

Sulfonate-bonded tin complexes for the production of diphenyl carbonate

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Abstract

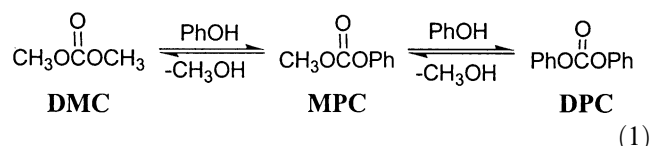
Various tin complexes including dibutyltin oxide and dibutyltin diacetate were tested for their activities in the transesterification between dimethyl carbonate (DMC) and phenol to produce diphenyl carbonate (DPC). The activities of tin complexes were significantly enhanced by the co-presence of alkyl or arylsulfonic acid, possibly due to the in situ formation of sulfonate-bonded tin complexes. Highly active triflate-bonded tin species, $[\text{Bu}_2\text{Sn}(\text{OH})(\text{OTf})_2]$ and $[\text{Bu}_2\text{Sn}(\text{OAc})(\text{OTf})_2]$, were isolated from the reaction of triflic acid with dibutyltin oxide and dibutyltin diacetate, and characterized by single crystal X-ray diffraction study.
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1. Introduction

Polycarbonate, one of the most important engineering thermoplastics, is being commercially produced by reacting bisphenol-A with phosgene [1,2]. This conventional phosgenation process, however, has the serious environmental problems such as the use of highly toxic phosgene, the formation of a stoichiometric amount of NaCl, and the use of a copious amount of methylene chloride as a solvent. Accordingly, there have been tremendous efforts to produce polycarbonate by using non-phosgene methods [3–5].

The most practical non-phosgene process seems to be the melt polymerization of bisphenol-A with diphenyl carbonate (DPC) which can be prepared from step-wise transesterification of dimethyl carbonate (DMC) with phenol with the continuous removal of methanol as shown in the following equation [6–8]:



However, due to the thermodynamically unfavorable equilibrium ($K = 3 \times 10^{-4}$ at 453 K) toward DPC, the reaction suffers from low yield and selectivity even at elevated temperature [9]. Various tin complexes have been applied as catalysts for the production of DPC by the transesterification between DMC and phenol, but their catalytic activities are not high enough for the industrial purpose [10,11].

We now report highly efficient catalytic system consisting of an alkyl or arylsulfonic acid and a tin complex for the transesterification between DMC and phenol as well as the X-ray structural characterization of $[\text{Bu}_2\text{Sn}(\text{OH})(\text{OTf})_2]$ and $[\text{Bu}_2\text{Sn}(\text{OAc})(\text{OTf})_2]$.

2. Results and discussion

The activities of various tin compounds have been tested for the transesterification between DMC and phenol. The transesterification reactions were performed

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Table 1
Activities of various tin complexes for the transesterification of dimethyl carbonate with phenol^a

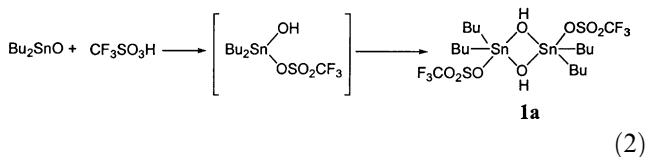
Entry	Catalyst	DMC conv. (%)	Yield (%)		
			DPC	MPC	Anisole
1	Bu ₂ SnO	21.0	4.0	16.7	0.3
2	Bu ₂ Sn(OAc) ₂	17.0	3.8	12.0	1.2
3	[Bu ₂ Sn(OPh)] ₄ (μ ₃ -O) ₂ , 3	22.9	4.9	17.2	0.8
4	Bu ₂ SnO/CF ₃ SO ₃ H	58.1	18.3	39.8	trace
5	Bu ₂ SnO/CH ₃ SO ₃ H	56.2	19.7	36.5	trace
6	Bu ₂ SnO/CH ₃ C ₆ H ₄ SO ₃ H	60.2	20.8	39.4	trace
7	Bu ₂ Sn(OAc)/CF ₃ SO ₃ H	57.5	19.1	38.4	0.1
8	[Bu ₂ Sn(OPh)] ₄ (μ ₃ -O) ₂ , 3 /CF ₃ SO ₃ H	58.0	20.4	37.6	trace
9	[Bu ₂ Sn(OH)(OTf)] ₂ , 1a	60.9	20.0	40.9	trace
10	[Bu ₂ Sn(OAc)(OTf)] ₂ , 2	58.1	19.6	38.5	trace

^a Dimethyl carbonate (40 mmol), phenol (200 mmol), catalyst (0.4 mmol based on Sn atom), sulfonic acid (0.4 mmol), benzene (40 ml), and molecular sieves (30 g), 180 °C, *t* = 3 h.

in the presence of molecular sieves (4A) at 180 °C for 3 h in a 100-ml stainless steel reactor equipped with an electrical heater.

