New aspects in the chemistry of multiple-bonds to heteroatoms*

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Abstract: The recent applications of an extremely bulky and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt in this article) to the kinetic stabilization of a variety of multiple-bonds to heteroatoms are described. The main topics are as follows: (i) the first isolation and characterization of stable antimony–antimony double-bond compound (distibene) and its bismuth analogue (dibismuthene), long-sought doubly bonded compounds between heavier group 15 elements, and (ii) the successful synthesis of stable silabenzene and 2-silanaphthalene, the first examples of stable silaaromatics.

INTRODUCTION

During the last two decades the chemistry of multiple-bonds to heteroatoms has made remarkable progress and many examples of new, stable multiple-bond compounds of heavier main group elements have been isolated and characterized [1]. Most of them have been synthesized as stable compounds by taking advantage of kinetic stabilization by using appropriate bulky substituents as steric protection groups.

On the other hand, in the course of our studies on sterically congested molecules we have developed a new type of steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter), which was found to be very efficient to stabilize highly reactive low-coordinate organoheteroatom compounds such as a series of group 14–group 16 double-bond compounds Tbt(R)M=X (**1**) [M = Si, Ge, Sn and Pb; X = O, S, Se and Te; we coin these species as *'heavy ketones'*] [2–11], i.e. the heavier congeners of a ketone. Most of them were isolated as stable crystalline compounds, the X-ray structural analysis and spectroscopic studies of which revealed that the heavy ketones have a trigonal planar geometry around their heavy carbonyl units and have a considerable degree of double-bond character (Scheme 1).

The successful isolation of the *'heavy ketones'* by taking advantage of the Tbt group prompted us to apply this efficient steric protection group to the kinetic stabilization of the unprecedented multiple-bond species of heavier elements such as the doubly bonded compounds of antimony and bismuth (distibene and dibismuthene) and novel silicon-containing aromatic compounds (silabenzene and silanaphthalene). In this article, the syntheses, structures, and reactivities of these novel heteroatom-containing double-bond species will be outlined.

## SYNTHESIS AND ISOLATION OF TEH FIRST STABLE DISTIBENE AND DIBISMUTHENE

Synthesis and structure of dibismuthene (TbtBi=BiTbt), the heaviest double bond

Synthesis of a dibismuthene by deselenation of an overcrowded triselenatribismane derivative

Since the first isolation of a stable diphosphene (ArP=PAr; Ar = 2,4,6-tri-*tert*-butylphenyl) [12] several examples of stable diphosphenes, phosphaarsenes (RP=AsR) [13], and diarsenes (RAs=AsR) [14b,15],

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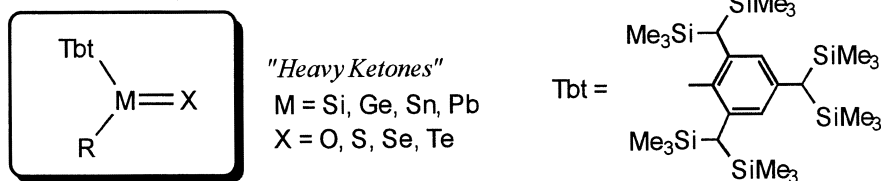
Scheme 1

i.e. the heavier congeners of an azo compound, have been synthesized by taking advantage of steric protection with bulky substituents. Although theoretical calculations predict that all the doubly bonded compounds between heavier group 15 elements can be isolated as stable species with appropriate steric protection groups [16], no examples of a stable distibene (RSb=SbR) and dibismuthene (RBi=BiR) are known.

