

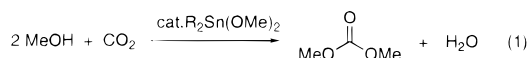
Reaction of Dialkyltin Methoxide with Carbon Dioxide Relevant to the Mechanism of Catalytic Carbonate Synthesis

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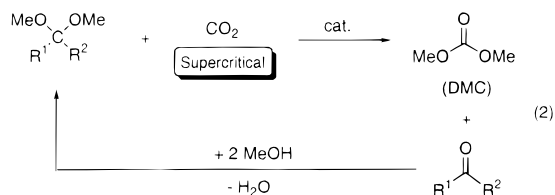
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Conversion of carbon dioxide to industrially useful compounds has been a challenge for synthetic chemists and has recently attracted much interest in view of the so-called “Sustainable Society”¹ and “Green Chemistry”.² One of the most attractive synthetic goals starting from CO₂ is dimethyl carbonate (DMC).³ Indeed, the straightforward reaction of methanol and CO₂ catalyzed by R₂Sn(OMe)₂ leading to DMC has been intensively studied although catalytic performance is still far from satisfactory (eq 1).⁴ Catalyst deactivation and hydrolysis of DMC caused by



coproduced water were postulated as the reason for the low productivity. We have recently enhanced the catalytic efficiency of R₂Sn(OMe)₂ using dehydrated derivatives of methanol (e.g., ortho esters and acetals) as a starting material^{5,6} under supercritical CO₂ conditions.⁷ Especially, the reaction of acetals is attractive because the starting material is much more inexpensive compared with ortho esters, and the coproduced carbonyl compounds can be recycled (eq 2). Hence, the reaction can be regarded as the



DMC synthesis from CO₂ and methanol. In these reactions, carbonate complexes generated via CO₂ insertion into the tin-oxygen bond of R₂Sn(OMe)₂ are proposed as a key intermediate. However, the structure and reactivity of the postulated complex

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(6) Reaction of acetals: submitted to *J. Org. Chem.* A part of the work was presented at the 75th Annual Meeting of Japan Chemical Society, Sakakura, T.; Saito, Y.; Sako, T., Matsuyama, Japan, September 14–19, 1998; Japan Chemical Society; Abstract IA604.

(7) As for homogeneous catalysis in supercritical CO₂, see (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Science* **1995**, *269*, 1065–1069. (b) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259–272. (c) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207–2221. (d) Morgenstern, D. A.; LeLacheur, R. M.; Morita, D. K.; Borkowsky, S. L.; Feng, S.; Brown, G. H.; Luan, L.; Gross, M. F.; Burk, M. J.; Tumas, W. In *Green Chemistry*; Anastas, P. T., Williamson, T. C., Eds.; ACS Symposium Series 626; American Chemical Society: Washington, DC, 1996; pp 132–151.

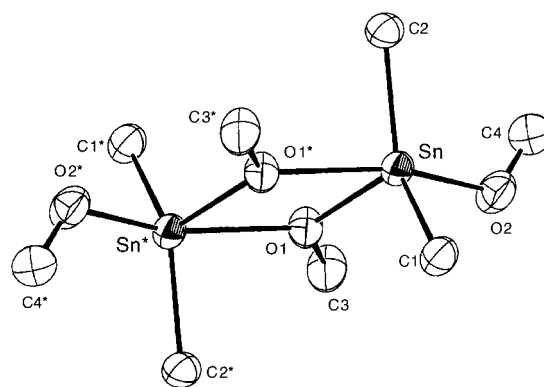


Figure 1. X-ray crystal structure of **1**. Selected bond distances (Å) and angles (deg): Sn(1)–O(1) 2.038(5); Sn(1)–O(1*) 2.324(6); Sn(1)–O(2) 2.038(7); Sn(1)–C(1) 2.121(9); Sn(1)–C(2) 2.130(8); O(1)–C(3) 1.445(10); O(2)–C(4) 1.30(1); O(1)–Sn(1)–O(1*) 68.9(2); O(1)–Sn(1)–O(2) 93.2(3); O(1)–Sn(1)–C(1) 110.0(3); O(1)–Sn(1)–C(2) 109.4(3); O(1*)–Sn(1)–O(2) 161.7(3); O(1*)–Sn(1)–C(1) 86.6(3); O(1*)–Sn(1)–C(2) 88.3(3); O(2)–Sn(1)–C(1) 96.4(3); O(2)–Sn(1)–C(2) 101.8(3); C(1)–Sn(1)–C(2) 135.1(3); Sn(1)–O(1)–Sn(1*) 111.1(2); Sn(1)–O(1)–C(3) 122.8(5).

has not been well defined. In this paper, we report (i) the crystal structures of Me₂Sn(OMe)₂ and its CO₂ insertion product, and (ii) DMC formation via thermolysis of the resulting carbonate complex. This is the first report to elucidate the transformation pathway of CO₂ to DMC by R₂Sn(OMe)₂ at a molecular level.

