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Synthesis and Transesterification of the Complexes of Methyl 2-Methyl-3-trichlorostannylpropoinate with Benzylmethylsulfoxide

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Abstract: The title complex, $Cl_3SnCH_2CH(CH_3)CO_2CH_3$•L (**1**), was synthesized by the reaction of methyl 2-methyl-3-trichlorostannylpropionate with benzylmethylsulfoxide (**L**) in solid state at room temperature and readily underwent transesterification into the corresponding analogues $Cl_3SnCH_2CH(CH_3)CO_2R$•L when reacted with an alcohol ROH. The structural features of these compounds were described, and the possible mechanism of transesterification was suggested.

Keywords: 2-Methyl-3-trichlorostannylpropionate complexes, solid state reaction, crystal structure, transesterification.

2-Methyl-3-trichlorostannylpropionate, $Cl_3SnCH_2CH(CH_3)CO_2R$, a novel type of mono-organotin compounds containing ester group, have received considerable attention since Hutton *et al.* reported their synthesis because of the variety of coordination geometry about tin atom[1-4]. Organotin compounds[5] like organotin carboxylates or oxides were already used as transesterification catalysts, however, little attention was paid to transestrifications of 2-methyl-3-trichlorostannylpropionate complexes in the literature. In this paper, we report the synthesis in solid state, crystal structure and transesterification of **1**.

The complex **1** was formed by grinding equal molar of methyl 2-methyl-3-trichlorostannyl- propionate and **L** at room temperature and readily converted into the corresponding 2-methyl-3-trichlorostannylpropionate analogues **2-8** with yields of 42-93%, when refluxed in corresponding alcohol ROH. The results were listed in **Table 1**.

$$Cl_3SnCH_2CH(CH_3)CO_2Me\bullet L + ROH \rightarrow Cl_3SnCH_2CH(CH_3)CO_2R\bullet L + MeOH$$

R = Me **1**; Et, **2**; *n*-Pr, **3**; *i*-Pr, **4**; allyl, **5**; *n*-Bu, **6**; *i*-Bu, **7**; cyclohexyl, **8**.

Table 1 The yield (%) and melting point (°C) of the compounds

No.	mp	yield	No.	mp	yield	No.	mp	yield	No.	mp	yield
1	131-2	82.3	**3**	98-99	89.5	**5**	104-6	90.2	**7**	96-7	78.4
2	118-9	92.8	**4**	120-2	48.3	**6**	82-3	88.4	**8**	156-8	41.6

Comparison of ν (C=O) (~1650 cm^{-1}) in the complexes with ν (C=O) (~1730m^{-1}) of

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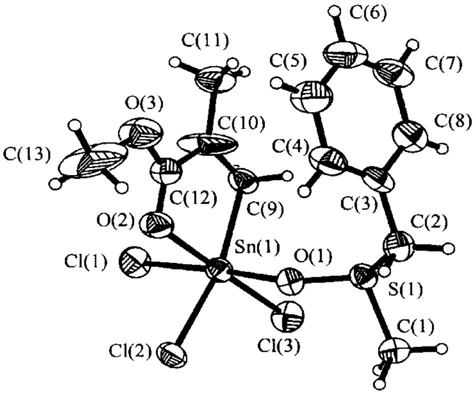
the free ester group indicated that the carbonyl oxygen atom is coordinated intramolecularly to the tin atom[2]. The complexation of the oxygen atom of **L** to the tin atom is confirmed by the decrease of the ν (S=O) (from 1016 to ~950 cm^{-1})[2]. The δ values of alkoxyl protons showed a downfield shift comparing with those in the fatty acid ester because the coordination of carbonyl to tin caused the deshielding of alkoxyl protons OCH. The result of X-ray single crystal diffraction of **1** (monoclinic, space group $P2_1/c$, a = 15.633(5), b = 8.658(8), c = 19.129(8) Å, β = 93.057(7)°, V = 2585.4(4) Å^3, Dc = 1.234 g cm^{-3}, Z = 4) is in agreement with the spectral analysis (see **Figure 1**)[6]. The complex contains a five-membered chelate ring formed *via* carbonyl oxygen to tin coordination (the Sn–O bond length is 2.354 Å). The tin atom is six-coordinated with Cl(1), Cl(2), Cl(3), O(1), O(2) and C(9) in a distorted octahedral arrangement.

Figure 1 Molecular structure of **1**



We attributed the occurrence of the novel transesterification to the intramolecular Lewis acid catalysis by the electrophilic $SnCl_3$ group. The coordination of the ester carbonyl to tin atom (C=O→Sn) polarized the carbonyl bond, thereby making the carbonyl carbon more susceptible to attack by a nucleophilic reagent alcohol to form tetrahedral intermediate. Our work provides a convenient way with higher yields, faster rate and easier operation for preparing 2-methyl-3-trichlorostannylpropionate complexes.

References and Note

1. R. E. Hutton, J. W. Burley, V. Oakes, *J. Organomet. Chem.*, **1978**, *156*, 369.
2. D. Maughan, J. L. Wardell, J. W. Burly, *J. Organomet. Chem.*, **1981**, *212*, 59.
3. R. Balasubramanian, Z. H. Chohan, R. A. Howie, et al., *polyhedron*, **1997**, *16*, 4283.
4. Z. F. Li, S. W. Wang, Y. X. Wang, *et al.*, *Chin. J. Struct. Chem.*, **2002**, *21*, 87.
5. J. Otera, *Chem. Rev.*, **1993**, *93*, 1449.
6. The data of elemental analysis, IR, ^{1}H NMR of all compounds and crystallographic parameters of **1** have been deposited in the editorial office of CCL.

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