Organometallics **2007,** *26,* 4080−4082

Dimeric Diorganotin Dications: Structure and Catalytic Activity in Alcohol Acetylation

Blanka Kašná,[†] Libor Dostál,[†] Ivana Císařová,[‡] and Roman Jambor*[,†]

Department of General and Inorganic Chemistry, University of Pardubice, nám. Čs. legií 565, CZ-532 10, Pardubice, Czech Republic, and Faculty of Natural Science, Charles University in Prague, Hlavova 2030, 128 40 Praha 2, Czech Republic

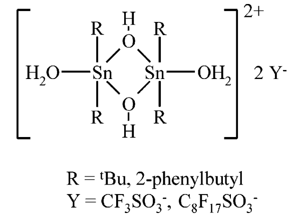
Received March 27, 2007

Summary: We report the stabilization of the Sn_2 *diorganotin(IV) dication* $[Ph(L^1)Sn(\mu\text{-}OH)_2Sn(L^1)Ph]^{2+}(1\text{-}CB_{11}H_{12})^-{}_2$ *(**2**), where* L^1 *is 1-{2,6-*$(MeOCH_2)_2C_6H_3$*}, which in contrast to the rare analogues prepared thus far does not contain a coordinated water molecule. Compound **2** exhibits high catalytic activity in the acetylation of alcohols.*

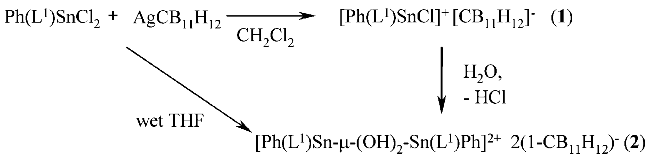
Introduction

Organotin cations, well-known as species with pronounced Lewis acidic character of the central tin atom, are important intermediates in the hydrolysis of organotin halides, a key step in the preparation of stannoxanes. An investigation of their long history showed a relatively large number of triorganotin cations[1] (the trimethyltin cation hydrates and ammoniates have been known since the 1960s),[2] while the preparation of diorganotin dications stabilized by coordination with alkynylborates and phosphine oxide was reported recently.[3] One of the most promising areas of organotin cations is the chemistry of cationic clusters. The Sn_{12} dications $[(RSn)_{12}O_{14}(OH)_6]^{2+}$ have received attention as nano building blocks for sol−gel-derived hybrid materials,[4] and the recently prepared Sn_2 dications $[R_2(H_2O)Sn(\mu\text{-}OH)_2Sn(H_2O)R_2]^{2+}Y^-{}_2$ ($Y = CF_3SO_3$, $C_8F_{17}SO_3$) were shown to be very efficient alcohol acetylation and C−C coupling bond catalysts.[5] As a consequence of hydrolysis, all Sn_2 dications contain a coordinated molecule of water (Chart 1).

Chart 1 Ionic Sn_2 Dications Prepared to Date



Scheme 1. Preparation of Compounds 1 and 2



Results and Discussion

In this context, we have prepared the Sn_2 dication $[Ph(L^1)Sn(\mu\text{-}OH)_2Sn(L^1)Ph]^{2+}(1\text{-}CB_{11}H_{12})^-{}_2$ (**2**), where L^1 is 1-{2,6-$(MeOCH_2)_2C_6H_3$}, which is free of any coordinated water molecule. Compound **2** exhibits high catalytic activity in the acetylation of alcohols.

Since the use of Y,C,Y-chelating ligands (Y = O in 2,6-$(MeOCH_2)_2C_6H_3$ and 5-^{t}Bu-1,3-$[P(O)(OEt)_2]_2C_6H_2$ and Y = N in 2,6-$(Me_2NCH_2)_2C_6H_3$) was shown to be a possible way to prepare organotin cations,[6] we attemted to prepare the diorganotin cation $[Ph(L^1)SnCl]^+[1\text{-}CB_{11}H_{12}]^-$ (**1**) by treating $Ph(L^1)SnCl_2$ with $Ag(1\text{-}CB_{11}H_{12})$ in CH_2Cl_2.[7] However, during our attempts to prepare single crystals for X-ray diffraction,

---

* To whom correspondence should be addressed. E-mail: roman.jambor@upce.cz. Fax: +420 466037068.

