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Di-tert-butylarsino(chloro)tin(II): A (μ-AsR$_2$)-Coordination Polymeric Stannylene

W.-W. DU MONT

Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, D-1000 Berlin 12, BRD

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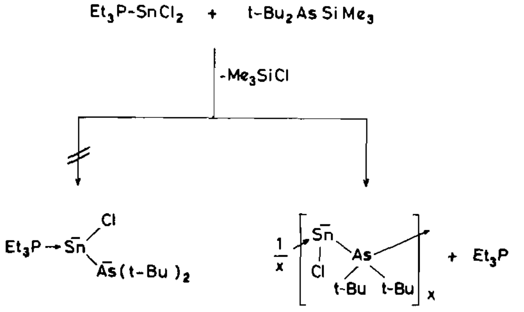
Since 1974 several groups reported the preparation of a variety of aminotin(II) compounds by lithioamination of $SnCl_2$. Amino-substituted stannylenes are strongly coloured and monomeric in solution when the NR_2 groups at tin are weakly basic and/or very voluminous (*e.g.*, R = Me_3Si) [1]. Sterically less hindered tin(II) amines like $Sn(NMe_2)_2$ are associated in solution and in the solid state [2]. Recently we reported the synthesis of chloro- and bromo(di-tert-butylphosphino)tin(II) and bis(di-tert-butylphosphino)tin(II). These phosphino-substituted stannylenes are polymeric (yellow t-Bu_2PSnCl and t-Bu_2PSnBr) or dimeric (orange–red (t-$Bu_2P)_2Sn$) with bridging phosphino groups [3]. P(III)–Sn(II) coordination is surprisingly strong, as shown also by the stability of trialkylphosphine tindihalide complexes R_3P-SnX_2 [4]. We thought that, if As(III)–Sn(II) association is significantly weaker than P–Sn coordination, it might be possible to obtain monomeric phosphine-stabilized arsinotin(II) compounds like R_3P–Sn(Cl)–AsR'_2.



The competition of P–Sn coordination *vs.* As–Sn association was experimentally realised by the reaction of triethylphosphinedichlorostannylene with the equimolar amount of di-tert-butyl(trimethylsilyl)arsine at about 0 °C in toluene. Under these conditions a dark red–brownish mixture was formed containing chlorotrimethylsilane, triethylphosphine and strongly coloured still unidentified Sn–As compounds in solution, from which yellow crystals of di-tert-butylarsino(chloro)tin(II) were separated by filtration after 2 h. Di-tert-butylarsino(chloro)tin(II) is the first arsino-substituted stannylene, it does not contain triethylphosphine, as shown also by its correct elemental analysis [5]. The compound is only sparingly soluble in dry benzene, toluene, ether and tetrahydrofurane. Its physical properties indicate strongly a μ-di-tert-butylarsino coordination polymeric structure, the basicity of triethylphosphine is apparently not sufficient for the formation of a stable monomeric phosphine adduct of the arsinostannylene. Evidence for terminal Sn–Cl moieties in t-Bu_2As–Sn–Cl comes from the i.r. tin–chlorine valence stretching vibration at 280 cm^{-1} which is very similar to that of t-Bu_2PSnCl (279 cm^{-1}) [3] and typical for terminal Sn(II)–Cl bonds. Thus the coordination polymeric structure of the arsinostannylene should consist of $(\text{–Sn–As–})_x$ chains with an ylidic type of bonding between Sn(II) (C.N. 3) and As(III) (C.N. 4) similar to dimeric (t-$Bu_2P)_2Sn$ [3].

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5 Calc.: C 27.80, H 5.28, Cl 10.32, Sn 34.56%; found: C 27.76, H 5.11, Cl 10.0, Sn 34.63%. Yield: 60%. The compound is very sensitive to air, moisture and protic solvents, but thermally stable at r.t. under Ar. It decomposes above 100 °C without melting.