^{29}Si NMR chemical shifts based on the crystallographic parameters reported by Lambert *et al* [29] at the IGLO II' level. There are two structures found in the crystal. The calculated ^{29}Si NMR chemical shifts for these two structures are δ 94.1 and δ 93.2. Thus the calculated ^{29}Si NMR chemical shifts on experimental structures are only about 10 ppm more deshielded than the experimental chemical shift of 83.2 ppm. The related p-(trimethylsilyl)toluenium ion **3** and (trimethylsilyl)benzenium ion **4** showed chemical shifts at δ^{29}Si 60.4 (63.3 at the IGLO II'//MP2/6-31G* level) and 77.9, respectively, at the IGLO II'//HF/6-31G* level. The reported experimental value for **4** is δ^{29}Si 83.6 [10].

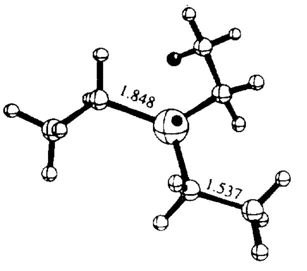
Table II. ^{29}Si NMR chemical shifts of **1-12** (in ppm)^a.

compound	II'//HF/6-31G*	expt
TMS (T_d)	0.0	0.0
1 $Et_3Si\ C_6H_5CH_3^+$	82.1	83.2
2 $Et_3Si\ C_6H_6^+$	104.6	92.3
3 $Me_3Si\ C_6H_5CH_3^+$	60.4 (63.3)^b	
4 $Me_3Si\ C_6H_6^+$	77.9	83.6
5 Et_3Si^+	376.6 (370.2)^c	
6 $Me_3Si\ C_6H_4(CH_3)_2^+$	48.4	
7 $Me_3Si\ C_6H_3(CH_3)_3^+$	44.3	
8 $(SiH_3)_3Si^+$	865.7	
9 $(Me_3Si)_3Si^+$	925.3	
10 $(SiH_3)_3SiH$	−139.2	
11 $(Me_3Si)_3SiH$	−124.2	−117.4
12 $(SiH_3)_3Si\ C_6H_6^+$	55.6	

^{a} See ref 30 for basis set description; ^{b} at IGLO II'//MP2/6-31G*, ^{c} at IGLO II//MP2/6-31G*.

We have also probed what the ^{29}Si NMR chemical shifts of planar trivalent silicon cation should be using *ab initio*/IGLO method [1]. The calculated ^{29}Si chemical shift of the planar trimethylsilyl cation is

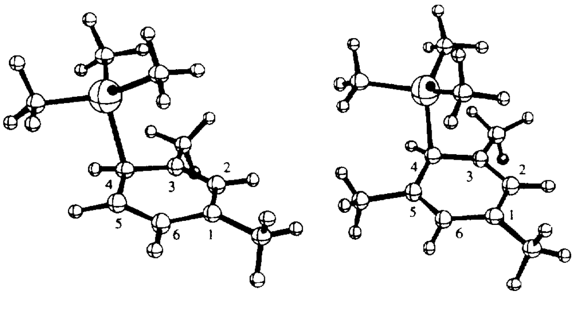
δ^{29}Si 355.7 at the IGLO II'//HF/6-31G* level and 351.2 at the IGLO II//MP2/6-31G* level (table II). We have now calculated the ^{29}Si shifts of the triethylsilyl cation (triethylsilicenium ion) **5** (see fig 3) at the IGLO II'//HF/6-31G* and IGLO II//MP2/6-31G* levels and found them to be δ^{29}Si 376.6 and 370.2, respectively. Clearly the almost 300 ppm difference between the calculated and experimentally observed values excludes the formation of long lived trialkylsilyl cation.



5 (C_{3h})

Fig 3. Selected MP2/6-31G* optimized parameters of structure **5**.