Here we report the first synthesis of a stable dibismuthene, TbtBi=BiTbt (**2**), i.e. the long-sought doubly bonded compound consisting of the heaviest stable element in the periodic table, by utilizing a novel synthetic methodology and an efficient steric protection group (Tbt). For the preparation of **2** we have developed a new synthetic method, i.e. deselenation reaction of triselenatribismane **3** with a phosphine reagent. As shown in Scheme 2, the precursor **3** was readily synthesized by treatment of TbtBiCl$_2$ (**4**) with Li$_2$Se in tetrahydrofuran. Triselenatribismane **3** thus isolated as a stable crystalline compound was then treated with an excess amount of hexamethylphosphorous triamide in toluene at 100 °C in a sealed tube. After being heating for 12 h the solution turned purple, and the dibismuthene **2**, which precipitated from the mixture on cooling, was isolated as deep purple single crystals by filtration in a glovebox filled with argon (Scheme 2) [17]. The dibismuthene **2** has a very low solubility probably due to its high symmetry in the molecular structure, thus making its isolation quite simple.
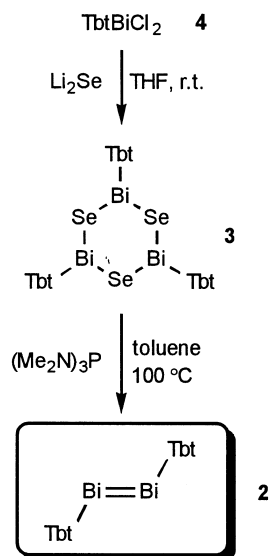
Scheme 2

Molecular structure of dibismuthene

Dibismuthene **2** is the first compound containing a bismuth–bismuth double bond which is the heaviest among those which consist of stable elements in the periodic table. The molecular geometry of **2** was determined by X-ray crystallographic structural analysis as shown in Fig. 1. Two important parameters in the structure of **2** are the Bi–Bi bond length [2.8206(8) Å] and the Bi–Bi–C angle [100.5(2)°]. The Bi–Bi bond in **2** is 6% (0.169 Å) shorter than the Bi–Bi single bond length of 2.990(2) Å in Ph$_2$Bi–BiPh$_2$ [18].
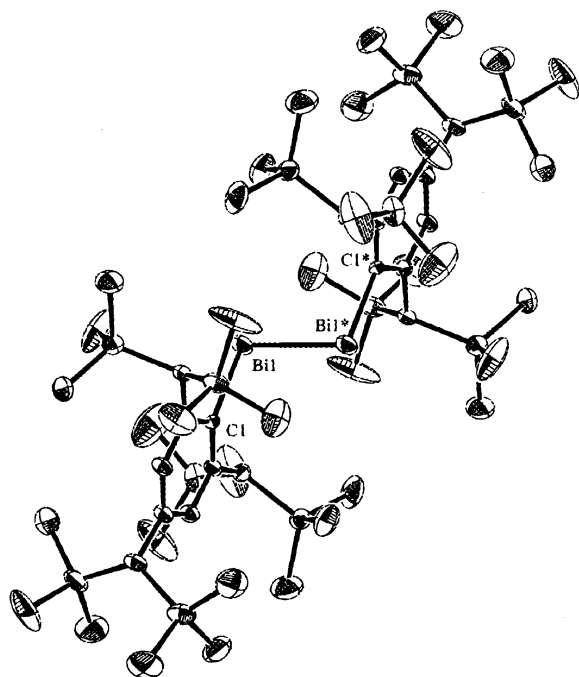
Fig. 1 ORTEP drawing of TbtBi=BiTbt (**2**) with thermal ellipsoid plot (30% probability).

This agrees reasonably well with the calculated bond shortening of 7% (0.214 Å) from $H_2Bi-BiH_2$ (3.009 Å) to HBi=BiH (2.795 Å) [17]. In addition, it is interesting that the bond shortenings are comparable with those reported for diphosphenes; the experimental value is 8% (0.183 Å) from $(PhP)_5$ [2.217(6) Å] [19] to ArP=PAr [2.034(2) Å; Ar = 2,4,6-tri-*t*-butylphenyl] [12], while the calculated value is 9% (0.200 Å) from H_2P-PH_2 (2.247 Å) to HP=PH (2.047 Å) [17]. The observed Bi–Bi–C angle of 100.5° deviates greatly from the ideal sp^2 hybridized bond angle (120°). This is due to the fact that the heavy Bi atom has the lowest tendency to form a hybrid orbital because the size-difference of the valence *s* and *p* orbitals increases upon going from N to Bi (the significant 6*s* orbital contraction originates mostly from the relativistic effect) and prefers to maintain the $(6s)^2(6p)^3$ valence electron configuration. The use of these three orthogonal 6*p* orbitals without significant hybridization leads to a bond angle of ≈ 90° at Bi [16]. The Bi–Bi–C bond angle in **2**, being close to 90°, is exactly the experimental evidence for the core-like nature of the 6*s* electrons, i.e. so called 'inert *s*-pair effect' or 'nonhybridization effect' [20].

