Highly Selective Methyl Transfer from Methylsilanes to Phenylthallium(III) Crown Ether Complexes

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*Summary: Reactions of (18-crown-6)phenylthallium(III) diperchlorate monohydrate (**1a**) with Me_3SiR (R = $PhCH_2$, Et, Ph, CH=CH_2, $SiMe_3$, $OSiMe_3$) proceeded at 60 °C to provide (18-crown-6)phenylmethylthallium(III) perchlorate (**3**) in good to excellent yields. Cleavage of the Me–Si bond in tetramethylsilane using **1a** also occurred at 25 °C, albeit for a long reaction time. The silicon-containing products of the reaction of **1a** with benzyltrimethylsilane were siloxanes. Intramolecular trapping of the silyl fragment by a hydroxy group using (1,7-DTC)phenylthallium(III) bis(trifluoromethanesulfonate) (**1b**) was employed with trans-2-((trimethylsilyl)methyl)-1-cyclohexanol, affording a bicyclic silyl ether in 92% yield.*

During the course of our study on the unique carbophilic property of $PhTl^{III}$(crown ether) complexes (**1**),[1] e.g., (18-crown-6)phenylthallium(III) diperchlorate monohydrate (**1a**) attacks not an oxygen but a carbon atom of phenols[1b] and not a nitrogen but a carbon atom of anilines,[1c] we have now found that the thallium(III) complexes can cause methyl group transfer to Tl(III) from methylsilicon compounds of the unactivated trialkyl- and tetraalkylsilanes type. The selectivity for the carbon–silicon bond cleavage is extremely high so that virtually only the methyl–silicion bond is cleaved in the presence of ethyl–, vinyl–, or phenyl–silicon bonds.

The present reaction is unique since generally the cleavage of a carbon–silicon bond is confined to ethynyl–, vinyl–, phenyl–, and allyl–silicon bonds, in which the carbon atoms are activated.[2] That unactivated tetraalkylsilanes are stable toward various reagents is best exemplified by the popular use of tetramethylsilane as an NMR reference. There have been a limited number of examples of the cleavage of an alkyl–silicon bond in unactivated tetraalkylsilane using electrophilic metal reagents[3-11] with varying degrees of efficiency and selectivity. The reaction described below stands out from the rest in the degree of efficiency and selectivity.

A representative example of a methyl-transfer reaction mediated by **1a** is shown in eq 1. The reaction of **1a**[12] with

$$\underset{\mathbf{1a}}{[PhTl(18\text{-crown-}6)](ClO_4)_2\cdot H_2O} + \underset{\mathbf{2}}{PhCH_2SiMe_3} \xrightarrow[60\ ^\circ C,\ 5\ h]{CD_3CN} \underset{\mathbf{3}\qquad >95\%\ \text{NMR yield}}{[Ph(Me)Tl(18\text{-crown-}6)]\ ClO_4} \tag{1}$$

benzyltrimethylsilane (**2**) (1:2) in CD_3CN at 60 °C resulted in quantitative formation of (18-crown-6)phenylmethylthallium(III) perchlorate (**3**) as revealed by the ^1H NMR spectrum. As will be discussed later the reaction also gave products arising from the hydrolysis of **2**. The observed high methyl selectivity is noteworthy since the benzyl group is generally more reactive than a methyl group either in electrophilic or nucleophilic displacement.[13]

The selective methyl transfer has been found general for several organosilicon compounds, and the results are given in Table I. Tetramethylsilane did react. Therefore, CHD_2CN contained in CD_3CN was used as an internal standard for NMR throughout these experiments. Within the accuracy of ^1H NMR spectroscopy any products obtainable by ethyl, phenyl,[14] or even vinyl transfer were

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[3] These reagents are BCl_3,[4] $GaCl_3$,[5] $Tl(OCOCF_3)_3$,[6] $HgCl_2$,[7,8] $Hg(NO_3)_2$,[8] $[(C_2H_4)PtCl_2]_2$,[9] and $H_2PtCl_6\cdot 6H_2O$.[10]

