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The reaction of $(p\text{-FC}_6\text{H}_4)_3\text{PE}$ (E = Se, S) with diiodine: The single crystal X-ray structures of $(p\text{-FC}_6\text{H}_4)_3\text{PSe}$, $(p\text{-FC}_6\text{H}_4)_3\text{PS}$, $(p\text{-FC}_6\text{H}_4)_3\text{PSeI}_2$, and $(p\text{-FC}_6\text{H}_4)_3\text{PSI}_2$

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Abstract

The reactions of the tris(p-fluorophenyl)phosphine chalcogenides $(p\text{-FC}_6\text{H}_4)_3\text{PE}$ (E = Se (**1**), E = S (**2**)) with diiodine have been performed. The products of these reactions are the 1:1 charge-transfer compounds $(p\text{-FC}_6\text{H}_4)_3\text{PSeI}_2$ (**3**), and $(p\text{-FC}_6\text{H}_4)_3\text{PSI}_2$ (**4**), which feature a linear E–I–I motif typical of these types of spoke or "molecular dart" adducts. The I–I bonds in **3** [I–I: 2.8888(12)/2.8950(11) Å] and **4** [I–I: 2.8042(17)/2.835(2) Å] are lengthened with respect to diiodine in the solid-state, which is consistent with donation of electron density from the chalcogen atom to the σ^* antibonding orbital of the diiodine molecule. The elongation of the I–I bonds is considerably lower in magnitude than is observed for many CT adducts of diiodine as a result of the relatively poor donating capability of the phosphine chalogenides **1** and **2**. A comparison with the non-fluorinated analogues Ph_3PEI_2 (E = S and Se) shows that the fluorine atom has little apparent effect upon the strength of the CT adduct formed, and that the I–I bond lengths appear to be more influenced by steric effects. The P–E–I angles in **3** and **4** are more acute than in the non-fluorinated Ph_3PEI_2 analogues, and as a result the steric influence of the aryl rings may be more strongly felt. This steric effect may act in competition with the electronic effect which would otherwise result in a more pronounced shortening of the I–I bond, compared to analogous Ph_3PEI_2 (E = S and Se) systems, although the differences are relatively small, and may also be due to packing effects.
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1. Introduction

The reactions of tertiary phosphine chalcogenides, R_3PE (E = S, Se, and Te) with dihalogens were first reported by Zingaro and co-workers in the 1960s [1–5]. Since then, a number of reports have shown that the adducts formed from these reactions show considerable structural diversity. The motif adopted by a particular adduct has been shown to be dependent on the identity of the halogen, the group 16 donor atom, the R groups bound to phosphorus, and in some cases, the solvent of recrystallisation. Typically, the adducts formed exhibit one of two structural types, *viz.* a T-shaped geometry at the chalcogen atom, Fig. 1a, formed by oxidative addition of the halogen, or a charge-transfer (CT) spoke adduct, Fig. 1b.

The reaction of R_3PSe with dichlorine has been only briefly studied as these reactions result in rapid cleavage of the P=Se bond. [6] The reaction initially forms the $[\text{R}_3\text{PSeCl}]\text{Cl}$ species at low temperature (characterised by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy), but these compounds decompose above −90 °C to yield $[\text{R}_3\text{PCl}]\text{Cl}$. Similarly, no compound of stoichiometry R_3PSCl_2 has been reported. However, Chivers and co-workers have recently reported that the reaction of Et_3PTe with dichlorine results in the

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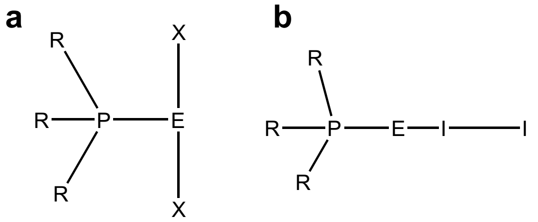

Fig. 1. Structural isomers for R_3PEX_2 (E = S, Se and Te) compounds; (a) T-shaped motif, (b) charge-transfer "molecular spoke" adduct.

formation of a stable compound, Et_3PTeCl_2 [7]. This compound has been crystallographically characterised and features a T-shaped motif at tellurium, as shown in Fig. 1a. Molecules of Et_3PTeCl_2 are linked by weak tellurium···chlorine interactions to form centrosymmetric dimers.