Dibismuthene **2** is purple in hexane and shows two absorption maxima at $\lambda_1 = 660$ nm (sh, ϵ 100) and $\lambda_2 = 525$ nm (ϵ 4000), which correspond to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the Bi=Bi chromophore, respectively. These red-shifts relative to the values reported for diphosphenes and diarsenes agree with the changes in the *n*, π and π^* orbital levels calculated for HE=EH (E = P, As, Sb and Bi). Meanwhile, in the FT-Raman spectrum a strong band attributable to the Bi–Bi stretching was observed at 134 cm^{-1} for the dibismuthene **2** (solid; excitation, He-Ne laser 632.8 nm). This is 31 cm^{-1} higher than the Bi–Bi stretching frequency of $Ph_2Bi-BiPh_2$ (103 cm^{-1}) [21], agreeing with the frequency shift of 34 cm^{-1} calculated for HBi=BiH (153 cm^{-1}) and $H_2Bi-BiH_2$ (119 cm^{-1}) [17]. Thus, the spectroscopic data here obtained indicate again that **2** features double bonding between the Bi atoms even in solution.

The first synthesis of a stable distibene and its unique crystalline-state reaction with molecular oxygen

Synthesis of a stable distibene (TbtSb=SbTbt)

The successful isolation of dibismuthene (**2**; TbtBi=BiTbt) prompted us to challenge the synthesis and characterization of the missing stable antimony–antimony double bond compound. Distibene (**5**; TbtSb=SbTbt) was synthesized by the same method as in the case of **2** [17], i.e. deselenation reaction of the 1,3,5,2,4,6-triselenatristibane **6** (E = Sb), which was prepared by the reaction of $TbtSbCl_2$ with Li_2Se

in THF, with excess amount of hexamethylphosphorous triamide in toluene at $100\,^\circ$C in a sealed tube. After heating 12 h the solution turned green and the expected distibene **5**, which precipitated from the mixture on cooling, was isolated as deep green single crystals in 94% by filtration in a glovebox filled with argon (Scheme 3) [22].
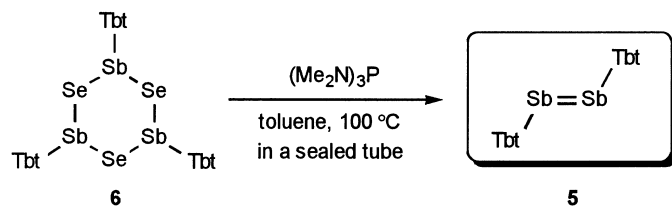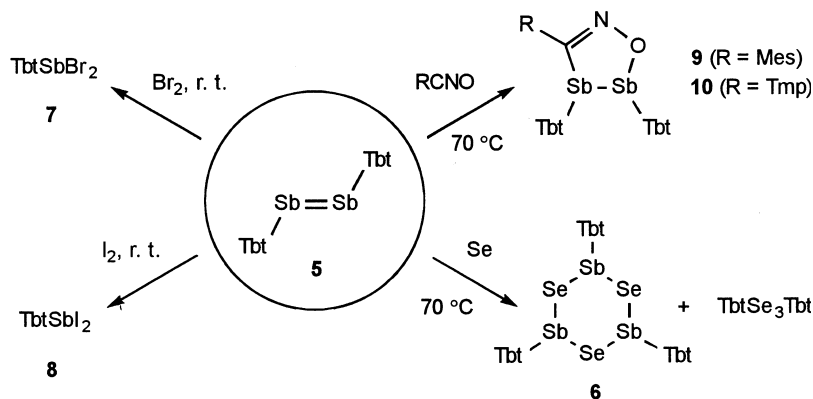