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[11] With various reagents. (a) Parnes, Z. N.; Bolestova, G. I.; Akhrem, I. S.; Vol'pin, M. E.; Kursanov, D. N. *J. Chem. Soc., Chem. Commun.* **1980,** 748. (b) Akhrem, I. S.; Chistovalova, N. M.; Airapetyan, S. M.; Mysov, E. I.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978,** 1126; *Chem. Abstr.* **1978,** *89,* 109684q. (c) Akhrem, I. S.; Avetisyan, D. V.; Vartanyan, R. S.; Shakhatuni, K. G.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975,** 2327; *Chem. Abstr.* **1976,** *84,* 44254z. (d) Akhrem, I. S.; Chistovalova, N. M.; Mysov, E. I.; Vol'pin, M. E. *J. Organomet. Chem.* **1974,** *72,* 163.

[12] The purified complex **1a** contained one molecule of water in the crystal. For the preparation of **1a**, see ref 1b.

[13] The benzyl group in $C_6H_5CH_2SiMe_3$ reacts also exclusively in the reaction with a single electron transfer mechanism. See: Baciocchi, E.; Crescenzi, M.; Fasella, E.; Mattioli, M. *J. Org. Chem.* **1992,** *57,* 4684.

[14] To the best of our knowledge, in only one case can methyl compete with phenyl. Preferential methyl cleavage was reported in the H_2PtCl_4-catalyzed redistribution reaction of $PhSiMe_3$ with chlorosilanes; see ref 10. On the other hand, it was reported that platinum complexes ($[(C_2H_4)PtCl_2]$[9] and $H_2PtCl_6\cdot 6H_2O$[11c,d]) brought about cleavage of a phenyl–silicon bond in $PhSiMe_3$ as usual.

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Table I. Reaction of 1a with Alkylsilanes and Siloxane[a]

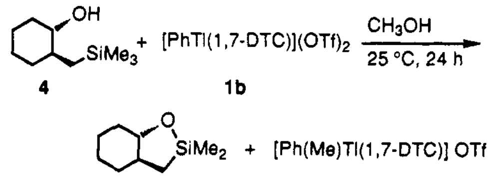
silane	temp, °C	time, h	yield of **3**,[b] %
$PhCH_2SiMe_3$	60	15 (5)[c]	60 (>95)[c]
Me_4Si	r.t.	240	34[d]
Me_3SiEt	60	12	80
Me_3SiPh	60	15	70
	60	15	50[e]
$Me_3SiSiMe_3$	60	5	83
$Me_3SiOSiMe_3$	60	42	77

[a] Reaction conditions: **1a** (0.1 mmol), silane (0.1 mmol), CD_3CN (0.5 mL). [b] Yields were quantified by ^1H NMR spectra by the use of CHD_2CN as an internal standard. [c] Reaction conditions: **1a** (0.1 mmol), silane (0.2 mmol), CD_3CN (0.5 mL). [d] Complex **1a** was recovered in 47% yield. [e] Diphenylthallium (Ph_2Tl^+) also formed in 15% yield.

not detected.[15] The high selectivity for a methyl group may be attributed to the steric congestion of the crown ether ligand in **1a**. A disilane and a siloxane reacted similarly.

The silicon-containing products of reaction 1 were siloxanes. From the reaction of **1a** (2.0 mmol) with $PhCH_2SiMe_3$ (4.0 mmol) in CH_3CN at 60 °C for 5 h, 0.64 mmol of $(PhCH_2Me_2Si)_2O$, 0.05 mmol of $Me_2(PhCH_2)SiOSi(CH_2Ph)MeOSi(CH_2Ph)Me_2$, and 0.08 mmol of $Me_3SiOSi(CH_2Ph)Me_2$ were obtained in addition to unreacted **2** (2.24 mmol) and **3** (1.74 mmol). The material balance with respect to Si was 96%. The formation of a siloxane having $SiMe_3$ indicated that cleavage of the $PhCH_2$–Si bond took place to a small extent with a cleaved $PhCH_2/CH_3$ ratio of 1:20.

