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A structural and spectroscopic study of *tris*-aryl substituted R₃PI₂ adducts

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ABSTRACT

A series of Ar_3Pl_2 adducts [$Ar = (o-OCH_3C_6H_4)$, ($m-OCH_3C_6H_4$), ($p-OCH_3C_6H_4$), ($o-SCH_3C_6H_4$), ($p-SCH_3C_6H_4$), ($(m-FC_6H_4)$, ($p-FC_6H_4$), ($p-CCL_6H_4$)] have been synthesized via the 1:1 reactions of Ar_3P with di-iodine. The ³¹P{¹H} NMR spectra of a series of Ar_3Pl_2 adducts has been examined to resolve previous inconsistent reports. Ar_3Pl_2 adducts do not ionize to [Ar_3Pl_1] in CDCl₃, and in many cases the molecular Ar_3Pl_2 "spoke" adduct is stable in solution, with the degree of stability being highly dependent on the nature of the aryl group. The structures of the majority of these adducts have been established by X-ray diffraction studies. Whilst P–I and I–I bond lengths are primarily influenced by electronic effects, steric and crystal packing effects may also have an influence, as shown by the different polymorphs of ($p-FC_6H_4$)₃Pl₂, where a change in the conformation of the aryl groups in one of the molecules results in a lengthening of the P–I bond and shortening of the I–I bond.

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1. Introduction

Molecules of formula R_3PX_2 (X = F, Cl, Br, I) have been known for many years, and are formed when tertiary phosphines are combined with a stoichiometric ratio of the appropriate halogen. The solid-state structures of R_3PX_2 adducts are surprisingly diverse, and encompass three main structural types (Fig. 1), (i) molecular five-coordinate trigonal bipyramidal species, (ii) ionic halo-phosphonium salts, and (iii) charge-transfer (CT) "spoke" adducts, R_3P-X-X , which feature a linear P-X-X angle. This linear arrangement is consistent with a CT interaction between the HOMO orbital of the phosphorus donor atom and the σ^* LUMO orbital on the I_2 acceptor. The structure favoured by a particular adduct is dependent on the identity of the halogen and the R groups, and also the solvent of preparation and/or recrystallisation [1].

The trigonal bipyramidal structure is favoured when X = F and is also observed for a number of R_3PCl_2 adducts with electron withdrawing R groups. In contrast, the majority of R_3PCl_2 and R_3PBr_2 adducts are ionic, $[R_3PX]X$, whilst the CT "spoke" structure, R_3PX-X , is most commonly observed when X = I. The interpretation of a particular structure as ionic or CT is often not straightforward as halo-phosphonium halides often exhibit strong cation–anion interactions between the P–X bound halogen atom and the halide anion [2–16], especially when X = I. The "spoke" compounds may be considered either as CT adducts with R_3P as the donor and X_2 as the acceptor, (10–I–2) CT systems, or alternatively as systems featuring $[R_3PX]^+$ as the acceptor and X^- as the donor [17]. This latter type of CT complex should feature shorter P–X bonds and long X–X bonds/soft–soft interactions.

Only four structures of ionic [R₃PBr]Br salts have been reported, where R = ⁱPr₃ [5], Et₃ [6], Ph₃ [4], and ^tBu₂ⁱPr [7]. The Br \cdots Br distances between the cation and anion in these structures vary between 3.12 and 3.42 Å, these distances being considerably shorter than the sum of the van der Waals radii for two bromine atoms (3.9 Å), but considerably longer than the Br–Br distances of 2.705(3)/2.717(1) Å observed for the CT complex Me₂SBr₂ [18,19]. This suggests that R₃PBr₂ adducts may be regarded either as ionic, or as CT adducts of the [R₃PBr]⁺ (acceptor)/Br⁻ (donor) type.