R₂Sn(OMe)₂ is an active catalyst for various reactions such as DMC synthesis from CO₂,^{5,6} polycarbonate synthesis from CO₂ and epoxides,⁸ stereoselective ring-opening polymerization of β-lactones,⁹ and so on. However, the structure of R₂Sn(OMe)₂ is still unclear and has long been a matter of discussion. Although some papers proposed the polymeric nature of R₂Sn(OMe)₂ (R = Me, Et, Bu) based on Mössbauer and NMR studies,¹⁰ further investigation was required to prove the structure. We have succeeded in obtaining single crystals of Me₂Sn(OMe)₂ from a *tert*-BuOH solution at room temperature. The X-ray structure of the crystal is different from the previously proposed polymeric one and exhibited a distinct methoxy-bridged dinuclear framework as shown in Figure 1.¹¹ The configuration of the tin center can be regarded as distorted trigonal-bipyramidal. A sharp ¹¹⁹Sn NMR signal in solution at δ –162 ppm is also consistent with the five-coordinated dimeric structure.

The reaction of **1** with excess CO₂ (4 equiv) quantitatively afforded a complex having two kinds of new methoxy groups based on the ¹H and ¹³C NMR data. ¹³C NMR also revealed the presence of a carbonyl group, indicating that CO₂ insertion occurred only at one of the two methoxy groups of **1** (eq 3). The



observation of a strong IR peak at 1682 cm⁻¹ was another support for the CO₂ insertion. On the other hand, low temperature ¹¹⁹Sn NMR exhibited one sharp signal at δ –171 ppm, indicating a five-coordinated structure. Broadening of the signal at around

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(11) Crystal data of **1**: monoclinic, P2₁/n, colorless; a = 8.03(1) Å, b = 8.162(6) Å, c = 11.375(8) Å; β = 91.78(8)°; V = 745(1) Å³; Z = 4; R = 0.051; GOF = 1.86.

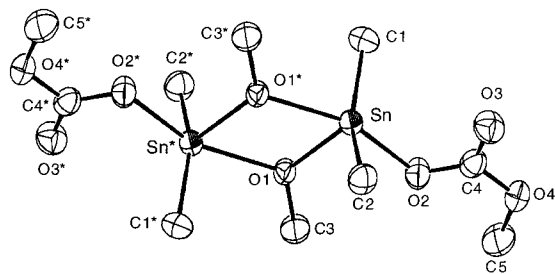
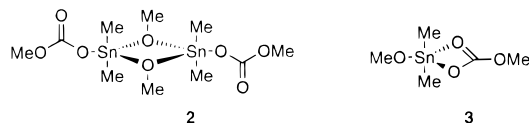


Figure 2. X-ray crystal structure of **2**. Selected bond distances (Å) and angles (deg): Sn(1)–O(1), 2.086(2); Sn(1)–O(1*) 2.223(2); Sn(1)–O(2) 2.192(2); Sn(1)–C(1) 2.102(3); Sn(1)–C(2) 2.110(3); O(1)–C(3) 1.413(4); O(2)–C(4) 1.292(4); O(3)–C(4) 1.201(4); O(4)–C(4) 1.353(4); O(4)–C(5) 1.426(5); O(1)–Sn(1)–O(1*) 71.79(9); O(1)–Sn(1)–O(2) 84.06(9); O(1)–Sn(1)–C(1) 102.1(1); O(1)–Sn(1)–C(2) 104.6(1); O(1)–Sn(1)–O(2) 155.85(9); O(1)–Sn(1)–C(1) 91.8(1); O(1)–Sn(1)–C(2) 91.6(1); O(2)–Sn(1)–C(1) 94.0(1); O(2)–Sn(1)–C(2) 93.8(1); C(1)–Sn(1)–C(2) 152.8(1); Sn(1)–O(1)–Sn(1*) 108.2(1); Sn(1)–O(1)–C(3) 124.3(2); O(2)–C(4)–O(3) 125.9(3); O(2)–C(4)–O(4) 115.9(3).

room temperature suggests a partial and rather slow dissociation process. Taking these NMR data into account, two kinds of carbonate complexes were readily postulated. One is a methoxy-bridged dinuclear complex (**2**) and the other is a mononuclear complex having an intramolecularly coordinated carbonyl group (**3**).