[†] University of Pardubice.

[‡] Charles University in Prague.

(1) (a) Rochow, E. G.; Seyferth, D. *J. Am. Chem. Soc.* **1953**, *75*, 2877 and references therein. (b) Okawara, R.; Rochow, E. G. *J. Am. Chem. Soc.* **1960**, *82*, 3285. (c) McGrady, M. M.; Tobias, R. S. *Inorg. Chem.* **1964**, *3*, 1157. (d) Clark, H. C.; O'Brien, R. J. *Inorg. Chem.* **1965**, *2*, 740. (e) Clark, H. C.; O'Brien, R. J.; Pickard, A. L. *J. Organomet. Chem.* **1965**, *4*, 43. (f) Birchall, T.; Manivannan, V. *J. Chem. Soc., Dalton Trans.* **1985**, 2671. (g) Lambert, J. B.; Kuhlmann, B. *J. Chem. Soc., Chem. Commun.* **1992**, 931. (h) Lambert, J. B.; Ciro, S. M.; Stern, C. L. *J. Organomet. Chem.* **1995**, *499*, 49. For a recent review of organotin cations, see: (i) Miller, T *Adv. Organomet. Chem.* **2005**, *53*, 155.

(2) Wada, M.; Okawara, R. *J. Organomet. Chem.* **1965**, *4*, 487.

(3) (a) Wrackmeyer, B.; Kehr, C.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1370. (b) Wrackmeyer, B.; Kehr, G.; Sebald, A.; Kümmerlen, J. *Chem. Ber.* **1992**, *125*, 1597. (c) Wirth, A.; Moers, O.; Blaschette, A.; Jones, P.G. *Z. Anorg. Allg. Chem.* **1999**, *625*, 982.

(4) (a) Banse, F.; Ribot, F.; Tolédano, P.; Maquet, J.; Sanchez, C. *Inorg. Chem.* **1995**, *34*, 6371. (b) Ribot, F.; Banse, F.; Sanchez, C.; Lahcini, M.; Jousseaume, B. *J. Sol-Gel Sci. Technol.* **1997**, *8*, 529. (c) Ribot, F.; Sanchez, C.; Willem, R.; Martins, J. C.; Biesemans, M. *Inorg. Chem.* **1998**, *37*, 911. (d) Eychenne-Baron, C.; Ribot, F.; Sanchez, C. *J. Organomet. Chem.* **1998**, *567*, 137.

(5) (a) Sakamoto, K.; Hamada, Y.; Akashi, H.; Orita, A.; Otera, J. *Organometallics* **1999**, *18*, 3555. (b) Sakamoto, K.; Ikeda, H.; Akashi, H.; Fukuyama, T.; Orita, A.; Otera, J. *Organometallics* **2000**, *19*, 3242. (c) Otera, J. *Acc. Chem. Res.* **2004**, *37*, 288. (d) Li, X.; Kurita, A.; Man-e, S.; Orita, A.; Otera, J. *Organometallics* **2005**, *24*, 2567.

(6) (a) Jastrzebski, J. T. B. H.; van der Schaaf, P. A.; Boersma, J.; van Koten, G.; de Wit, M.; Wang, Y. D.; Heijdenrijk, Y. D.; Stam, C. H. *J. Organomet. Chem.* **1991**, *407*, 301. (b) Růžička, A.; Dostál, L .; Jambor, R.; Buchta, V.; Brus, J.; Císařová, I.; Holčapek, M.; Holeček, J. *Appl. Organomet. Chem.* **2002**, *16*, 315. (c) Peveling, K.; Henn, M.; Löw, C.; Mehring, M.; Schürmann, M.; Costisella, B.; Jurkschat, K. *Organometallics* **2004**, *23*, 1501. (d) Kašná, B.; Jambor, R.; Dostál, L.; Růžička, A.; Císařová, I.; Holeček, J. *Organometallics* **2004**, *23*, 5300.