The situation for R₃PI₂ adducts has been the subject of some controversy as I-I distances in reported structures of R₃PI₂ adducts vary considerably, between 3.021(1) Å for (Mecarb)ⁱPr₂PI₂ [Mecarb = $1-(2-Me-1,2-C_2B_{10}H_{10})$ [11], and 3.6389(14) Å for $[({}^{n}Pr_2N)_3]$ PI I [14]. The length of the I...I interaction in these systems is clearly highly sensitive to the nature of the R groups bound to the phosphorus atom. Adducts such as (Mecarb)ⁱPr₂PI₂ [11], (o-CH₃C₆H₄)₃PI₂, *d*(I–I): 3.0727(4) Å [12], and Ph₃PI₂, *d*(I–I): 3.161(2) Å [3], feature relatively short I–I interactions, and are intensely coloured yellow or orange materials. On the basis of these observations a (10-I-2) CT assignment is appropriate for these compounds. R₃PI₂ adducts of tri-alkyl or tris-(alkylamino) substituted phosphines are usually pale yellow or cream solids, and often feature long I–I distances, i.e. [^tBu₃PI]I, d(I–I): 3.326(1) Å [2], and [ⁱPr₃PI]I, d(I–I): 3.383(1)/3.372(1) Å [10]. These I–I distances are still well within the sum of the van der Waals radii for two iodine atoms (3.96 Å) [20], and these adducts can either be regarded as ionic (with significant soft-soft, cation-anion interactions), or as CT adducts of the $[R_3PI]^+$ (acceptor)/ I^- (donor) type. The propensity



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Fig. 1. Main structural types observed for R_3PX_2 adducts; (a) trigonal bipyramidal, (b) ionic halo-phosphonium, (c) charge-transfer molecular "spoke" adduct.



Fig. 2. (a) Dimer pairs formed by $(EF)_6$ embrace between two back-to-back molecules of $(o-CH_3C_6H_4)_3Pl_2$. (b) Formation of six edge-to-face tolyl ring embraces.

for R_3Pl_2 compounds to display soft-soft I \cdots I contacts is illustrated by the fact that $[N(CH_2CH_2N^iBu)_3PI]I$ is the only structure of an R_3Pl_2 adduct to feature no I \cdots I contact below the sum of the van der Waals radii for two iodine atoms, the closest approach being 7.18 Å [21].

While the electronic properties of the R groups are an important influencing factor in the magnitude of the P–I and I–I bond lengths in R_3PI_2 adducts, other factors such as steric effects and crystal

packing also play a significant role. The structures of the series of tolyl-substituted adducts, *o*-, *m*- and *p*-(CH₃C₆H₄)₃Pl₂ show that the *o*-substituted adduct displays a significantly longer P–I bond, and significantly shorter I–I bond [2.5523(12) and 3.0727(4)Å, respectively] than either the *m*- or *p*-substituted analogues [2.472(4)–2.477(4)/3.1807(6)–3.1807(13), respectively] [12,16]. This reflects the cone angles of the tolyl-phosphine groups in these three adducts; 192.2° for (*o*-CH₃C₆H₄)₃Pl₂ compared to 154.5° for (*m*-CH₃C₆H₄)₃Pl₂ and 145.0° for (*p*-CH₃C₆H₄)₃Pl₂ [16]. The particularly large cone angle in (*o*-CH₃C₆H₄)₃Pl₂ is due to the phosphine adopting a sterically demanding *exo*₃ conformation, (where an *exo* substituent is defined as a group pointing towards the apex of a pyramid consisting of the three para hydrogens as the base and the atom bound to phosphorus as the apex) [22].