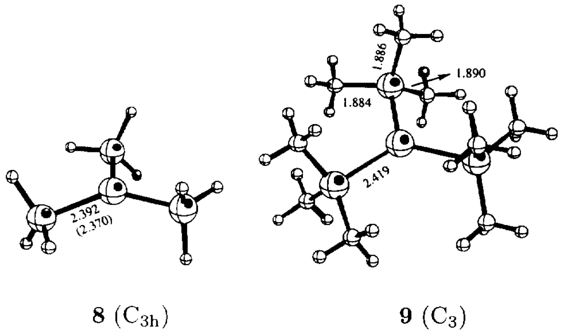
In experiments with *m*-xylene and mesitylene as solvents (superior π-bases compared with toluene) the ^{29}Si chemical shift becomes further shielded to 75.9 and 64.5 ppm, respectively. (A relative shielding of *ca* 6-7 ppm for *m*-xylene and 17-18 ppm for mesitylene compared with toluene.) These results were also probed theoretically. We have calculated the ^{29}Si chemical shift of models $(CH_3)_3$Si *m*-xylene$^+$ **6** and $(CH_3)_3$Si mesitylene$^+$ **7** at the IGLO II'//HF/6-31G* level (fig 4 and table II). The calculated ^{29}Si chemical shifts of **6** and **7** are 48.4 and 44.3, respectively. The relative shielding values of 12.0 ppm for **6** and 4.1 ppm for **7** compared with **3** agree well with the observed data. These observations are in full accord with σ-bonding interaction of the aromatic with the electron deficient silicon center leading to arenium ions.



6 (C_1) **7** (C_s)

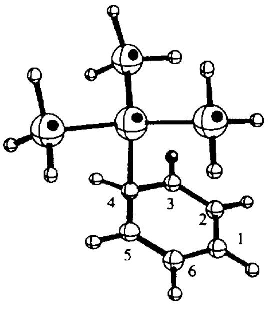
Fig 4. HF/6-31G* optimized structures of **6** and **7** (see table I for parameters).

Lambert *et al* [10] found a deshielding of 228.5 ppm between tris(trimethylsilyl)silane $(Me_3Si)_3SiH$ (δ^{29}Si −117.4) and the observed ion, $(Me_3Si)_3Si\ C_6H_6^+$ (δ^{29}Si 111.1). They explained this as being due to the substantial free silicenium ion. Later Olsson and Cremer [17] predicted a ^{29}Si chemical shift value of 245 ppm for the central Si atom of $(Me_3Si)_3Si^+$ by comparing the ^{29}Si chemical shifts of $(Me_3Si)_3SiH$, SiH_4 and calculated value of SiH_3^+. We have now calculated the ^{29}Si chemical shift of Si^+ atom of $(SiH_3)_3Si^+$ **8** and $(Me_3Si)_3Si^+$ **9** ions and found them to be 866.3 and 925.9 ppm, respectively, at the IGLO II'//HF/6-31G* level. At the same level of calculation the ^{29}Si chemical shift of central Si atom of $(SiH_3)_3SiH$ **10** and $(Me_3Si)_3SiH$ **11** are −138.6 and −123.6 ppm, respectively. Thus a chemical shift difference of 1050 ppm can be expected between a free $(Me_3Si)_3Si^+$ **9** ion and its parent silane $(Me_3Si)_3SiH$ **11**. This is in excess of 800 ppm more deshielding than that observed by Lambert *et al* [10]! The optimized geometries of $(SiH_3)_3Si^+$ and $(Me_3Si)_3Si^+$ ions are given in fig 5 and chemical shifts are listed in table II. In contrast, when we calculated model the trisilylsilylbenzenium ion **12**, the calculated ^{29}Si chemical shift of central Si atom of $(SiH_3)_3Si\ C_6H_6^+$ **12** (see fig 6) is δ^{29}Si 55.6, deshielded by 194.2 ppm from $(SiH_3)_3SiH$, which compares very well with the observed deshielding of 228.5 ppm in the case of $(Me_3Si)_3Si\ C_6H_6^+$ [10].



8 (C_{3h}) **9** (C_3)

Fig 5. Selected HF/6-31G* optimized parameters (MP2/6-31G*) of structure **8** and **9**.



12 (C_s)

Fig 6. HF/6-31G* optimized structures of **12** (see table I for parameters).