R_3PSeBr_2 adducts were first reported by Williams and Wynne in 1976 ($R_3 = Ph_3$, (*m*-tolyl)$_3$ and (*p*-tolyl)$_3$) [8], who assigned a T-shaped geometry to these adducts on the basis of vibrational spectroscopic data. A T-shaped geometry has subsequently been confirmed crystallographically for a series of R_3PSeBr_2 compounds, R = $(Me_2N)_3$, Cy_3 [9], $^iPr_3$, $^iPr_2{}^tBu$, $^iPr^tBu_2$ [10], and for a number of dibromine adducts of bidentate phosphine selenides, $dppmSe_2Br_4$ and $dppeSe_2Br_4$ [11]. These selenium(II) compounds feature a T-shaped geometry as predicted by VSEPR theory (based on a pseudo trigonal bipyramidal arrangement, taking into account the two lone pairs on selenium). Typically, in such compounds the Br–Se–Br angle should be distorted from linear as a result of repulsion from the lone pairs. These adducts do show distorted Br–Se–Br angles, but the distortion appears to be *towards* the lone pairs and away from the bulky groups on the phosphine. The distortion is more extreme where there is a higher degree of steric hindrance, e.g., in the structure of $^iPr^tBu_2PSeBr_2$, where Br–Se–Br: 159.16(4)° [10]. A T-shaped geometry has also been observed for the only reported R_3PTeBr_2 adduct, Et_3PTeBr_2 [7], although here the Br–Te–Br angle is distorted away from the lone pairs, possibly as a consequence of the presence of weak intermolecular tellurium···bromine interactions: similar interactions are not observed in the T-shaped selenium compounds. In contrast, the reactions of tertiary phosphine sulfides, R_3PS, with dibromine usually result in cleavage of the P–S bond and subsequent formation of R_3PBr_2 [12]. Some exceptions are known, for example, R_3PSBr_2 can be isolated when R = Cy (although this compound also undergoes P–S bond cleavage in polar solvents), and the reaction of dibromine with $(Me_2N)_3PS$ results in formation of an S_3 bridged dinuclear ionic species, $[(Me_2N)_3P–S–S–S–P(NMe_2)_3][Br_3]_2$ in moderate yield [12].

The reaction of Et_3PTe with diiodine also yields a T-shaped compound, Et_3PTeI_2 [7], but the reactions of R_3PE (E = S and Se) result in the formation of charge-transfer (CT) spoke adducts of the type shown in Fig. 1b [2,5,11–16]. These adducts consist of a 3c–4e CT system, and display I–I bonds which are lengthened with respect to diiodine in the solid state, 2.715(6) Å [17], as a consequence of donation of electron density from the chalcogen atom to the σ^* antibonding orbital of the diiodine molecule. Tertiary phosphine selenides are better donors towards diiodine than the analogous tertiary phosphine sulfides, as illustrated by a comparison of $(Me_2N)_3PSeI_2$ and $(Me_2N)_3PSI_2$. In the former, the I–I distances are 2.959(2)/2.965(2) Å [13], considerably longer than the I–I bond in the latter, 2.856(1) Å [12], and consistent with the greater donating ability of the phosphine selenide. The geometry at the chalcogen atom is bent in the CT adducts as a result of the presence of the two lone pairs at selenium. The P–E–I (E = S and Se) angles in these molecules are typically 100–108° and thus show distortion from the idealised angle for a pseudo-tetrahedral arrangement due to a combination of repulsion from the lone pairs, and retention of some double bond character in the phosphorus–chalcogen bonds, unlike the situation observed in the T-shaped R_3PSeBr_2 compounds, which feature single P–Se bonds. This phenomenon is illustrated by a comparison of the P–Se bond lengths between $(Me_2N)_3PSeBr_2$, where there is a P–Se single bond of 2.262(2) Å [9], $(Me_2N)_3PSeI_2$, where the P–Se bonds range between 2.185(7) and 2.175(8) Å [13], and $(Me_2N)_3PSe$, which has a P=Se double bond of 2.114(1) Å [18]. These observations agree with spectroscopic data *viz.* (i), a reduction in ^1J(PSe) coupling constants in the $^{31}P\{^1H\}$ NMR spectra, and (ii), a shift to lower frequencies of the ν(P–Se) band in the IR spectra upon adduct formation. Addition of excess iodine to the R_3PSeI_2 systems results in the formation of either $[R_3PSeI]^+$ or $[R_3PSe–I–SePR_3]^+$ cations linked by weak I–I interactions to polyiodide anions [19–21].

The only reported adducts of R_3PE with interhalogens are the IBr and ICl adducts of Ph_3PS, both of which display a CT spoke motif, as observed for the I_2 analogues [22]. In both cases the interhalogen is bound by the heavier iodine atom. In contrast, the Ph_3PS/I_2 system is more complex, and despite the fact that the 1:1 Ph_3PSI_2 adduct was identified in solution, it was initially believed it could not be isolated in the solid-state due to the poor donating capability of Ph_3PS [4]. The 2:3 adduct $Ph_3PSI–I–I_2–I–ISPPh_3$ was instead isolated and crystallographically characterised [23]. Later work by Kaur and Lobana showed that formation of the 1:1 adduct was solvent dependent, and could be synthesised in CH_2Cl_2, whilst the 2:3 adduct was favoured in CCl_4 [24]. The 1:1 adduct, Ph_3PSI_2, was subsequently crystallographically characterised by Bricklebank and coworkers [14], and shown to adopt the same linear E–I–I motif as Ph_3PSeI_2. A 3:1 adduct has also been reported when excess iodine is added to the system, and consists of a 1:1 Ph_3PSI_2 adduct interacting with two further molecules of diiodine in a head-to-tail fashion [25].

We now present the results obtained from the reactions of the related fluoro-substituted phosphine chalcogenides

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