These observations suggest that it is the large steric bulk of the exo_3 (o-CH₃C₆H₄)₃P group which is responsible for the lengthening of the P–I bond and concomittant shortening of the I–I bond. The exo_3 conformation appears to be preferred over the less sterically demanding exo_2 conformation, since the exo_3 conformation allows two (o-CH₃C₆H₄)₃Pl₂ molecules to pack back-to-back as a dimer pair (Fig. 2a), whereby a number of concerted multiple embraces between the tolyl rings are set up. The dimer pair in (o-CH₃C₆H₄)₃Pl₂ are linked by six edge-to-face (EF) embraces between the rings (Fig. 2b). This (EF)₆ aryl embrace has been shown by Dance and co-workers to be one of the most commonly observed ring embracing motifs in structures containing Ph₃P and [Ph₄P]⁺ groups [23–26]. In the structure of (o-CH₃C₆H₄)₃Pl₂ the embracing pairs are further linked by hydrogen bonding between the iodine and protons on the tolyl ring.

The conformation adopted by the Ar_3P groups in Ar_3PI_2 adducts has an impact on the steric properties, which may change significantly with a change in orientation of the aryl rings, particularly when the rings are substituted. These changes in the steric profile in turn has an effect on the magnitude of the P–I and I–I bond lengths.

We have therefore widened our studies on Ar_3Pl_2 adducts in order to establish how the substitution of different groups in different positions on the aryl rings affects both the steric and electronic properties of the Ar_3P fragment, and what influence these changes have on the magnitude of the P–I and I–I bond lengths.

2. Results and discussion

2.1. Synthesis of R₃PI₂ adducts and Raman spectroscopic data

The series of *tris*-aryl substituted R_3Pl_2 adducts were synthesized via the reaction of the appropriate phosphine with one equivalent of iodine in dry diethyl ether as shown in Scheme 1.

The adducts formed are typically orange-yellow in colour (except for **4** which is red, and **7** which is olive-green), and were treated as moisture sensitive. All of the compounds have been characterized by elemental analysis, multinuclear NMR spectros-copy, Raman spectroscopy and in most cases by single-crystal X-ray diffraction (except for **1** and **4** which exhibit poor solubility in a range of common solvents). Elemental analytical results confirmed the formation of a 1:1 adduct in all cases.

The deep red colour exhibited by $(o-SCH_3C_6H_4)_3PI_2$ (**4**), is unusual, and was initially suggestive of the formation of an $[I_3]^-$ containing salt. However, the bulk solid of **4** analyses to a 1:1 R₃P:I₂ stoichiometry, but the poor solubility prevented us from obtaining crystals. The Raman spectrum of **4** also shows a significant difference to that of the other adducts. The spectra of **1–3** and **7–8** all show peaks between 130 and 160 cm⁻¹ (**5** and **6** fluoresce and decompose in the laser beam), which have been assigned as v(P-I) stretches in previous studies of R₃PI₂ compounds [8,27–29].

$$Ar_3P + I_2 \longrightarrow Ar_3PI_2$$

 $\begin{array}{l} \mathsf{Ar} = \textit{o}-\mathsf{OCH}_3\mathsf{C}_6\mathsf{H}_4 \ (\textbf{1}), \ \textit{m}-\mathsf{OCH}_3\mathsf{C}_6\mathsf{H}_4 \ (\textbf{2}), \ \textit{p}-\mathsf{OCH}_3\mathsf{C}_6\mathsf{H}_4 \ (\textbf{3}), \ \textit{o}-\mathsf{SCH}_3\mathsf{C}_6\mathsf{H}_4 \ (\textbf{4}), \\ \textit{p}-\mathsf{SCH}_3\mathsf{C}_6\mathsf{H}_4 \ (\textbf{5}), \ \textit{m}-\mathsf{FC}_6\mathsf{H}_4 \ (\textbf{6}), \ \textit{p}-\mathsf{FC}_6\mathsf{H}_4 \ (\textbf{7}), \ \textit{p}-\mathsf{ClC}_6\mathsf{H}_4 \ (\textbf{8}) \end{array} \right) \\ \end{array}$

Scheme 1. Reactions of Ar₃P with I₂.

³¹P{¹H} NMR spectroscopic data for Ar₃P, Ar₃Pl₂, [Ar₃POH]⁺, [Ar₃POH]⁺/[{Ar₃PO}₂H]⁺, and [Ar₃PH]⁺ species, (chemical shifts given in ppm, coupling constants in Hz).