As can be seen in Table 1, Bu₂SnO gave low yields of DPC and methyl phenyl carbonate (MPC) along with the formation of a by-product, anisole. However, when an alkyl or aryl sulfonic acid was used in conjunction with dibutyltin oxide, the yields of DPC and MPC greatly increased, while the formation of anisole decreased. Similarly, the activity of dibutyltin diacetate also increased significantly by the presence of a sulfonic acid. No appreciable changes in catalytic activities of dibutyltin oxide and dibutyltin diacetate were observed with the variation of substituent on the sulfonic acid.

To have a better understanding of the role of sulfonic acid, we have carried out a reaction of dibutyltin oxide with an equimolar amount of triflic acid in CH₂Cl₂ for 2 h at an ambient temperature Eq. (2). Following addition of *n*-hexane into the reaction mixture produced a white solid, which turned out to be a highly active intermediate species for the transesterification reaction,



¹H, ¹³C, ¹⁹F, and ¹¹⁹Sn NMR spectra show that the white solid is a tin complex containing *n*-butyl and triflate ligands. Due to the ambiguity of the spectroscopic data of the complex, we have conducted a single crystal X-ray diffraction study. Interestingly, as shown in Figs. 1 and 2, the X-ray diffraction analysis reveals that the crystal unit cell contains mutually interacting two anhydrous and hydrated molecules, [Bu₂Sn(OH)(OTf)]₂, **1a** and [Bu₂Sn(OH)(OTf)(H₂O)]₂, **1b** (Table 2). Each tin atom in **1a** and **1b** is six-coordinated and adopts a distorted octahedral geometry [12,13]. The distance between Sn and the triflate oxygen for the hydrated

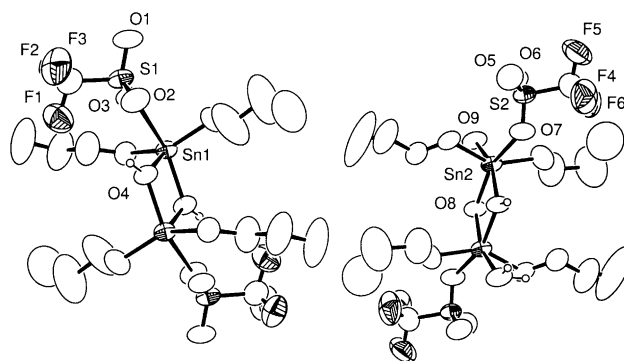


Fig. 1. Molecular structures of **1** (**1a**–**1b**). The hydrogen atoms on carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–O(4) 2.090(4), Sn(1)–O(4*) 2.120(4), Sn(1)–O(3) 2.492(5), Sn(2)–O(8) 2.064(4), Sn(2)–O(8*) 2.138(4), Sn(2)–O(7) 2.863(3), Sn(2)–O(9) 2.364(5), O(4)–Sn(1)–O(4*) 80.07(2), Sn(1)–O(4)–Sn(1*) 109.59(2), O(8)–Sn(2)–O(8*) 71.11(2), Sn(2)–O(8)–Sn(2*) 108.89(2).

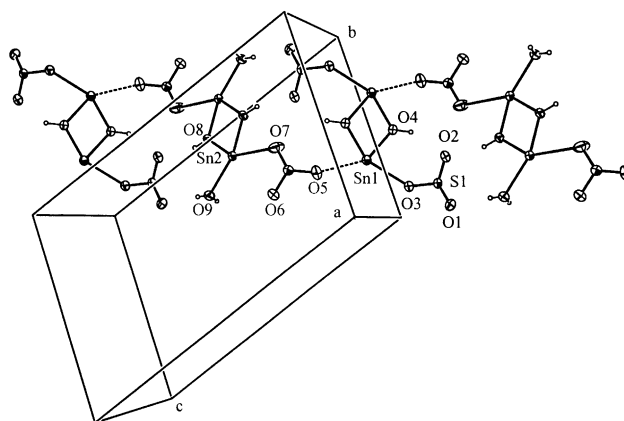


Fig. 2. Packing diagram of the complexes **1** (**1a**–**1b**) viewed along the *c* axis of the unit cell. The butyl and trifluoromethyl groups have been omitted for clarity. Intermolecular interactions between triflate oxygen in complex **1a** and tin atom in complex **1b** are represented by dashed line.