(7) $Ag(1\text{-}CB_{11}H_{12})$ (0.33 g, 1.0 mmol) was added to a stirred solution of $Ph(L^1)SnCl_2$ (0.432 g, 1.0 mmol) in CH_2Cl_2 (10 mL). The suspension was stirred for 2 days at ambient temperature. After this time, the AgCl was filtered off and the solvent was evaporated in vacuo. The residue was washed with pentane to afford **1** as a white solid. Yield: 0.52 g (96%). Mp: 145−148 °C. Anal. Calcd for $C_{17}H_{30}B_{11}ClO_2Sn$ (mol wt 539.50): C, 37.85; H, 5.60. Found: C, 37.81; H, 5.39. Mol wt: 540. MS: *m/z* 397, 100%, $[M - CB_{11}H_{12}]^+$; *m/z* 143, 100%, $[CB_{11}H_{12}]^-$. ^{1}H NMR ($CDCl_3$; δ (ppm)):2.15 (s, cage CH); 3.86 (s, 6H, CH_3); 5.19 (AB spin system, 4H, CH_2, $^nJ(^1H,^1H) = 12.3$ Hz); 7.43−7.87 (complex pattern, 8H, SnPh, SnC_6H_3). ^{13}C NMR ($CDCl_3$; δ (ppm)): 42.60 (s, cage *C*H); 61.10 (CH_3), 74.0 (CH_2, $^nJ(^{119}Sn,^{13}C) = 36.10$ Hz); SnC_6H_3, 131.73 (C(1)), 140.82, 125.08, 121.03; SnPh, 133.88 (C′(1)), 135.74, 131.31, 134.31. ^{119}Sn NMR ($CDCl_3$; δ (ppm)): −88.13. ^{11}B NMR ($CDCl_3$; δ (ppm)): −10.03 (s, 1B, B(12)); −16.38 (s, 5B, B(7−11)); −20.37 (s, 5B, B(2−6)). IR (suspension in Nujol; cm^{-1}): ν(BH) 2569.