Ar ₃ P system	$\delta_{\rm P} \ {\rm R}_{\rm 3} {\rm P}$	$\delta_P R_3 P I_2$ spoke	$\delta_{\rm P}^{\rm a} [{\rm R}_3 {\rm PI}]^+$	$\delta_{P} [R_{3}POH]^{+}/[\{R_{3}PO\}_{2}H]^{+}$	$\delta_{\mathrm{P}} \left[\mathrm{R}_{3} \mathrm{PH} \right]^{+} \left({}^{1} J_{\mathrm{PH}} \right)$
Ph₃P	-7.7	-23.4	+12.0	+44.7	-5.1 (514)
(o-CH ₃ C ₆ H ₄) ₃ P	-37.2	-21.5	-8.6	+48.6	-10.9 (504)
$(m-CH_3C_6H_4)_3P$	-10.2	-13.1	+6.0	+48.2	-5.6 (518)
$(p-CH_3C_6H_4)_3P$	-7.3	-11.1	+4.6	+47.3	-5.0 (513)
$(o-OCH_3C_6H_4)_3P(1)$	-39.2	-34.6	-15.8	+56.5	-17.9 (551)
$(m-OCH_{3}C_{6}H_{4})_{3}P(2)$	-2.6	-18.5	+5.5	+47.8	-5.6 (525)
$(p-OCH_{3}C_{6}H_{4})_{3}P(3)$	-9.5	-12.7	+5.7	+50.9	-8.6 (531)
$(o-SCH_3C_6H_4)_3P(4)$	-30.6	-31.4	N/A	+40.7	-12.9 (548)
$(p-SCH_3C_6H_4)_3P(5)$	-8.3	-16.3	+5.9	+47.9	-3.8 (515)
$(m-FC_6H_4)_3P(6)$	-5.6	-29.8	-14.7	+40.6	N/A
$(p-FC_{6}H_{4})_{3}P(7)$	-8.4	-20.2	-4.2	+39.8	N/A
$(p-ClC_6H_4)_3P(8)$	-7.8	-14.1	-5.1	+35.0	N/A

^a Data for [R₃PI]⁺ cationic species from reported [R₃PI][I₃] salts [37].

Table 1

The spectrum of **4** also displays a peak within this region (at 160 cm^{-1}), but this peak is much more intense than the v(P-I) bands in the spectra of the other adducts. This may be suggestive that in the case of **4** this band is due to v(I-I), not v(P-I).

The v_1 Raman active (I–I) mode for free I_2 is observed at 180 cm⁻¹ [30], and has been observed to fall to lower frequencies upon formation of donor complexes D-I-I (D = donor atom) [31-33]. This lowering of the $v_1(I-I)$ mode is consistent with donation of electron density from the donor non-bonding orbital into the LUMO di-iodine σ^* antibonding orbital. Deplano et al. have correlated $v_1(I-I)$ Raman data with I-I bond lengths for many donor: I_2 adducts [32,34]. Where the I-I bond order is higher than 0.6. (relative to a bond order of 1.0 corresponding to that of free di-iodine at 2.715(6) Å) [35], then the adduct is classified as being of the D-I-I type (10-I-2) CT system, where the I-I bond is typically between 2.8 and 3.0 Å. v_1 (I–I) bands for this type of adduct are commonly observed between 150 and 180 cm^{-1} , and the data for 4 suggests that this adduct may be of this type, which would be consistent with the deep red colour of the compound. This would be extremely unusual for a D-I₂ complex where the donor is phosphorus, as the I–I bond order in these adducts is typically less than 0.4, with I–I bonds over 3.01 Å. An alternative assignment of the structure of **4** (based on Raman v(I-I) data), could be a perturbed intercalated R₃P···I-I···PR₃ structure, as observed in the structure of (Mecarb)Ph₂P···I–I···PPh₂(Mecarb) [36]. However, this is ruled out as the microanalytical data suggests that the R₃P:I₂ ratio of **4** is 1:1.