Scheme 3

Physical properties of TbtSb=SbTbt

Distibene **5** is the first example of a stable antimony–antimony double bond, and the green solution of **5** in hexane showed two absorption maxima at $\lambda_1 = 599$ nm (ϵ 170) and $\lambda_2 = 466$ nm (ϵ 5200). The absorption maxima thus obtained for **5** lie between those for the previously reported stable diarsenes and those for the dibismuthene **2** [17], and the experimentally observed red-shifts for the double-bond systems of heavier group 15 elements on going from P to Bi agree with the changes in the n, π and π^* orbital levels calculated for HE=EH (E = P, As, Sb and Bi) [20]. Distibene **5** showed a strong Raman line at $207\ \mathrm{cm}^{-1}$ (solid; excitation, He-Ne laser 632.8 nm) which is much higher than the frequencies observed for distibines (e.g. Ph_2Sb–$SbPh_2$ $141\ \mathrm{cm}^{-1}$) [23].

X-ray crystallographic analysis of the green crystal revealed the molecular geometry of distibene **5**, which was found to be completely isomorphous with the dibismuthene **2**. Considerable bond shortening (7%) of the Sb–Sb bond length (2.642[1] Å) in **5** as compared with that reported for Ph_2Sb–$SbPh_2$ [2.837 Å] [23] clearly indicates its double-bond character, while the observed Sb–Sb–C bond angle of $101.4(1)^\circ$, which deviates greatly from the ideal sp^2 hybridized bond angle (120°) and approaches to 90°, suggests that **5** has a nonhybridized Sb–Sb double bond due to the core-like nature of Sb atom as in the case of dibismuthene **2**.

Novel reactions of an overcrowded distibene

With the stable distibene **5** in hand, we have examined the reactivity of the Sb–Sb double bond towards several reagents (Scheme 4) [22]. Treatment of **5** with bromine and iodine in carbon tetrachloride at room temperature resulted in the cleavage of the Sb–Sb bond to give the corresponding dihalostibines $TbtSbBr_2$ **7** and $TbtSbI_2$ **8** in quantitative yields, respectively, while the reaction of **5** with elemental selenium in tetrahydrofuran at $70\,^\circ$C gave the precursor **6** (23%) together with a triselenide $TbtSe_3Tbt$ (16%). On the other hand, distibene **5** underwent a [2+3]-cycloaddition reaction with bulky aryl-substituted nitrile oxides ArCNO [Ar = 2,4,6-trimethylphenyl (Mes) or 2,4,6-trimethoxyphenyl (Tmp)] to afford the corresponding adducts **9** and **10** in 59 and 58% yields, respectively.

Scheme 4

Furthermore, during the course of our investigations on the chemistry of **5**, we found a unique and interesting reaction of distibene **5** with oxygen. Although distibene **5** reacts with oxygen in solution quite rapidly to give quantitatively the corresponding colorless 1,3,2,4-dioxadistibetane derivative **11, 5** is relatively stable in the solid state in the open air. The crystals of **5** remained dark green for several hours, but they slowly reacted with atmospheric oxygen to give **11** quantitatively. Of particular note is that in the crystalline state **5** reacts with molecular oxygen while retaining its crystallinity (Scheme 5). Thus, the reaction proceeds from single crystals of **5** to single crystals of **11** [22].
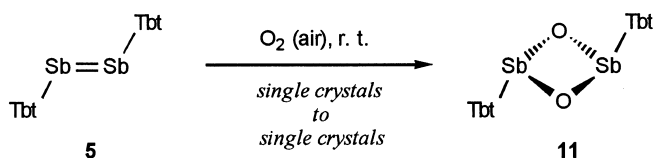
Scheme 5

This unique oxidation process of **5** in the crystalline phase was successfully monitored by repeated measurements of the cell dimensions using an X-ray diffraction technique with an imaging plate Weissenberg diffractometer [24]. The data clearly indicate that the crystal dimensions of **5** abruptly changed to those of **11** within 10 h after an induction period ($\approx$ 30 h). After completion of the transformation of the unit cell dimensions three dimensional intensity data of **11** were collected using the identical crystal initially used for the structural analysis of **5**.

