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Supersilylating Agents from Chlorosilanes

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Abstract: The addition of R_3SiCl to $B(OTf)_3$ gives "supersilylating agents" formulated as $R_3SiB(OTf)_3Cl$. The catalytic properties of these species are similar to those of the previously-described (but less accessible) $R_3SiB(OTf)_4$. Copyright © 1996 Elsevier Science Ltd

Electron-deficient organosilicon compounds have attracted widespread interest, on theoretical grounds¹ and as reagents for organic synthesis.² In the latter respect, the "supersilylating agents" $R_3SiB(OTf)_4$ 1 (Tf = SO₂CF₃), discovered in this laboratory,³ are probably the most potent " R_3Si^+ -equivalents" readily accessible to the synthetic chemist. However, while their preparation from R_3SiOTf and $B(OTf)_3$ (eq. 1) is straightforward, the required trialkylsilyl triflates may be less available (and are certainly less convenient to handle) than the corresponding chlorotrialkylsilanes 2. We now report that treatment of $B(OTf)_3$ with 2 provides a new source of supersilylating species which facilitates access to this promising class of reagents.

$$B(OTf)_{3} + R_{3}SiOTf \xrightarrow{CH_{2}Cl_{2} \text{ or } CHCl_{3}} R_{3}SiB(OTf)_{4}$$
(1)

$$B(OTf)_{3} + R_{3}SiCl \xrightarrow{} R_{3}SiB(OTf)_{3}Cl$$
(2)

$$2 \qquad 3$$

$$a R = Me \qquad b R_{3}Si' = Bu^{t}Me_{2}Si \qquad c R = Pr^{t}$$

Addition of **2a-c** in CH₂Cl₂ to freshly-prepared⁴ B(OTf)₃ yielded a series of homogeneous pale yellow solutions with overall stoichiometry **3** (eq. 2). The catalytic properties of these solutions clearly indicated that supersilylating species were present. Previously demonstrated applications of the triflate-derived agents 1 had included (a) catalysis of the addition of allyltrimethylsilane to aldehydes by 1a,^{3a} and (b) the use of hindered analogues to catalyse the Mukaiyama aldol reaction with enhanced Cram-type diastereoselectivity.^{3b} To a good approximation, solutions of **3** matched those of 1 for both reaction types. For example, **3a** at 1-2 mol% was a potent catalyst for the allylation of benzaldehyde and 2-phenylpropanal (4) with allyltrimethylsilane (CH₂Cl₂, room temperature, MeOH/HCl work-up). Homoallylic alcohols **5** and **6** (*syn:anti::*2:1) were formed in yields of 79% and 92% respectively, both reactions being complete within 15 minutes.



Similarly, **2a-c** catalysed the Mukaiyama additions shown in eq. 3-5 (general conditions; 5 mol% catalyst, 1 h at -80 °C in CH₂Cl₂, followed by NaHCO₃/H₂O work-up). The yields and (especially) stereoselectivities recorded are closely similar to those achieved by the corresponding $1.^{3b}$ Although the solutions of **3** decomposed in a matter of days at room temperature, they retained their activity for several weeks provided they were stored at -18 °C.



The nature of **3a** was explored using NMR in toluene-d₈ at -20 °C, conditions which appeared to maximise the stability of the reagent. The ¹¹B spectrum was dominated by a sharp singlet at δ -3.17 p.p.m. (W₁₂ = 7 Hz), consistent with a tetracoordinate boron atom with approximate (time-average) spherical symmetry.⁵ The ²⁹Si signal at δ 45 p.p.m. appeared at somewhat higher field than that of **1a** (62 p.p.m. in CH₂Cl₂ at 20 °C), although the difference may be partly due to the change in conditions. In any case this relatively low chemical shift⁶ leaves little doubt that the silicon is tetracoordinate, probably in rapid exchange between different points on the counterion. The Si-C one-bond coupling constant of 59 Hz, measured from the ¹³C spectrum, also supports sp³ hybridization at Si.^{3a}

Aside from its practical advantages, the use of chlorosilanes increases the range of readily-accessible supersilylating agents. For example, while $Bu^{1}Ph_{2}SiCl(7)$ is commercially available, the corresponding triflate has seldom been prepared.⁷ Treatment of 7 with $B(OTf)_{3}$ does indeed yield a supersilylating species, whose catalytic and stereodirecting properties will be described in a forthcoming paper.

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References and Footnotes

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- 4. From BBr₃ and TfOH. See Olah, G. A.; Farooq, O.; Farnia, S. M. F.; Olah, J. A. J. Am. Chem. Soc. 1988, 110, 2560.
- 5. The similarity of this signal to that of Me₃SiB(OTf)₄ (see ref. 3a) raises the possibility of ligand exchange at boron.
- 6. *cf.* ref 1a; $\delta_{si} = 115$ p.p.m. has been recorded for the "silylium-like" silyl group in Prⁱ₃Si(Cl₆CB₁₁H₆).
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