Journal of Organometallic Chemistry, 471 (1994) C4–C5

Preliminary Communication

Trialkyltin cation in solution

Mitsuo Kira, Taro Oyamada and Hideki Sakurai

Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980 (Japan)

(Received September 29, 1993; in revised form December 22, 1993)

Abstract

Definitive evidence for the formation of a long-lived trivalent tin cation was obtained by using a well-defined reaction, *i.e.* the abstraction of hydride from tributyltin by trityl tetrakis[3,5-bis(trifluoromethyl)phenyl]borate in dichloromethane-d_2. The ^{119}Sn resonance at around 360 ppm is indicative of no significant interaction between the tin cation and the counteranion.

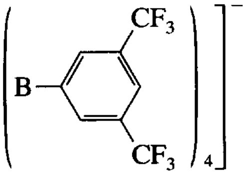
Key words: Tin; Borate; Cation; Group 14

Convincing evidence for the existence of Group-14 metal cations in the condensed phase is very sparse. We have recently pointed out that correct choice of the counter anion as well as of the solvent is essential for the formation of persistent silicenium ions because of the high electrophilicity of silicenium ions [1]; abstraction of hydride from a silane by trityl cation gave no evidence for the corresponding silicenium ion as indicated by NMR spectroscopy even if the less nucleophilic tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB$^-$) was used as a counteranion in dichloromethane. A similar reaction in the presence of diethylether gave a rather stable diethylsilyloxonium ion, a silicenium ion adduct to ether. Since this report, two groups found that *closo*-6,7,8,9,10-Br_5-$CB_9H_5^-$ and tetrakis(pentafluorophenyl)borate ions serve as extremely weakly coordinating counteranions for silicenium ions [2,3]. There has been until now no definitive evidence for tricoordinate germanium cations in solution [4]. We present evidence for the formation of trivalent tin cations by using a well-defined reaction, *i.e.* the abstraction of hydride from tributyltin by trityl-TFPB in dichloromethane-d_2. Very recently, tricoordinate tin cations have been indicated by ^{119}Sn NMR (Birchall and Manivannan [5] and Lambert and Kuhlmann [6]) by the use of rather unusual methods of preparation.

When the abstraction of hydride from tributylstannane by trityl-TFPB, newly generated by the reaction of trityl chloride and NaTFPB, was effected in CD_2Cl_2 at −70°C, the quantitative formation of tributyltin cation (**1**) accompanied by the quantitative formation of triphenylmethane was indicated by NMR spectroscopy [7*]. All experiments were performed in carefully dried dichloromethane-d_2 by the use of vacuum-line techniques.

$$Bu_3SnH + Ph_3C^+TFPB^- \xrightarrow[-70°C]{CD_2Cl_2} \underset{\mathbf{1}}{Bu_3Sn^+TFPB^-} + Ph_3CH \quad (1)$$

TFPB$^-$ =



The ^{119}Sn resonance for **1** was found at δ 356 at −20°C; reported values are δ 360 for $(Bu_3Sn)[B(C_6F_5)_3H]$ in benzene [6] and δ 322 for $(Me_3Sn)(SO_3F)$ in HSO_3F [5]. The ^{119}Sn resonance shifted to slightly higher fields with decreasing temperature; δ 348 at −70°C. The ^{1}H and ^{13}C resonances for α-methylene groups appeared at 1.65 and 22.8 ppm at −40°C, respectively, which were rather lower than the corresponding resonances for Bu_3SnH ($\delta_H = 0.9$, $\delta_C = 8.3$) and Bu_3SnCl ($\delta_H = 1.3$, $\delta_C = 17.2$). The signals due to **1** disappeared below −20°C. No interaction of the tin cation with the TFPB anion through any of the fluorine atoms was indicated by ^{19}F NMR spectroscopy; a signal due to fluorines of the TFPB anion was observed at −61.9 ppm as a sharp singlet. There is no significant difference of ^{119}Sn resonances between the Lambert cation in benzene and **1** in dichloromethane-d_2. The rather high ^{119}Sn resonance (245 ppm) for tributyltin perchlorate in dichloromethane-d_2 [6] suggests that the tin perchlorate is not fully ionic but that it has significant Sn–O covalent character. It is interesting to note that a similar experiment using trimethylsilane instead

---

Correspondence to: Prof. M. Kira or Prof. H. Sakurai.

* Reference number with asterisk indicates a note in the list of reference.