2.2. ³¹P{¹H} NMR spectroscopic studies

Conflicting data has previously been reported regarding the ${}^{31}P{}^{1}H{}$ NMR spectra of R_3PI_2 adducts. It was initially reported that all R_3PI_2 adducts ionized to $[R_3PI]I$ in CDCl₃ solution, irrespective of whether the solid-state structure of the adduct was CT or ionic [3,27]. The reported chemical shifts are highly dependent on the nature of R, but when R is an aryl group the resonances assigned to $[Ar_3PI]^+$ species have been reported to lie between +40 and +50 ppm [3,8,27]. However, in the solid-state, MAS ${}^{31}P{}^{1}H{}$ NMR studies showed that shifts for R_3PI-I "spoke" adducts are observed

at much lower frequencies, i.e. -17.8 ppm for the CT form of Ph₃Pl₂ [27].

Subsequently, Deplano et al. studied the reaction between Ph₃P and varying ratios of I₂ using ³¹P{¹H} NMR spectroscopy. They showed that δ_P was highly dependent on the ratio of Ph₃P:I₂, with continuous shifting of $\delta_{\rm P}$ as the ratio of I₂ is increased [17]. Initially, δ_P shifts to lower frequency, from -7.7 ppm (Ph₃P) to -23.4 ppm when a 1:1 ratio is present. This value is consistent with that obtained for the spoke form in solid-state ³¹P{¹H} NMR spectroscopic studies (-17.8 ppm), and shows that the CT spoke form is present in solution, as well as in the solid-state. Addition of excess iodine resulted in continuous shifts to higher frequency, up to a maximum of +12.0 ppm when the I₂:Ph₃P ratio exceeded 2:1. This suggests that the correct shift for the [Ph₃PI]⁺ cation is +12.0 ppm, not +44.8 ppm as initially reported [3]. It therefore seems likely that the shifts previously reported for the ionized forms of Ar₃Pl₂ adducts (between +40 and +50 ppm), are incorrect, and arise from hydrolysis of the cation to form either [Ar₃POH]⁺ or [{Ar₃PO}₂H]⁺ species, which have been shown to be the major hydrolysis products obtained when R₃PI₂ compounds are exposed to water or moist air [10]. We have observed that the CT spoke form of (o- $CH_3C_6H_4)_3PI_2$ is also stable in CDCl₃ solution, as the ³¹P{¹H} NMR spectrum of this adduct shows a broad signal at -21.5 ppm [12].

In view of the conflicting data regarding the behaviour of R_3Pl_2 adducts in solution we have carefully monitored the ³¹P{¹H} NMR spectra of **1–8** over a period of several weeks, and re-examined the data for Ph_3Pl_2 and $(o/m/p-CH_3C_6H_4)_3Pl_2$ adducts for comparative purposes. In all cases the aryl phosphine was dissolved (or suspended) in CDCl₃ and one equivalent of iodine added. The reactions were performed (a) in the dry box using CDCl₃ dried over molecular sieves, and (b) in air using standard-grade CDCl₃, in order to determine which resonances are due to hydrolysis products. The different species observed for each system and their shifts are summarised in Table 1, along with data for $[R_3PI]^+$ cationic species from $[R_3PI][I_3]$ salts [37].

The ${}^{31}P{}^{1}H$ NMR spectra of the 1:1 mixtures of the aryl phosphine and I₂ performed in anhydrous conditions initially display a broad peak in the region -10 to -35 ppm. These peaks are usually shifted to lower frequencies from that of the starting phosphine, except for $(o-CH_3C_6H_4)_3PI_2$ and $(o-OCH_3C_6H_4)_3PI_2$ **1**, where



Fig. 3. ORTEP representation of the molecular structure of (*m*-OCH₃C₆H₄)₃Pl₂ (**2**). Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: P(1)–I(1): 2.454(2), I(1)–I(2): 3.2123(7), P(1)–C(1): 1.790(7), P(1)–C(8): 1.802(7), P(1)–C(15): 1.793(7), P(1)–I(1)–I(2): 177.42(5), I(1)–P(1)–C(1): 111.2(2), I(1)–P(1)–C(8): 107.3(3), I(1)–P(1)–C(15): 112.0(3), C(1)–P(1)–C(8): 108.4(3), C(1)–P(1)–C(15): 107.8(3), C(8)–P(1)–C(15): 110.3(3).