SYNTHESIS OF THE FIRST STABLE SILAAROMATIC SYSTEMS

Synthesis of a stable 2-silanaphthalene

Much attention has been focused on the chemistry of silaaromatic compounds, i.e. Si-containing $[4n+2]\pi$ ring systems and a number of reports on the formation and reactions of transient silaaromatics such as sila-and disilabenzenes have appeared in the past few decades [25]. Although some of these species were characterized spectroscopically in low-temperature matrices no isolation of silaaromatic compounds has been reported due to their high reactivity. As for a neutral silaaromatic compound, Märkl *et al.* have already reported the synthesis of a monomeric silabenzene, 2,6-bis(trimethylsilyl)-1,4-di-*t*-butylsila-benzene [26]. However, it was observed only in solution (THF/Et$_2$O/petroleum ether = 4:1:1) below $-100\,°C$, due apparently to stabilization by coordination of the solvent Lewis base judging by the relatively high field ^{29}Si NMR chemical shift ($\delta_{Si} = 26.8$).

Although the only generation of a silanaphthalene ever reported, transient 2-methyl-2-silanaphthalene, was deduced by MeOD trapping of the reaction products in the flow pyrolysis of 2-allyl-2-methyl-1,2-dihydro-2-silanaphthalene [27], our successful application of the Tbt group to the kinetic stabilization of silaaromatic species has now led to the first isolation of 2-silanaphthalene **12**.

The 2-silanaphthalene **12** was synthesized as a colorless, stable crystalline compound (m.p. 151–155 °C) in 80% yield by treatment of **13** with one equivalent of *t*-BuLi in hexane (Scheme 6) [28]. The structure of **12** was confirmed by its ^{1}H, ^{13}C and ^{29}Si NMR spectral data, which were in quite good agreement with chemical shifts computed for the parent and substituted 2-silanaphthalenes **14–16** (GIAO–B3LYP). The ^{29}Si NMR chemical shift ($\delta_{Si} = 87.35$) observed for the ring silicon of **12** is comparable to those for the previously reported sp^2 silicon compounds [25c]. All the ^{1}H NMR signals of
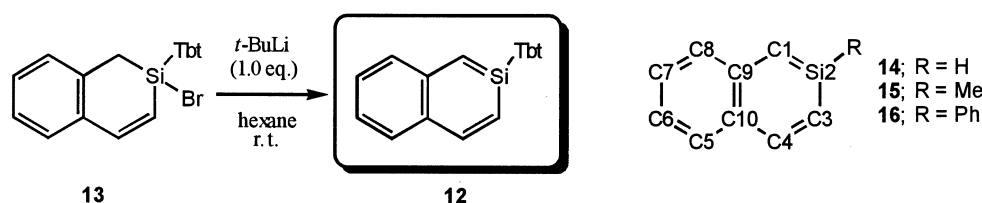
Scheme 6

the ring protons of **12** were observed in the aromatic region (6.99–8.48 p.p.m.) and the ^{13}C NMR signals of the ring carbons were located in the sp^2 region (116.01–148.95 p.p.m.). The coupling constants between the ring Si atom and the two adjacent ring carbons [92 Hz for $J_{Si-C(1)}$ and 76 Hz for $J_{Si-C(3)}$, respectively,] both exceed normal values for C–Si(sp^3) ($\approx$ 50 Hz) [29] and are similar to those reported for Si=C systems (83~85 Hz) [25c]. These results clearly indicate that the 2-silanaphthalene ring has delocalized double bonds.