10.1021/om7002893 CCC: $37.00

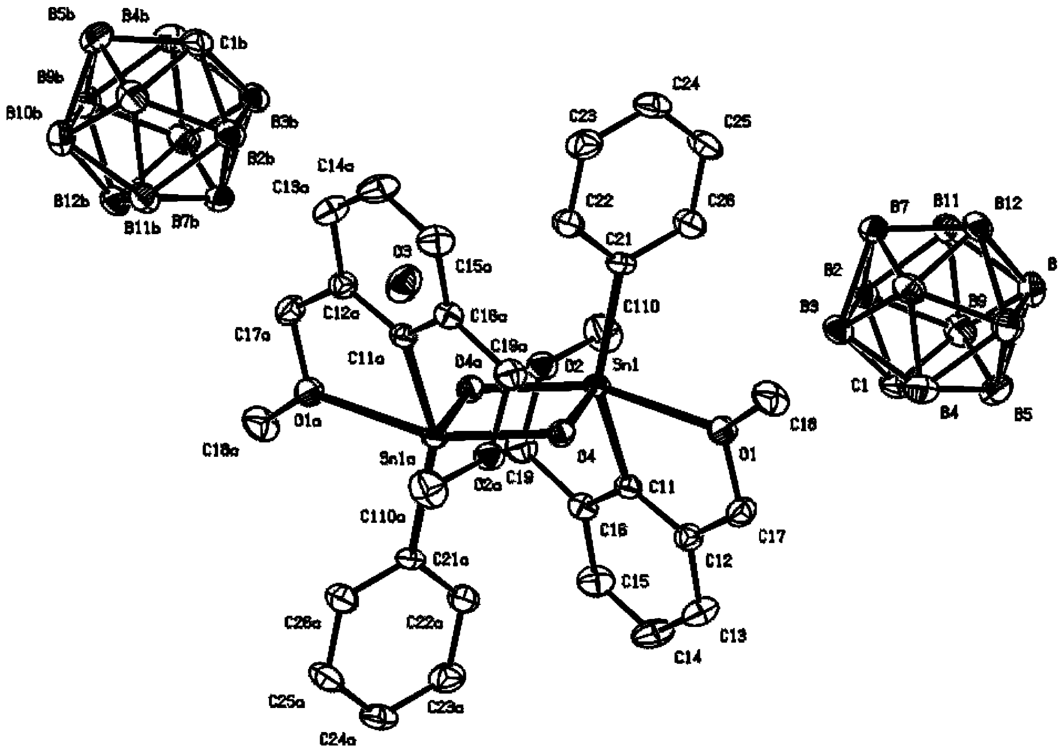


Figure 1. ORTEP view of **2**. The thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Sn1−O4 = 2.0744(11), Sn1−O4a = 2.0942(11), Sn1−C11 = 2.0933(15), Sn1−C21 = 2.1062(16), Sn1−O1 = 2.3502(11), Sn1−O2 = 2.6414(13), Sn1a−O2a = 2.6414(13); O4−Sn1−C11 = 104.40(5), O4−Sn1−O4a = 70.82(5), C11−Sn1−O4a = 104.35(5), O4−Sn1−C21 = 103.30(5), C11−Sn1−C21 = 146.73(6), O4a−Sn1−C21 = 101.88(5), O4−Sn1−O1 = 79.75(4), C11−Sn1−O1 = 73.85(5), O4a−Sn1−O1 = 149.18(5), C21−Sn1−O1 = 93.45(5).

Table 1. Acetylation of Alcohol by 2[a]

$$\mathrm{ROH} \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{Ac_2O/cat.}} \mathrm{ROAc}$$

ROH	concn, mol %	reacn time, min	yield, %[b]
$CH_3(CH_2)_6OH$[c]	0.01	5	48
	0.01	9	99
$CH_3CH(OH)CH_3$[d]	0.01	5	17
	0.01	20	100

[a] Reaction conditions: ROH (5 mmol); Ac_2O (5 mL). [b] Determined by GC. [c] Yields (0.1 mol % concentration, reaction time 60 min): 12% (without catalyst), 22% ($Ph(L^1)SnCl_2$). [d] Yields (0.1 mol % concentration, reaction time 60 min): 0% (without catalyst), 0% ($Ph(L^1)SnCl_2$).

Table 2. Comparison of Catalytic Activities of 2, 3a, and 3b in the Acetylation of 2-Phenylethanol[a]

$$\mathrm{Ph(CH_2)_2OH} \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{Ac_2O/cat.}} \mathrm{Ph(CH_2)_2OAc}$$

compd	concn, mol %	reacn time, min	yield, %[b,c]
2	0.01	10	97
	0.005	30	91
3a[d]	0.01	10	93
	0.005	30	93
3b[d]	0.01	10	95
	0.005	30	90

[a] Reaction conditions: ROH (5 mmol); Ac_2O (5 mL). [b] Determined by GC. [c] Yields (0.1 mol % concentration, reaction time 60 min): 2% (without catalyst), 29% ($Ph(L^1)SnCl_2$). [d] See ref 5a.

compound **2** was isolated. Compound **1** underwent facile hydrolysis. Compound **2** was prepared directly in wet THF in 40% yield as an air-stable solid (Scheme 1).[8]

The ^{119}Sn NMR spectrum of **1** in $CDCl_3$ exhibited a singlet at −88.1 ppm, diagnostic of [3 + 2] coordinated organotin cations,[9] shifted downfield compared to the signal for the starting material $Ph(L^1)SnCl_2$ (−204.2 ppm). The formation of prochiral **1** was further confirmed by the ^{1}H NMR spectrum, where an AB spin system at 5.2 ppm was observed for CH_2O groups, indicating their diastereotopicity.[10] The ^{119}Sn NMR spectrum of **2** exhibited a singlet at −315.1 ppm, which is shifted upfield compared to the signal for the starting material $Ph(L^1)SnCl_2$. The ^{1}H NMR spectrum showed a broad singlet at 5.0 ppm for the CH_2 groups. Three resonances in a 1:5:5 ratio found in the ^{11}B NMR spectra of **1** and **2** indicate the presence of a free $CB_{11}H_{12}$ anion.[11] Figure 1 illustrates the structure of **2**, determined by single-crystal X-ray analysis.[12]