Table 2
Crystallographic data for compounds **1** and **2**

	1 (1a · 1b)	2
Molecular formula	C ₃₆ H ₈₀ F ₁₂ O ₁₈ S ₄ Sn ₄	C ₂₂ H ₂₆ F ₆ O ₁₂ S ₂ Sn ₂
(empirical formula)	(C ₁₈ H ₄₀ F ₆ O ₉ S ₂ Sn ₂)	(C ₁₁ H ₂₃ F ₃ O ₆ SSn)
Formula weight	816.06	459.54
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Z	4	4
Cell constants		
<i>a</i> (Å)	9.811(2)	8.963 (2)
<i>b</i> (Å)	11.995(2)	9.120(2)
<i>c</i> (Å)	14.628(3)	12.128(2)
α (°)	87.78(3)	105.69(3)
β (°)	72.63(3)	96.06(3)
γ (°)	81.97(3)	100.10(3)
Volume (Å ³)	1626.8(6)	927.3(3)
μ (mm ⁻¹)	1.736	1.538
<i>D</i> _{calc} (g/cm ³)	1.666	1.644
2 θ _{max} (°)	51.8	51.8
No. of reflections used in refinement (<i>I</i> > 2 σ (<i>I</i>))	6372	3625
No. of parameters	338	202
Residuals ^a : <i>R</i> ₁ ; <i>wR</i> ₂	0.05; 0.13	0.04; 0.11
Goodness-of-fit	1.03	0.75

GOF = $[\sum_{hkl} (w(|F_o^2| - |F_c^2|)^2 / (n_{\text{data}} - n_{\text{vari}}))]^{1/2}$.
^a $R_1 = \sum (||F_o| - |F_c||) / \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$;
 $w = 1 / [\sigma^2(F_o^2) + (0.0932P)^2 + 0.0000P]$ for **1** and $1 / [\sigma^2(F_o^2) + (0.1156P)^2 + 2.1798P]$ for **2**, where $P = (F_o^2 + 2F_c^2) / 3$.

complex **1b** is longer by 0.372 Å in comparison with that in the non-hydrated complex **1a**, implying a significant electron donation from H₂O to the electrophilic Sn atom. The anhydrous and hydrated tin complexes are likely to form a polymeric structure through interaction of triflate oxygen of hydrated complex **1b** to the tin atom of anhydrous complex **1a** [14,15]. The interaction between two molecules can be clearly seen in the packing diagram shown in Fig. 2, where triflate oxygen O(5) is closely located to Sn(1) with the distance of 2.630(4) Å.

Triflate-bonded tin complex **2** was similarly prepared by the reaction of the dibutyltin diacetate with triflic acid in CH₂Cl₂ and characterized by ¹H, ¹³C, ¹¹⁹Sn NMR, and X-ray crystallography (Table 2). Complex **2** was crystallized as a hydrated form. The molecular structure of **2** depicted in Fig. 3 reveals that Sn(1), O(4), Sn(1*), and O(4*) constitute a square planar and one of the oxygen atoms of the acetate ligand interacts intermolecularly with tin atom of the different molecule. This is why one of the Sn–O bond lengths of acetate substituent is slightly longer than the other (Sn(1)–O(4) = 2.402(4) Å and Sn(1)–O(5) = 2.256(3) Å).

As expected, complex **1a** exhibited a similar activity to the corresponding catalytic system consisting of Bu₂SnO and triflic acid. This result strongly suggests that the transesterification reaction in the presence of the catalytic system composed of Bu₂SnO and triflic acid is, indeed, catalyzed by in situ formed **1a**.

