

Organotin(IV) Trifluoromethanesulfonate Chemistry: Isolation and Characterization of Novel 1,10-Phenanthroline-based Derivatives

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The first study describing the synthesis of organotin trifluoromethanesulfonates dates back to the 1970s [1]. Since then, this class of compounds has attracted much interest in synthesis and homogeneous catalysis, acting as efficient *Lewis* acid catalysts. Beneficial effects have been described for the aldol reaction of *Mukaiyama* [2], the *Robinson* annulation [3], the acetylation of alcohols [4], the transesterification of dimethyl carbonate (DMC) with phenol [5], and the direct synthesis of DMC from methanol and carbon dioxide [6, 7].

In the course of our ongoing studies on the reactivity of $[n-Bu_2Sn(\mu-OH)(H_2O)(CF_3SO_3)]_2$ (1) toward nitrogen-containing heterocyclic compounds [8, 9], we report herein the synthesis and characterization of two novel diorganotin trifluoromethanesulfonate derivatives, $[n-Bu_2Sn(\mu-OH)(phen)]_2[CF_3SO_3]_2$ (5) and $[n-Bu_2Sn(\mu-OH)(phen)]_2[CF_3SO_3]_2$ (5) $Bu_2Sn(phen)_2[CF_3SO_3]_2$ (6) [10]. They result from the reaction of 1 with 1,10-phenanthroline (phen) with the latter acting as bidentate ligand. Complexes **5** and **6** were fully characterized by IR, ¹H, ¹¹F, ¹³C, and ¹¹⁹Sn{¹H} NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray diffraction analysis. Monitoring of the reaction by 119 Sn{ 1 H} NMR spectroscopy in solution (CD₃CN) and as a function of the amount of phen added, revealed the successive *in-situ* formation of additional species 2, 3, and 4. While compounds 2 and 4 were already described in the literature, further investigations were carried out to isolate and identify species 3. Furthermore, by changing the solvent conditions from acetonitrile to dichloromethane, and in a 1:1 molar ratio of 1 and phen, an unprecedented mononuclear hydrated di-n-butyltin cation, [n- $Bu_2Sn(phen)(OH)(H_2O)][CF_3SO_3]$ (7), was isolated, with the tin centre N,N-chelated by a bidentate phen ligand and bearing a terminal hydroxyl group. The structural and spectroscopic characterizations of these compounds, as well as their relationships, will be detailed in the poster.



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