For the formation of these siloxanes, water contained in **1a** may be responsible. It seemed to us that the use of nucleophiles other than water would be interesting and important. After various attempts we have found the reaction conditions which enable clean intramolecular trapping of the silyl fragment by a hydroxy group using $[PhTl^{III}(1,7\text{-DTC})](OTf)_2$ (**1b**)[16] (eq 2). This result opens



4 **1b**

5 **6** (2)

92% GLC yield

a new possibility for the use of tetraalkylsilanes (such as **4**) in organic synthesis, since the presence of at least one electronegative functional group (such as that in **5**) on the silicon atom is required for the application of Tamao oxidative cleavage[17] and reaction 2 provides a method for the required functionalization[18] of tetraalkylsilanes.

Further studies on the unique carbophilic properties of (crown ether)phenylthallium(III) complexes are in progress.

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Supplementary Material Available: Text describing synthetic procedures and spectral data for all new compounds (5 pages). Ordering information is given on any current masthead page.

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(15) In an NMR tube was placed **1a** (74.4 mg, 0.1 mmol), and then these solids were dissolved in 0.5 mL of acetonitrile-d_3. To this solution was added the silane (0.1 mmol). This tube was sealed, and the resulting solution was heated at 60 °C or was kept at 25 °C. The progress of the reaction was monitored by ^1H NMR spectroscopy. Complex **3** was obtained in 60–80% NMR yield. An example of a preparative-scale reaction is given by the preparation of (18-crown-6)phenylmethylthallium(III) perchlorate (**3**): In a 20-mL two-necked flask was placed **1a** (1.488 g, 2.0 mmol), and the flask was charged with argon. The solids were dissolved in 10 mL of acetonitrile, and then benzyltrimethylsilane (0.656 g, 4.0 mmol) was added to this solution. This mixture was heated at 60 °C for 5 h with stirring. The reaction mixture was transferred into a 300-mL flask, and 200 mL of diethyl ether was added to enforce precipitation of the product. The precipitates were filtered. After purification from CH_3CN/Et_2O (5 mL/100 mL), (18-crown-6)phenylmethylthallium(III) perchlorate (**3**) was obtained in 87% yield (1.149 g, 1.74 mmol): mp 273 °C dec. ^1H NMR (CD_3CN, 100 MHz): δ 3.65 (s, 24 H, 18-crown-6), 1.16 (d, J_{TlH} = 485 Hz, 3 H, CH_3), 7.61 (dd, J_{TlH} = 402 Hz, J_{HH} = 7.0 Hz, 2 H, H_2), 7.55 (dt, J_{TlH} = 123 Hz, J_{HH} = 7.0 Hz, 2 H, H_3), 7.39 (dt, J_{TlH} = 37 Hz, J_{HH} = 8.0 Hz, 1 H, H_4). IR (Nujol): 1578 w, 1354 s, 1286 s, 1250 s, 1100 s, 1022 m, 1000 w, 962 s, 870 w, 836 m, 700 m, 620 s, 534 w, 450 w cm^{-1}. Anal. Calcd for $C_{19}H_{32}ClO_{10}Tl$: C, 34.56; H, 4.89. Found: C, 34.55; H, 4.89.

(16) 1,7-DTC stands for 1,7-dithia-4,10,13,16-tetraoxacyclooctadecane. Complex **1b** was prepared by a modification of our published method (see ref 1b). After the reaction of **1b** with **4**, diethyl ether was added to precipitate the thallium complexes. The ether layer was washed with $NaHCO_3$(aq) and dried with $MgSO_4$. The products were isolated as usual.

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(18) For recent examples of oxidative cleavage into diols of organosilicon compounds having bicyclic structure similar to that of **5**, see: Sieburth, S. M.; Fensterbank, L. *J. Org. Chem.* **1992**, *57*, 5279. Stork, G.; Chan, T. Y.; Breault, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 7578.