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A SULPHUR DIOXIDE ADDUCT OF TRIPHENYLINDIUM

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Summary

The product from the reaction of triphenylindium with sulphur dioxide, previously considered to be *O*-benzenesulphinatodiphenylindium(III), is now formulated as the 1/1 adduct, $Ph_3In(O_2S)$.

Introduction

Sulphur dioxide frequently inserts into metal—carbon bonds to afford metal sulphinates, which are also of interest because of their desulphination reactions giving organometallics and because of the ambidentate nature of sulphinate ligands [1—4]. It was recently shown that trimethylindium undergoes sulphur dioxide insertion to give tris(methanesulphinato)indium(III) [5], whilst under carefully controlled conditions, (methanesulphinato)dimethylindium(III) is obtained [5,6]. An analogous product, $Ph_3In(O_2S)$, from the reaction of triphenylindium with sulphur dioxide, was considered to be (benzenesulphinato)diphenylindium(III) with unidentate *O*-sulphinate coordination [5]. We now present evidence for the formulation of this compound as a sulphur dioxide adduct of triphenylindium. Reported adducts of sulphur dioxide with main group element organometallics appear restricted to those of Group V elements [7—12]. (However, $Ph_3Bi(O_2S)_2$ [12] has been reformulated as the insertion product, $PhBi(O_2SPh)_2$ [13,14].

Results and discussion

The 1/1 stoichiometry of the product from the reaction of triphenylindium with sulphur dioxide has been established by elemental analysis [5] and by tensiometric titration with sulphur dioxide. Loss of sulphur dioxide occurs under mild conditions (readily in vacuo or in solution at room temperature, and more slowly in air). By contrast, sulphur dioxide elimination (or desulphination [4]) reactions of main group element *O*-sulphinate complexes take place at temperatures above 100° [15—17]. The mass spectrum of $Ph_3In(O_2S)$

TABLE 1

SELECTED INFRARED DATA[a]

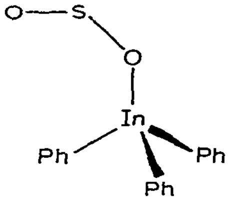
Ph_3In[b]	Ph_3InOSO[b]	$(PhSO_2)_3In$[b]	$PhHgO_2SPh$[c,d]	$PhSO_2Na$[c]	Assignments
		1449 vs	1440 m	1442 vs	n $\nu(CC)$ PhS
1433 s	1433 s		1431 s		n $\nu(CC)$ PhM
	1053 ms(br)	963 vvs	1048 vs	1041 vs(br)	$\nu_{as}(SO_2)$
	854 ms	930 vs	838 vs(br)	992 vs(br) 976 vs(br)	$\nu_s(SO_2)$
		766 vs	751 s	757 vs 751 vs	f $\gamma(CH)$ PhS
741 vvs 736 vvs	740 vvs 736 vvs		731 s		f $\gamma(CH)$ PhM
	586 ms	599 vs	582 s	587 vs	$\delta(SO_2)$
		523 w	519 m	490 m	y 'X-sens.' PhS
473 s(sh) 470 vs	473 s(sh) 469 vs		447 m		y 'X-sens.' PhM
		422 mw	415 m	421 m	t 'X-sens.' PhS

[a] In Nujol mull; frequencies in cm^{-1}. [b] From ref. 5; other phenyl bands are at similar frequencies for all these compounds. [c] From ref. 15. [d] *O*-Sulphinate isomer.

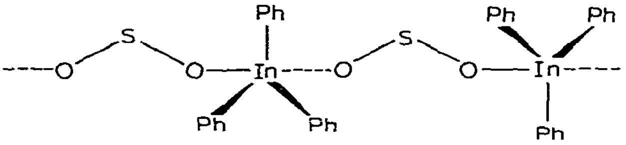
shows no evidence for the presence of the benzenesulphinate ligand. Furthermore, if the compound was an insertion product, the $\nu(SO_2)$ frequencies (Table 1) would strongly indicate [2,15] a unidentate *O*-sulphinate with three-coordinate indium, whereas all established sulphinatoindium(III) complexes, including tris(benzenesulphinato)indium(III), possess bridging bidentate *O*-sulphinate groups with four- or six-coordinate indium [5,6].