Fig. 4. ORTEP representation of the molecular structure of (p-OCH₃C₆H₄)₃Pl₂ (**3**). Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: P(1)-I(1): 2.448(4), I(1)-I(2): 3.2575(15), P(1)-C(1): 1.66(3), P(1)-C(8): 1.802(16), P(1)-C(15): 1.757(18), P(1)-I(1)-I(2): 170.75(12), I(1)-P(1)-C(1): 115.4(7), I(1)-P(1)-C(8): 106.6(5), I(1)-P(1)-C(15): 107.5(6), C(1)-P(1)-C(8): 108.0(8), C(1)-P(1)-C(15): 108.5(9), C(8)-P(1)-C(15): 110.8(8).

the shift is slightly to higher frequency. For the other o-substituted adduct, $(o-SCH_3C_6H_4)_3PI_2$ **4**, the shift to lower frequency is very small. These broad peaks are often located at similar chemical shifts to those of the free phosphine, and may have been mistaken

in the past for unreacted starting material. When the same samples are made up in air (with no attempt to exclude moisture), two peaks are typically seen in each spectrum. The peak for the spoke adduct is again observed, along with a second peak found between



Fig. 5. ORTEP representation of the molecular structure of (p-SCH₃C₆H₄)₃Pl₂ (**5**). Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: P(1)–I(1): 2.468(2), I(1)–I(2): 3.1946(8), P(1)–C(1): 1.783(7), P(1)–C(8): 1.795(7), P(1)–C(15): 1.783(7), P(1)–I(1)–I(2): 173.55(5), I(1)–P(1)–C(1): 110.5(2), I(1)–P(1)–C(8): 107.5(3), I(1)–P(1)–C(15): 111.2(2), C(1)–P(1)–C(8): 110.6(3), C(1)–P(1)–C(15): 109.9(4), C(8)–P(1)–C(15): 107.1(3).

Table 2

Comparison of P-I and I-I bond lengths, and P-I-I angles in reported R₃PI₂ structures.

