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Preliminary communication

SYNTHESIS OF *o*-PHENYLENEBIS(DIMETHYLSTIBINE) AND SOME TRANSITION METAL DERIVATIVES

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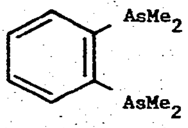
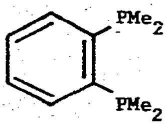
Summary

The new chelating agent *o*-phenylenebis(dimethylstibine) has been synthesised and shown to form the expected palladium(II) and platinum(II) complexes.

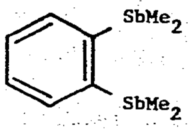
Since the isolation of *o*-phenylenebis(dimethylarsine) (I) by Chatt and Mann [1] and the demonstration of ability to stabilise high and low oxidation states in transition metal complexes, often with unusual stereochemistries [2], much interest has been shown in preparing similar chelating agents. The corresponding ditertiary phosphine [3] (II) and the mixed donor atom bidentates, for example, the amino- [4], thioether- [5], and phosphino-arsines [6] (IV) and the amino- [7] and arsino-stibines [8] (V), are typical additions to the class of reagent. We report here the synthesis and some of the properties of the antimony analogue of the ditertiary arsine (I) and phosphine (II), namely *o*-phenylenebis(dimethylstibine) (III).



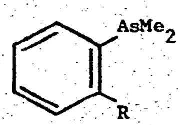
(I)



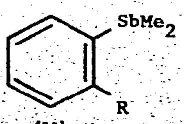
(II)



(III)



(IV)
(where R = NMe_2, SMe or PEt_2)

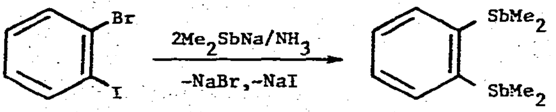


(V)
(where R = NMe_2 or $AsMe_2$)

The ditertiary distibine (III) is a yellow air-sensitive liquid, b.p. 124—125°/ 0.5 mm which is obtained in 5—8.7% overall yield from antimony trichloride from the following series of reactions:

$$SbCl_3 \xrightarrow[-3MgClI]{3MeMgI} SbMe_3 \xrightarrow{Br_2} Me_3SbBr_2$$

$$Me_3SbBr_2 \xrightarrow[-MeBr]{\Delta} Me_2SbBr \xrightarrow[-NaBr]{2Na/NH_3} Me_2SbNa$$



In addition to a correct elemental analysis the PMR spectrum of (III) in $CDCl_3$ shows a sharp singlet at δ 0.98 and a broad multiplet at δ 7.08—7.62 with an intensity ratio corresponding to the methyl and aromatic protons, respectively. The product (III) gives the molecular ion in the mass spectrum and the fragmentation pattern of this ion is in most respects similar to that observed in other related *o*-phenylene derivatives [9]. From a geometrical point of view the ditertiary distibine (III) is ideally suited to form chelate complexes and although tertiary distibines have not been used widely as ligands [10, 11] our preliminary work indicates that the ligand undergoes many of the reactions characteristic of ditertiary bidentates involving Group V donor atoms. For example, the compounds (distib)MX_2 (where M = Pd or Pt; X = Cl, Br, I or SCN) form readily under the usual reaction conditions; they have been fully characterised and occur as pale-yellow to orange-red crystalline solids which are non-electrolytes in nitrobenzene and whose PMR spectra in $CDCl_3$ show a typical downfield shift of the Sb—CH_3 resonance (0.65—0.91 ppm) upon coordination. It is noteworthy that although these distibine derivatives are not unusual, for Pd^{II} and Pt^{II} compounds direct preparations of the corresponding platinum compounds of the diarsine (I) have not been described. The compound (diars)$PtCl_2$ [12] (where diars = *o*-phenylenebis(dimethylarsine)) has been prepared, however, from $(PhCN)_2PtCl_2$ by replacement of the two benzonitrile groups with the diarsine.

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