The most convincing evidence for its formulation as an adduct stems from its infrared spectrum [5], the relevant features of which are compared with those of suitable reference compounds in Table 1. Assignments are based on those for sodium benzenesulphinate [15] and diphenylthallium(III) bromide [18], and the nomenclature is that of Whiffen [19]. The infrared spectrum of $Ph_3In(O_2S)$ shows bands attributable to sulphur—oxygen stretching and bending vibrations, in addition to those assignable to modes of the phenyl groups, the latter being virtually superimposable on those of triphenylindium (Table 1). A comparison of the spectra of $In(O_2SPh)_3$ and Ph_3In indicates that the $\nu(CC)$ mode n, the $\gamma(CH)$ mode f, and the 'X-sensitive' mode y are at significantly higher frequencies in the former than in the latter (Table 1). This suggests that the spectrum of the insertion product, $Ph_2In(O_2SPh)$, would be expected to exhibit distinct absorptions due to the n, f, and y modes of both the PhS and PhIn groups. Two or three of these modes of the PhS and the PhM (M = Hg or Bi) groups are clearly distinguishable in the infrared spectra of the complexes, $PhHg(O_2SPh)$ (both the *O*-and the *S*-sulphinate isomers) [15], $Ph_2Bi(O_2SPh)$ [14], and $PhBi(O_2SPh)_2$ [14]. Moreover, $Ph_3In(O_2S)$ shows no absorption due to the 'X-sensitive' mode t of the PhS group in contrast with $In(O_2SPh)_3$ (mode t of PhIn may be expected below 400 cm^{-1}). Thus, infrared evidence clearly favours the formulation of $Ph_3In(O_2S)$ as an adduct and not as $Ph_2In(O_2SPh)$.

In $Ph_3In(O_2S)$ the sulphur dioxide is presumably acting as a Lewis base and, since In^{III} is a hard acid [20], as exemplified by the preference for *O*-sulphinate coordination [5], structure (I) appears most likely, although the possibility of it being a five-coordinate polymer, (II), cannot be entirely excluded in view of



(I)



(II)

the fact that this coordination number can be readily attained by triarylindium compounds (e.g. in the complex $(C_6F_5)_3In(OSMe_2)_2$ and the polymeric $(C_6F_5)_3In$(1,4-dioxane) [21]). However, the polymeric structure, (II), is perhaps inconsistent with the large splitting between the $\nu(SO_2)$ frequencies (Table 1). Coordination of oxygen is known in only one other sulphur dioxide adduct, viz. $SbF_5(O_2S)$ [22]. By contrast, sulphur dioxide acts as an *S*-bonded Lewis acid in most main group element adducts, e.g. $R_3N—SO_2$ [7—9], $R_3P—SO_2$ [11], $[I—SO_2]^-$ [23] and $PtMe(PPh_3)_2[I—SO_2]$ [24], and as an *S*-bonded σ-donor and π-acceptor in transition metal derivatives [24]. The shifts of the $\nu(SO_2)$ frequencies from the free ligand values (1340 and 1150 cm^{-1}) [25] are larger than those of any reported sulphur dioxide adduct [24]. For *S*-bonded derivatives, a larger shift implies a more strongly bonded adduct [24], but the correlation may not be applicable to *O*-bonded complexes, since $Ph_3In(O_2S)$ has lower thermal stability than $SbF_5(O_2S)$, for which only small shifts are observed.

Experimental

The preparation of the adduct and its physical properties were previously described [5]. Tensiometric titration was performed in a conventional Pyrex glass vacuum line equipped with a spiral gauge and other accessories for pressure measurements [26].

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