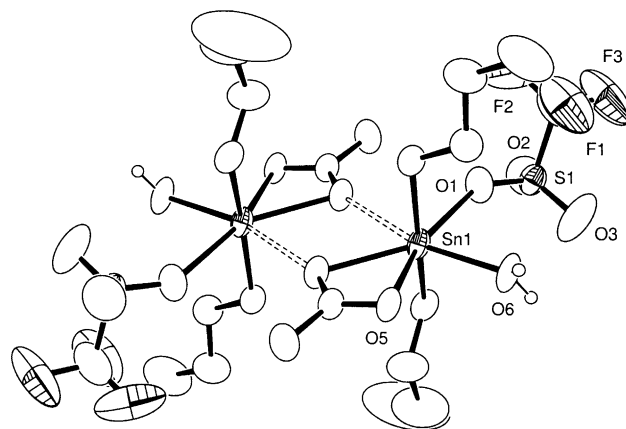
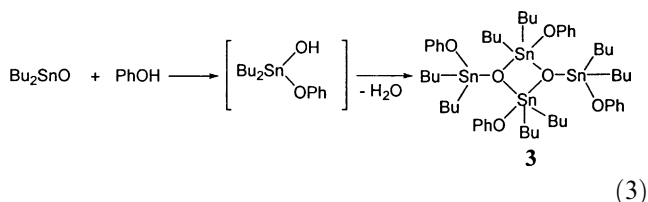
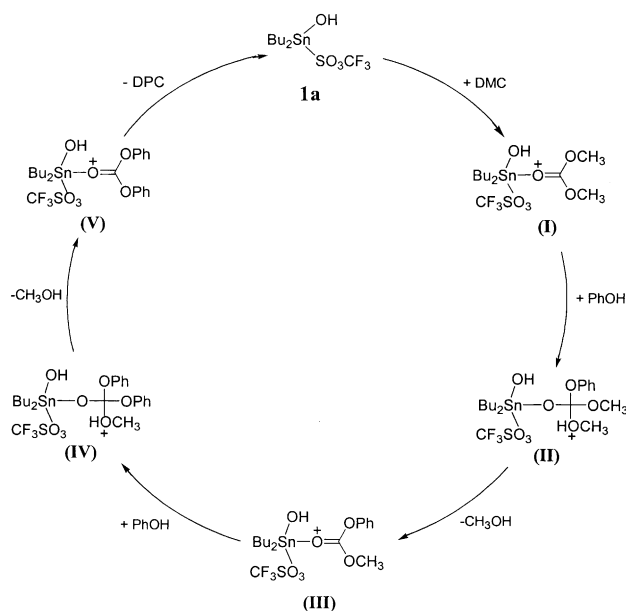


Fig. 3. Molecular structures of **2**. The hydrogen atoms on carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–O(4) 2.402(4), Sn(1)–O(5) 2.256(3), Sn(1)–O(4*) 2.612(4), Sn(1)–O(1) 2.472(4), Sn(1)–O(6) 2.210(3), Sn(1)–O(4)–Sn(1*) 115.51(7), O(4)–Sn(1)–O(1) 143.30(1), O(4)–Sn(1)–O(5) 55.13(1), C(4)–Sn(1)–C(8) 163.4(2).

The higher activity of **1a** compared with dibutyltin oxide can be largely ascribed to the presence of electronegative triflate ligands coordinated to Sn atoms. As a result of a triflate bonding, the Sn atom becomes highly electrophilic or Lewis acidic, thereby facilitating the nucleophilic attack of DMC on Sn atom. On the other hand, in the absence of triflic acid, dibutyltin oxide easily reacts with phenol to produce a less active and sterically crowded tetrameric tin complex, [Bu₂Sn(OPh)]₄(μ₃-O)₂, **3** [16],



The catalytic activity of **3** also increased by the co-presence of triflic acid (entry 8), possibly due to the formation of an active intermediate species with triflate ligands. The formation of triflate-bonded complex with the liberation of phenol is evident from the ¹H NMR spectrum (not shown here). The increase in electrophilicity due to the triflate bonding is supported by the comparison of ¹¹⁹Sn NMR spectral data for **1a** and **3**, which show a singlet at –156.3 ppm for **1a** and two singlets at –178.5 and –177.8 ppm for **3**. The two singlets can be ascribed to the presence of the four- and five-coordinated tins, respectively. The strong Lewis acidic character of Sn atoms in complex **1a** is obvious from the coordination of water molecules to complex **1a** to give complex **1b**. Based on the experimental and spectroscopic results as well as the structural analysis, a plausible mechanism of the transesterification with **1a** is



Scheme 1. Plausible mechanism for the transesterification of DMC with phenol in the presence of **1a**.

proposed in Scheme 1. For clarity, only a monomeric portion of **1a** is depicted.

Coordination of DMC to complex **1a** is likely to occur first to give species **I**. An attack of phenol on the carbonyl carbon of the coordinated DMC followed by the elimination of methanol would give **III**. The MPC-coordinated species **III** either loses MPC to generate complex **1a** or reacts with an additional phenol to give species **IV**. The subsequent elimination of methanol and DPC from species **IV** would regenerate **1a**.

Effort to tune the catalytic activity of complex **1a** by modifying the ligand set is in progress.