Compound	P–I (Å)	I–I (Å)	P–I–I (°)	Ref.
(Mecarb) ^{<i>i</i>} Pr ₂ PI ₂ ^a	2.5978(14)	3.021(1)	177.49(3)	[11]
$(0-CH_3C_6H_4)_3PI_2$	2.5523(12)	3.0727(4)	174.32(3)	[12]
$(p-FC_6H_4)_3PI_2$, 7b ^b	2.507(3)	3.0807(12)	177.76(7)	This paper
	2.461(3)	3.1529(11)	173.07(7)	
$(p-ClC_6H_4)_3Pl_2$, 8	2.488(2)	3.1332(9)	178.86(6)	This paper
$(m-FC_6H_4)_3PI_2, 6^{c}$	2.476(4)	3.1347(13)	177.58(10)	This paper
	2.475(4)	3.1500(14)	174.10(10)	
$(o-PhC_6H_4)Ph_2PI_2$	2.485(3)	3.1463(11)	170.02(8)	[15]
Ph ₃ Pl ₂	2.481(4)	3.161(2)	178.23(6)	[3]
$(m-CH_3C_6H_4)_3PI_2$	2.479(3)	3.1815(13)	173.82(8)	[16]
$(p-CH_3C_6H_4)_3PI_2$	2.472(5)	3.1809(17)	178.75(9)	[16]
$(p-SCH_3C_6H_4)_3PI_2$, 5	2.468(2)	3.1946(8)	173.55(5)	This paper
$(p-FC_6H_4)_3PI_2$, 7a ^d	2.460(3)	3.1985(11)	171.91(8)	This paper
$(m-OCH_3C_6H_4)_3PI_2$, 2	2.454(2)	3.2123(7)	177.42(5)	This paper
$(p-OCH_3C_6H_4)_3PI_2$, 3	2.448(4)	3.2575(15)	170.75(12)	This paper
^t Bu ₃ PI ₂	2.461(2)	3.326(1)	177.6(1)	[2]
[2,4,6-(MeO) ₃ C ₆ H ₂] ₃ PI ₂	2.482(1)	3.3394(5)	174.52(5)	[9]
ⁱ Pr ₃ Pl ₂	2.409(2)/2.420(2)	3.383(1)/3.372(1)	174.11(6)/179.06(5)	[10]
Me ₂ PhPI ₂	2.410(2)	3.408(2)	177.01(6)	[8]
$[(C_4H_8N)_3PI]I$	2.4303(17)	3.5170(6)	167.97(4)	[14]
[(Et ₂ N) ₃ PI]I	2.4730(8)	3.6168(4)	171.97(2)	[14]
[{(Me ₂ N) ₃ PI}I] ₆ CH ₃ CN	2.427(3)-2.448(5) ^e	3.6378(14)	175.08(8)	[13]
$[(^{n}\mathrm{Pr}_{2}\mathrm{N})_{3}\mathrm{PI}]\mathrm{I}$	2.455(4)	3.6389(14)	161.12(9)	[14]
[N(CH ₂ CH ₂ N ⁱ Bu) ₃ PI]I	2.5814(8)	7.18 ^f	N/A	[21]

^a (Mecarb) = 1-(2-Me-1,2-*closo*-C₂B₁₀H₁₀).

^b Triclinic form (orange) of $(p-FC_6H_4)_3PI_2$ with two independent molecules in the asymmetric unit.

^c Two independent molecules in the asymmetric unit.

^d Monoclinic form (olive-green) of (*p*-FC₆H₄)₃PI₂.

^e Value for P–I in cation interacting with an I^- is 2.427(3) Å.

^f Closest I...I contact in the structure, no linear P–I...I motif observed.

-20 and 0 ppm, (with the exception of **6**, **7** and **8** which show very broad peaks assigned to the spoke adducts, and a second prominent peak around +40 to +45 ppm, assigned to hydrolysis products, see below). We have shown that δ_P for [Ar₃PI]⁺ cations in [Ar₃PI][I₃] salts is typically observed between +10 and -10 ppm [37], and it

was therefore assumed that the species observed between -20 and 0 ppm in the above reactions were due to ionization of the Ar₃Pl₂ spoke adducts to [Ar₃Pl][I]. However, when the ³¹P NMR spectra are recorded proton coupled the resonances in this region all appear as doublets with couplings in the range 500–560 Hz.

Couplings of this magnitude are consistent with ¹*J*(PH) coupling for [R₃PH]⁺ cationic species. Previous literature data for [R₃PH]⁺ is sparse, however data for [Ph₃PH][HBr₂] (δ_P : -4.6 ppm, ¹*J*(PH) = 532 Hz) [38], [{0-CH₃C₆H₄}PH][HB(C₆F₅)₃] (δ_P : -12.1 ppm, ¹*J*(PH) = 485 Hz in CD₂Cl₂) [39] and [{p-CH₃C₆H₄}PH][HBr₂] (δ_P : -4.2 ppm, ¹*J*(PH) = 529 Hz in CD₂Cl₂) [38], are consistent in all three cases with the second species observed in the ³¹P NMR spectra of Ph₃Pl₂, (o-CH₃C₆H₄)₃Pl₂ and (p-CH₃C₆H₄)₃Pl₂, see Table 1. It would therefore appear that [Ar₃PI]⁺ cationic species are not observed in the ³¹P{¹H} NMR spectra of Ar₃Pl₂ compounds, either in anhydrous conditions, or in samples prepared in air. This certainly contrasts with analogous tri-alkyl phosphine systems such as ¹Pr₃. Pl₂, which has been shown to exhibit an ionic structure in solution [10].