Molecular structure of 2-silanaphthalene

The molecular structure of 2-silanaphthalene **12** was also established by X-ray crystallographic analysis (Fig. 2). The 2-silanaphthalene ring system in **12** was found to be almost planar and to be oriented perpendicular to the benzene ring of the Tbt group, suggesting essentially no conjugative interaction of the π-electrons of Tbt group with those of the silanaphthalene ring. The 360° bond angle sum shows the completely planar trigonal geometry around the silicon atom.
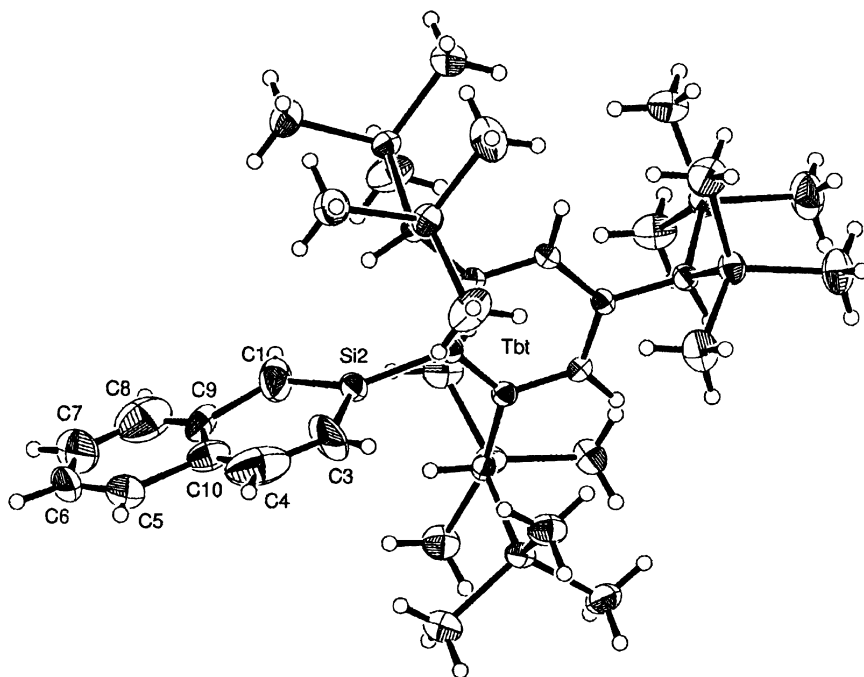

Fig. 2 Molecular structure of 2-silanaphthalene (**12**).

The Raman spectrum of **12** showed a strong line with a maximum intensity at 1368 cm^{-1}, compared with the most intense Raman line observed at 1382 cm^{-1} for naphthalene. The strongest Raman shifts observed for **12** and naphthalene are in good agreement with the calculated vibrational frequencies (1377 cm^{-1} for 2-silanaphthalene **14**, 1378 cm^{-1} for 2-phenyl-2-silanaphthalene **16** and 1389 cm^{-1} for naphthalene, computed at the B3LYP/6-31G* level and scaled by 0.98). Furthermore, the calculated vibration modes of 2-phenyl-2-silanaphthalene showed a close resemblance to those of naphthalene, suggesting the aromatic character of the 2-silanaphthalene ring system in **12**. The UV-vis spectrum of **12** in hexane showed three absorption maxima [267 (ε, 2×10^4), 327 (7×10^3) and 387 (2×10^3) nm] most likely assignable to the E_1, E_2 and B bands. These are red shifted compared to those for naphthalene [221 (ε, 1.33×10^5), 286 (9.3×10^3) and 312 (289) nm], suggesting the aromatic character of this conjugated ring system.

2-Silanaphthalene **12** was found to be very stable thermally even on heating in benzene at 100 °C in a sealed tube in an inert atmosphere. No dimerization product was detected, although **12** is air- and moisture-sensitive due to its Si=C moiety. Its thermal stability, obviously due to the steric protecting ability of the Tbt group, is in sharp contrast to that of 1,4-di-*t*-butylsilabenzene, which cannot be isolated as a monomer and undergoes facile dimerization even at 0 °C (Scheme 7) [30].

