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Preliminary communication

Ylid complexes of organotin and -lead halides

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SUMMARY

Carbonyl-stabilised ylids form complexes of varying stoichiometries with organotin and -lead halides.

Triphenylphosphinemethylene has previously been shown to form ionic complexes with trimethyltin bromide and dimethyltin dichloride and dibromide in which the phosphorus is linked to tin by the methylene group[1]. The resonance-stabilised *C*-acyl substituted phosphorus and arsenic ylids, however, are potentially ambidentate, and may coordinate via either the carbanionic carbon atom or the carbonyl oxygen.

With triorganotin and -lead halides, stabilised ylids such as triphenylphosphine-*C*-acetyl-, -*C*-benzoyl- or -*C*-carbomethoxy-methylene (Ia–Ic respectively), triphenylphosphine-*C*-methyl-*C*-carbomethoxy-methylene (Id), and triphenylarsine-*C*-benzoylmethylene (Ie) yield crystalline 1/1 adducts, $R_3MX\cdot$(ylid) (II), irrespective of the ylid or the metal halide employed. The stoichiometry of the adducts obtained with diorganotin dichlorides, however, depends on the nature of the ylid and the groups bound to tin. Whilst with dimethyltin dichloride, the ylids Ia and Ic give adducts of the stoichiometry $3R_2SnCl_2\cdot4$(ylid) (IIIa), the ylids Ib and Id yield products of stoichiometry $5R_2SnCl_2\cdot4$ (ylid) (IIIb). The adduct obtained from di-n-propyltin dichloride and Ia is also of the latter type. With diphenyltin dichloride, the adducts obtained are generally of the stoichiometry $3R_2SnCl_2\cdot2$(ylid) (IIIc). These stoichiometries seem best rationalised on the basis of the ionic formulations $R_2Sn(\text{ylid})_4{}^{2+}$ $2R_2SnCl_3{}^-$ (IIIa), $R_2Sn(\text{ylid})_2{}^{2+}$ $2R_2SnCl_3{}^-$ $R_2SnCl_4{}^{2-}$ (IIIb), and $R_2Sn(\text{ylid})_2{}^{2+}$ $2R_2SnCl_3{}^-$ (IIIc).

The infrared carbonyl stretching frequency has been used previously as a criterion to distinguish *O*- *versus* *C*-modes of attachment of stabilised phosphorus ylids in mercuric halide complexes[2]. The latter derivatives exhibit a band close to that in the

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parent phosphonium halides (ca. 1670 cm^{-1}), whereas in the resonance stabilised ylids, the analogous band occurs at ca. 1530 cm^{-1}. In the present case the adducts II exhibit an intense band in the range 1465–1510 cm^{-1}, and the ylid residue is therefore considered to be attached via the carbonyl oxygen, as has been confirmed by an X-ray crystal structure in one case[3]. In contrast, the adduct of triphenyltin chloride and Ie exhibits a carbonyl stretching mode at 1665 cm^{-1}, and is assigned the alternative *C*-bonded structure. Save for the dimethyltin dichloride adduct of Ia in which the carbonyl band occurs at 1505 cm^{-1}, all the diorganotin dichloride adducts exhibit a carbonyl stretching frequency in the range 1675–1740 cm^{-1}, and hence are also considered to be *C*-bonded.

The tin-119m Mössbauer spectra of all the 1/1 adducts II consist of quadrupole split doublets with splitting $\geqslant$ 3 mm·s^{-1} as expected for derivatives possessing the *trans*-R_3SnX_2 configuration, *e.g.* $Ph_3SnCl \cdot Ph_3PCH \cdot CO \cdot Me$ I.S. 1.30 mm·s^{-1}, Q.S. 2.99 mm·s^{-1}; $Me_3SnCl \cdot Ph_3PCH \cdot CO \cdot Me$ I.S. 1.29 mm·s^{-1}, Q.S. 3.44 mm·s^{-1}. Surprisingly, the spectra of the adducts III also consisted of two peaks only, although more than one type of tin must necessarily be present in the derivatives, *e.g.* $5Pr_2SnCl_2 \cdot 4Ph_3PCH \cdot CO \cdot Me$ I.S. 1.72 mm·s^{-1}, Q.S. 3.90 mm·s^{-1}; 3 $Me_2SnCl_2 \cdot 4Ph_3AsCH \cdot CO \cdot Ph$ I.S. 1.59 mm·s^{-1}, Q.S. 3.73 mm·s^{-1}, and hence the spectra must represent the sum envelope of absorptions due to all tin species present. This kind of behaviour has been observed previously for terpyridyl complexes of organotin halides[4].

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