Single crystals of **2** were obtained from a CO₂-saturated CH₂-Cl₂-Et₂O solution at 4 °C; **2** is unstable in solution at room temperature under nitrogen and easily releases CO₂. The X-ray crystal structure of **2** was dinuclear as exhibited in Figure 2 and was completely consistent with the above-stated NMR data.¹² The interaction, if any, between the carbonyl oxygen and the tin center is very weak because the bond length between these atoms is rather long (2.822 Å) and the ¹¹⁹Sn NMR chemical shift is in the range of those of five-coordinated complexes.¹³ Although no precise structural information on the CO₂ insertion products of R₂Sn(OMe)₂ is available,¹⁴ polymeric structures rather than dimeric ones were proposed for R₃SnOC(O)OSnR₃.¹⁵ On the other

(12) Crystal data of **2**: triclinic, *P* $\bar{1}$, colorless; *a* = 8.160(3) Å, *b* = 8.724(2) Å, *c* = 6.641(2) Å; α = 92.77(2)°, β = 110.46(3)°, γ = 93.01(2)°; *V* = 441.2(2) Å³; *Z* = 2; *R* = 0.026; GOF = 1.70.

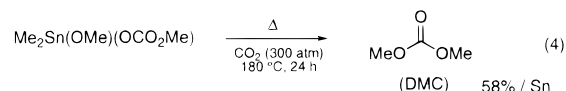
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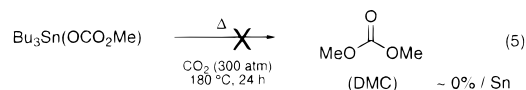
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hand, Darensbourg et al. have very recently reported the X-ray structure of the CS₂ insertion product of Cd(OAr)₂; the structure is dimeric with a thiocarbonyl group coordinating to the metal center.¹⁶ Unfortunately, the quality of the X-ray data was not good (*R* = 12%) and the attempt to identify the CO₂ insertion products failed.

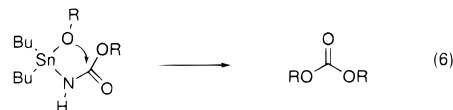
As we succeeded in elucidating the structure of the CO₂ insertion product of R₂Sn(OMe)₂, we next investigated the DMC formation from **2**. Upon heating to 180 °C under supercritical CO₂ (300 atm), **2** was converted to DMC in a reasonable yield as shown in eq 4.¹⁷ Very interestingly, the carbonate complex



prepared from Bu₃Sn(OMe),^{14c} which is inactive for catalytic DMC formation,^{5,6} did not give DMC under the same conditions (eq 5). Thus, the reactivities in stoichiometric reactions correspond



well with the difference in catalytic activities between Bu₂Sn(OMe)₂ and Bu₃Sn(OMe). Although precise mechanistic discussion is premature, an intramolecular pathway is presumably important to obtain DMC from **2**. Such an intramolecular process was discussed for a dialkyltin-catalyzed carbonate synthesis from carbamates (eq 6).¹⁸



In summary, we elucidated the structure of Me₂Sn(OMe)₂ and its CO₂ insertion product, Me₂Sn(OMe)(OCO₂Me), by X-ray crystallography. Thermolysis of the latter complex resulted in DMC formation, while thermolysis of Bu₃Sn(OCO₂Me) did not produce DMC. These results are enlightening for understanding the mechanism of CO₂ transformation catalyzed by metal complexes and will stimulate the development of a more efficient catalysis.

Supporting Information Available: Synthesis, NMR data, and thermolysis procedure of **2**, and crystal data for **1** and **2** (tables of crystal data, structure solution and refinement, atomic coordinates, bond length and angles, and anisotropic thermal parameters (PDF) and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) Although we could observe ¹¹⁹Sn NMR signals at the position close to **1** and **2** after the thermolysis, the reaction produced several unidentified Sn species, and it is difficult to clarify the material balance completely.

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