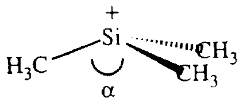
It has also been surmised that "silyl cation herein easily distorts from the plane to relieve external sources of strain. This distortion explains why the ^{29}Si NMR chemical shift (δ 92.3 in benzene) moves approximately

Table III. Calculated energies (-a.u.) and ^{29}Si NMR chemical shifts (in ppm) of **13**[a].

compound	MP2/6-31G*// MP2/6-31G*	rel energy[b]	IIc// HF/6-31G*	IIc// MP2/6-31G*
TMS (T_d)			0.0	0.0
13 $(CH_3)_3Si^+(C_{3h})$[d]	407.98877	0.0	355.7	351.2
13 (α=120.0°)	407.98819	0.4	355.5	351.3
13 (α=114.0°)	407.97394	9.3	368.2	362.5
13 (α=109.5°)	407.95913	18.6	397.0	392.0

[a] Structures of **13** were optimized with C_{3v} symmetry and by keeping C-Si-C bond angles constant; [b] in kcal/mol based on MP2/6-31G*// MP2/6-31G* energies; [c] see ref 30 for basis set description; [d] trimethyl silicenium ion, $(CH_3)_3Si^+$, with C_{3h} symmetry is the global minimum at the both HF/6-31G* and MP2/6-31G* levels.

90 ppm from the position of hydride (δ 0.2) rather than 300 ppm or so expected for planar structure" [12]. We have calculated by IGLO the ^{29}Si NMR chemical shifts of distorted trimethylsilicenium ion **13** with C-Si-C angle (α) 114.00 and 109.47° and found to be further deshielded at 368.2 and 397.0 ppm, respectively (see table III, corresponding distortion energies are also reported). Moreover, distorted silicenium ions are not stabilized by any other interactions. Thus, the suggestion by Lambert *et al* to explain the observed highly shielded ^{29}Si NMR shift (by some 270 ppm) is clearly incorrect.



13 (C3v)

Our studies unequivocally show that the reported structure [12] of triethylsilyl tetrakis(pentafluorophenyl) borate obtained from toluene solution is indeed that of a *p*-silylated toluenium cation, **1** (Wheland intermediate or σ-complex). In addition we found all other reported ions [10, 31] (**2**, **4**, **6**, **7** and **12**) are in fact silylated arenium ions with no indication of free trialkylsilicenium (R_3Si^+) or trisilylsilicenium $(R_3Si)_3Si^+$ ion character in the condensed phase. Toluene and related π-aromatic hydrocarbons not unlike such *n*-donor heteroorganics as ethers, nitriles, ketones, haloalkanes etc are unsuitable solvents to observe stable long-lived trivalent tricoordinate silicenium cations. Trialkylsilicenium cations, which are more reactive electrophiles than their carbocation analogs, will inevitably react very readily with good electron donor (nucleophilic) solvents or with their anions. At the same time we want to reemphasize that trialkylsilicenium cations are thermodynamically more stable than their carbon counterparts and are readily observed in the gas phase. It is their kinetic instability (*ie* reactivity) against *n*- or π- (or even σ-) electron donors (in the counter ions or solvents) that so far has prevented their observation under long lived ion conditions.

Much was made recently in the literature of non-coordinating anions/or in some cases of somewhat more cautions claims to "least coordinating or weakly coordinating" anions. "The myth of the non-coordinating anions" was discussed by Rosenthal [32] more than 20 years ago. His conclusion, "it is clear that the notion of the non-coordinating anion should be put to rest alongside the notion of the non-coordinating solvent" is as valid today. In superacidic systems nucleophilic coordination with electron deficient species, such as carbocations, is minimized. Silicenium ions however exert even stronger attraction to fluorine, oxygen, etc containing anions and thus do not exist as long-lived free species in superacids. Nucleophilicity and electrophilicity are relative terms, explored in great detail by physical-organic chemists. Even if the nomenclature is different, the concepts are the same and should be recognized as such by practitioners of inorganic coordination chemistry. There is no special case for silicenium ions and with existing systems no long-lived silicenium intermediates have been observed (due to their great electrophilic reactivity against both *n*- and π- or even σ-donors). However, this does not affect their well-recognized thermodynamic stability, reflected by gas phase studies or their possible involvement as reactive, short-lived intermediates in solution chemistry.

Acknowledgment

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