3. Experimental

3.1. General

Dimethyl carbonate and phenol were purchased from Aldrich Chemical Co. and distilled just before use. All other chemicals were obtained from Aldrich Chemical Co. and used as received. Catalysts were prepared under Ar atmosphere. ¹H, ¹³C, ¹⁹F, and ¹¹⁹Sn NMR measurements were carried out using a Varian UNITYplus-300. CF₃CO₂H and SnMe₄ were used as external references for ¹⁹F and ¹¹⁹Sn, respectively.

3.2. Preparation of sulfonate-bonded tin complexes

Triflic acid (10 mmol) was reacted with a dibutyltin compound (10 mmol) in 50 ml CH₂Cl₂ in a 100-ml round-bottomed flask at room temperature for 3 h. After the reaction, the reaction mixture was filtered off

to remove unreacted dibutyltin compounds. The addition of *n*-hexane into the resulting solution produced triflate-bonded tin complex as a white solid.

3.2.1. Complex **1a**

Yield: 95.4%; ¹H NMR (300 MHz, CDCl₃) δ = 0.85 (t, 6H; CH₃), 1.34 (m, 4H; CH₂), 1.71 (m, 8H; CH₂CH₂), 5.28 (s, OH); ¹³C NMR (CDCl₃, 75 MHz) δ = 13.6 (CH₃), 26.4 (CH₂), 26.7 (CH₂, ²J(¹³C–^{117/119}Sn) = 115/120 Hz), 29.1 (CH₂Sn, ¹J(¹³C–^{117/119}Sn) = 322/336 Hz), 119.4 (CF₃, ¹J(¹³C–¹⁹F) = 317.8); ¹⁹F NMR (external reference CF₃CO₂H) δ = –1.63 (s, CF₃); ¹¹⁹Sn NMR (external reference SnMe₄); δ = –156.26(s).

3.2.2. Complex **2**

Yield: 95.1%; ¹H NMR (300 MHz, CDCl₃) δ = 0.99 (t, 6H; CH₃), 1.45 (m, 4H; CH₂), 1.80 (m, 4H; CH₂), 2.02 (m, 4H; CH₂Sn), 2.27 (m, 3H; CH₃CO₂); ¹³C NMR (CDCl₃, 75 MHz): δ = 13.5 (CH₃), 21.2 (CH₃CO₂), 26.4 (CH₂, ²J(¹³C–^{117/119}Sn) = 111/116 Hz), ³J(¹³C–^{117/119}Sn) = 36.9 Hz), 30.2 (CH₂Sn, ¹J(¹³C–^{117/119}Sn) = 384/401 Hz), 119.4 (CF₃, ¹J(¹³C–¹⁹SnF) = 318), 185.2 (CH₃CO₂); ¹¹⁹Sn NMR (111 MHz, CDCl₃): δ = –165.7 (s).

3.3. Transesterification reaction

All the transesterification reactions were conducted in a 100-ml stainless-steel high-pressure reactor equipped with an electrical heater and a 60-ml stainless steel column. The reactor was charged with dimethyl carbonate (40 mmol), phenol (200 mmol), and benzene (40 ml) as a solvent, an appropriate catalyst or a catalytic system, and *t*-butyl benzene (2 g) as an internal standard. Molecular sieves (30 g) were placed in the 60-ml stainless-steel column mounted on the lid of the reactor. The reactor was evacuated to remove air from the molecular sieves and then heated to 180 °C at the rate of 10 °C/min. After the reaction, the reactor was cooled to room temperature and the resulting solution was analyzed by gas chromatography (HP-6890) and gas chromatography–mass spectroscopy (GS–MS, HP-6890N GC-5973MSD).

3.4. X-ray crystallography

Suitable crystals for **1** and **2** were obtained by slow diffusion of hexane into a methylene chloride solution of the complexes at ambient temperature. The crystals used in data collections were glued onto the end of thin glass fiber. X-ray intensity data were measured at 293 K on an Enraf CAD-4 automated diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The unit cells were determined by using search, center, index, and least-squares routines. The intensity data were corrected for Lorentz and polarization effects and for anisotropic decay.

Both compounds **1** and **2** crystallized in the triclinic system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. All structures were solved by the application of direct methods using the SHELXL 86 [17] and were refined by full-matrix least-squares on F^2 by using SHELXL 93 [18]. For each structure, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located and refined using isotropic thermal parameters.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 203808 for compound **1** and CCDC No. 226718 for **2**. Copies of this data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge BD2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://ccdc.cam.ac.uk>).

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