17; X = D, Y = OD
18; X = H, Y = OMe

19

20

21
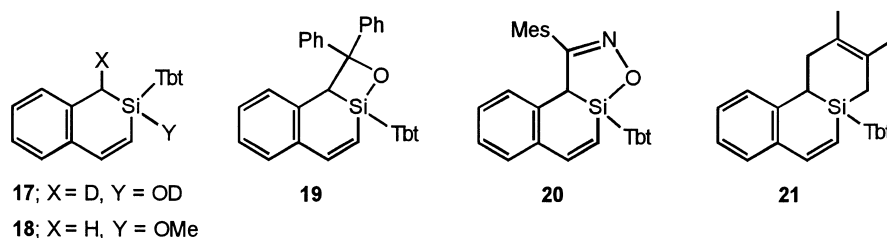
Scheme 7

Interestingly, **12** retains its high reactivity towards small molecules such as D_2O and methanol which afford the corresponding 1,2-addition products **17** and **18** in 59% and 72% yields, respectively. Furthermore, **12** was found to undergo cycloaddition reactions with benzophenone, mesitonitrile oxide and 2,3-dimethyl-1,3-butadiene giving the corresponding [2+2], [2+3] and [2+4] adducts **19–21** across its Si=C moiety in 62%, 77% and 72% yields, respectively. The aromatic character of the 2-silanaphthalene ring system was evaluated by computing the NICS (Nucleus Independent Chemical Shifts) [31] of 2-silanaphthalene together with the related silaaromatic compounds and the parent hydrocarbons. The large negative NICS values obtained for the possible three silanaphthalenes, comparable to the parent naphthalene suggest that the aromatic character will not be much reduced by the replacement of a ring carbon by a silicon atom, which agrees with the experimental evidence discussed above for the Tbt-substituted 2-silanaphthalene **12**.

Synthesis of the first silabenzene stable in solution at room temperature

As a goal of this project, we have attempted the synthesis of kinetically stabilized silabenzene **22** by taking advantage of the Tbt group. After overcoming several synthetic problems, we were able to obtain the bromosilacyclohexadienes **23a,b** as an inseparable mixture starting from stannacyclohexadiene **24**. With the expected precursors **23** in hand, we have treated the mixture of **23a,b** with *t*-butyllithium (0.9 equiv.) in cyclohexane-d_{12} at room temperature in a sealed NMR tube as in the case of 2-silanaphthtalene **12**. The monitoring of the reaction by ^{1}H NMR spectroscopy showed the formation of a new set of signals due to a Tbt group and, in the ^{29}Si NMR spectrum of this reaction mixture, a characteristic low-field shifted signal ($\delta_{Si} = 92.5$) assignable to that of the sp^2 silicon of silabenzene **22** was observed (Scheme 8).

24

23a

23b

t-BuLi (0.9 eq)
cyclohexane-*d*$_{12}$, r.t.
in a sealed tube

22 δ_{Si} 92.5
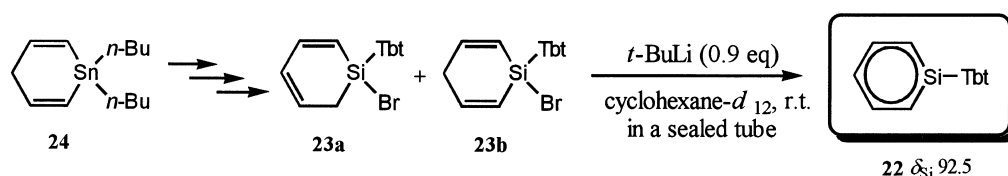
Scheme 8

Silabenzene **22** was found to be stable in solution at room temperature for at least several days under inert atmosphere. The stability of **22** is again in sharp contrast to those of previously reported 1,4-di-*t*-butylsilabenzene [30] and 1,4-di-*t*-butyl-2,6-bis(trimethylsilyl)silabenzene [26], both of which cannot be isolated as stable compounds at room temperature (*vide supra*). Unfortunately, we have not succeeded yet in the isolation of single crystals of **22** suitable for its X-ray structural analysis.

Further studies on the structure and reactivities of silabenzene **22** are now in progress.

ACKNOWLEDGEMENTS

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