0022-328X/94/$7.00
SSDI 0022-328X(94)24410-K

of tributyltin gave no evidence by NMR spectroscopy for the persistent silicenium ion; only the signals due to trimethylfluorosilane and trimethylchlorosilane were observed [1]. Silicenium ions, even if they were generated, would be much more highly electrophilic than the corresponding tin cations.

As expected, when a small amount of ether was added to the solution of **1** at -70°C, the ^{119}Sn signal was found at δ 165 at -20°C. The higher-field shift is indicative of the formation of the ether complex of tributyltin cation (**2**) [8*]. The sharp ^{1}H and ^{13}C signals due to the diethyl ether part may be ascribed to degenerate nucleophilic substitution of **2** by diethyl ether being faster than the corresponding reaction for silyloxonium ions, in which significant line-broadening was observed in the presence of diethyl ether [1].

$$\mathrm{Bu_3SnH + Ph_3C^+TFPB^-} \xrightarrow[-70^\circ\mathrm{C}]{\mathrm{CD_2Cl_2/Et_2O}} \underset{\mathbf{2}}{[\mathrm{Bu_3Sn\text{-}OEt_2}]^+\mathrm{TFPB^-}} + \mathrm{Ph_3CH} \qquad (2)$$

Acknowledgement

We thank the Ministry of Education, Science, and Culture of Japan for financial support (Grants in Aid for Specially Promoted Research No. 02102004 and Scientific Research on Priority Areas No. 04217202).

References and notes

1 M. Kira, T. Hino and H. Sakurai, *J. Am. Chem. Soc.*, *114* (1992) 6697; M. Kira, T. Hino and H. Sakurai, *Chem. Lett.*, (1992) 55; M. Kira, T. Hino and H. Sakurai, *Chem. Lett.*, (1993) 153.

2 J.B. Lambert and S. Zhang, *J. Chem. Soc., Chem. Commun.*, (1993) 383; J.B. Lambert, S. Zhang, C.L. Stern and J.C. Huffman, *Science, 260* (1993) 1917.

3 Z. Xie, D.J. Liston, T. Jelinek, V. Mitro, R. Bau and C.A. Reed, *J. Chem. Soc., Chem. Commun.*, (1993) 384.

4 J.B. Lambert and W. Schilf, *Organometallics*, 7 (1988) 1659.

5 T. Birchall and V. Manivannan, *J. Chem. Soc., Dalton Trans.*, (1985) 2671.

6 J.B. Lambert and B. Kuhlmann, *J. Chem. Soc., Chem. Commun.*, (1992) 931.

7 **1**: ^{1}H NMR (CD_2Cl_2, 230 K) δ 0.88 (brs, 9H), 1.32 (brs, 6H), 1.65 (brs, 12H), 7.61 (s, 4H), 7.81 (s, 8H); ^{13}C NMR (CD_2Cl_2, 230 K) δ 13.5, 22.8, 27.1, 27.7, 117.5, 124.5 (q, $^1J(^{13}C-^{19}F) = 273$ Hz), 128.6 (q, $^2J(^{13}C-^{19}F) = 31.6$), 134.7, 161.8 ($^1J(^{13}C-^{11}B) = 49.9$ Hz); ^{119}Sn NMR (CD_2Cl_2, 253 K) δ 356.

8 **2** (with 10.3 equiv of Et_2O): ^{1}H NMR (CD_2Cl_2, 230 K) δ 0.91 (t, 9H, $J = 6$ Hz), 1.3–1.4 (m, 12H), 1.60 (brs, 6H), 1.19 (t, 62H, $J = 7.0$ Hz, CH_3CH_2O–), 3.50 (q, 41H, $J = 7.0$ Hz, CH_3CH_2O–), 7.65 (s, 4H), 7.85 (s, 8H); ^{13}C NMR (CD_2Cl_2, 230 K) δ 13.7, 15.1 (CH_3CH_2O–), 18.5, 27.3, 28.0, 66.0 (CH_3CH_2O–), 117.6, 124.6 (q, $^1J(^{13}C-^{19}F) = 272$ Hz), 128.8 (q, $^2J(^{13}C-^{19}F) = 28.8$ Hz), 134.8, 161.8 (q, $^1J(^{13}C-^{11}B) = 49.7$ Hz); ^{119}Sn NMR (CD_2Cl_2, 230 K) δ 164.6. Neither increasing temperature from 230 to 270 K nor increasing the amount of diethyl ether from 5 to 20 equiv produced significant change of the NMR data.