The whole molecule consists of a dimeric organotin dication compensated by two $CB_{11}H_{12}$ anions. Although the tin atoms

---

(8) Yield: 0.42 g (40%). Mp: 185−189 °C. Anal. Calcd for $C_{34}H_{62}B_{22}O_6Sn_2$ (mol wt 1042.11): C, 39.19; H, 6.00. Found: C, 39.21; H, 6.02. Mol wt: 1042. MS: *m/z* 379, 100%, $[(M - 2CB_{11}H_{12})]^{2+}$; *m/z* 143, 100%, $[CB_{11}H_{12}]^-$. ^{1}H NMR ($CDCl_3$; δ (ppm)): 2.24 (bs, 1H, cage CH); 3.47 (s, 6H, CH_3); 5.04 (s, 4H, CH_2); 7.47−7.71 (complex pattern, 8H, SnPh, SnC_6H_3). ^{13}C NMR ($CDCl_3$; δ (ppm)): 59.84 (CH_3); 68.12 (cage *C*H); 71.12 (CH_2, $^nJ(^{119}Sn,^{13}C)$ = 29.21 Hz); SnC_6H_3, 126.49 (C(1)), 144.67, 126.75, 133.06; SnPh, 135.26 (C′(1)), 136.03, 131.04, 133.46. ^{119}Sn NMR ($CDCl_3$; δ (ppm)): −315.07. ^{11}B NMR ($CDCl_3$; δ (ppm)): −5.05 (s, 1B, B(12)); −11.41 (s, 5B, B(7−11)); −14.40 (s, 5B, B(2−6)). IR (solution in $CHCl_3$; cm^{-1}): ν(BH) 2539. IR (suspension in Nujol; cm^{-1}): ν(BH) 2543, ν_{as}(SnOSn) 721, ν_s(SnOSn) 439.

(9) (a) These ^{119}Sn values were found in the pentacoordinate phenyl cations C_3Sn^+ with trans-trigonal-bipyramidal geometry in triorganotin compounds containing Y,C,Y-chelating ligands, and the downfield shift of $\Delta[\delta(^{119}Sn)]$ = 116 ppm as one goes from the starting molecular complex $Ph(L^1)SnCl_2$ to **1** is typical for an ionization process where a Sn−X bond is cleaved. (b) Kašná, B.; Jambor, R.; Dostál, L.; Kolářová, L.; Císařová, I.; Holeček, J. *Organometallics* **2006**, *25*, 148.

(10) For the proposed structure of **1**, see the Supporting Information.

Table 3. Selective Acetylation of Primary Alcohol over Secondary Alcohol under Catalysis of 2[a]

$$\begin{bmatrix} Ph(CH_2)_2OH & \xrightarrow[30\ °C]{Ac_2O/cat.\ \mathbf{2}} & Ph(CH_2)_2OAc \\ CH_3CH(OH)CH_3 & & CH_3CH(OAc)CH_3 \end{bmatrix}$$

ROH	concn, mol %	reacn time, min	yield, %[b]	ratio
$Ph(CH_2)_2OH$	0.01	10	86	95:5
$CH_3CH(OH)CH_3$			5	
$Ph(CH_2)_2OH$	0.005	30	84	89:11
$CH_3CH(OH)CH_3$			10	

[a] Reaction conditions: $Ph(CH_2)_2OH$ (2.5 mmol)/$CH_3CH(OH)CH_3$ (2.5 mmol); Ac_2O (5 mL). [b] Detected by GC.

are ionic, they are free of any solvated molecule. The Sn_2 dication contains hydroxyl bridges, thus forming a four-membered Sn_2O_2 ring. The values of the Sn1−O1, Sn1−O2 and Sn1a−O1a, Sn1a−O2a bond lengths demonstrate the presence of strong and medium-strong Sn−O interactions. Tin atoms Sn1 and Sn1a are both hexacoordinated as a consequence of the presence of those interactions. This is also the reason that **2** does not contain additional water molecules coordinated to the tin atoms, although these molecules are present in the crystal cell of **2**. A similar ionic but solvated structure has been characterized for $[R_2(H_2O)Sn(\mu\text{-}OH)_2Sn(H_2O)R_2]^{2+}Y^-{}_2$ (Y = CF_3SO_3, $C_8F_{17}SO_3$), where bulky substituents were used.[5]

As a consequence of the increased Lewis acidity of the tin atom in the Sn_2 dication, compound **2** is an efficient catalyst for alcohol acetylation (Table 1).

Remarkably, the desired acetates were obtained at 30 °C in 10 min, and a 0.01 mol % concentration of **2** was sufficient for quantitative yields.

The catalytic activity of **2** is comparable with those of the previously prepared Sn_2 dications $[R_2(H_2O)(OTf)Sn(\mu\text{-}OH)_2\text{-}Sn(H_2O)(OTf)]$ (**3a**, R = ^{n}Bu; **3b**, R = ^{t}Bu). The catalytic activity of these compounds in the acetylation of 2-phenylethanol is given in Table 2, from which is seen that only a 0.005 mol % concentration of **2** is sufficient for quantitative yields of the desired 2-phenylethyl acetate.

Since the selective acetylation of primary alcohols in the presence of secondary alcohols is of great synthetic value, we have tried to investigate the competition in acetylation between primary and secondary alcohols under catalysis of **2**.

As shown in Table 3, there is a preference for primary alcohols and particularly notable are the high selectivities together with high conversions. Compound **2** maintains a high primary/secondary acetate ratio with over 90% conversion.

In summary, we have prepared a Sn_2 diorganotin dication which in contrast to the rare analogues prepared thus far does not contain a coordinated water molecule. Compound **2** exhibits high catalytic activity in the acetylation of alcohols as a consequence of its ionic nature. Other possible applications together with the preparation of similar cations are currently of interest to us.

Acknowledgment. We wish to thank The Ministry of Education of the Czech Republic (Project Nos. VZ0021627501 and LC523) for financial support.

Supporting Information Available: Text and a figure giving details of the catalytic experiments and a CIF file giving further details of the structure determination of **2**, including atomic coordinates, anisotropic displacement parameters, and geometric data. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for compound **2** have also been deposited with the Cambridge Crystallographic Data Centre (file no. CCDC 634588).

OM7002893

---

(11) (a) Knoth, W. H. *J. Am. Chem. Soc.* **1967**, *89*, 1274. (b) Knoth, W. H. *Inorg. Chem.* **1971**, *10*, 598. (c) Plešek, J; Jelínek, T.; Drdáková, E.; Heřmánek, S.; Štíbr, B. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1559.

(12) Crystallographic data for **2**: $C_{32}H_{38}O_6Sn_2 \cdot 2CH_{12}B_{11} \cdot 2H_2O$, triclinic, $P\bar{1}$ (No. 2), colorless, $a = 9.5000(2)$ Å, $b = 12.0520(3)$ Å, $c = 13.0070(3)$ Å, $\alpha = 62.773(1)°$, $\beta = 76.968(1)°$, $\gamma = 76.994(1)°$, $V = 1277.28(5)$ Å^3, $T = 150(2)$ K, $Z = 1$, $M_w = 1078.07$, $D_x = 1.402$ Mg m^{-3}, 5869 unique reflections, 5495 observed reflections ($I > 2\sigma(I)$), $R(I > 2\sigma(I)) = 0.021$, wR2(all data) = 0.050, GOF = 1.066.