The ³¹P{¹H} NMR spectra of the Ar₃Pl₂ adducts were examined over time, with those prepared in air showing a peak in the region +35 to +50 ppm becoming the predominant species, and are assigned as $[Ar_3POH]^+/[{Ar_3PO}_2H]^+$ hydrolysis species [10]. Peaks in this region only appear over many days for the samples prepared in anhydrous conditions, again except for **6**, **7** and **8** which appear to be much more sensitive to moisture and show exclusively hydrolysed species after several hours. In the cases of the bulky *o*-substituted compounds the molecular spoke resonance persists even in moist solution for many days, with the two new peaks only appearing gradually over several weeks.

It therefore seems that hydrolysis of the Ar₃Pl₂ adducts occurs fairly rapidly with initial formation of HI, resulting in [Ar₃PH]⁺ species, followed by a slower hydrolysis to [Ar₃POH]⁺/[{Ar₃PO}₂H]⁺. In many cases the shift of [Ar₃PH]⁺ is very close to that of the starting phosphine, which may have resulted in previous incorrect assignments of these peaks if the ³¹P NMR spectrum is recorded with proton decoupling. The colour of all of the solutions darkens considerably over time, suggesting that the counter anion is [I₃]⁻, not [I]⁻, although mixtures with the same cationic species may be formed, as du Mont and co-workers have crystallised both [ⁱPr₃-POH]I and [[ⁱPr₃PO]₂H][I₃] from the hydrolysis of ⁱPr₃PI₂ [10].

2.3. Structural studies of Ar₃PI₂ adducts

2.3.1. Structures of anisyl- and thioanisyl-substituted Ar_3Pl_2 adducts Crystals of the di-iodide adducts (m-OCH₃C₆H₄)₃Pl₂ **2**, (p-OCH₃C₆H₄)₃Pl₂ **3**, and the related thioanisyl-substituted adduct (p-SCH₃C₆H₄)₃Pl₂ **5**, were obtained by layering dichloromethane solutions of each with diethyl ether. Unfortunately, suitable crystals of the *o*-analogues of both series (compounds **1** and **4**) could not be obtained due to the poor solubility of these adducts in a range of common solvents. The molecular structures of **2**, **3** and **5** are shown in Figs. 3–5, along with selected bond lengths and angles.

The structures of all three adducts show the expected CT "spoke" motif, with P-I-I angles typically close to linear, e.g. between 170.76(12)° for 3, and 177.42(5)° for 2. The P-I and I-I bond lengths for all three adducts fall within the range observed for other Ar₃PI₂ compounds (see Table 2). The P-I bond lengths are all somewhat shorter than the P–I bond in Ph₃PI₂, [2.454(2) Å for 2, 2.448(4) Å for 3, and 2.468(2) Å for 5], whilst the I-I distances show an elongation in comparison to Ph_3PI_2 , [3.2123(7)Å for 2, 3.2575(15) Å for **3**, and 3.1946(8) Å for **5**]. A comparison of the crystallographic cone angles of the phosphine fragments in the three adducts shows that there is little difference in size between the three, with crystallographic cone angles [40,41] of 148.8° for 2, 152.5° for 3, and 147.0° for 5. All three adducts show shorter P–I bonds and longer I–I bonds than Ph₃Pl₂, as expected for more electron donating phosphines, but there are only relatively small variations in the P-I and I-I bond lengths between the three adducts.

It would appear that steric arguments are less important when ring substitution is in the *m*- or *p*-positions, where any variations in the P-I and I-I bond lengths are due to changes in the electronic properties of the aryl groups. The adduct displaying the shortest P-I bond of the three compounds, $(p-OCH_3C_6H_4)_3PI_2$ **3**, displays the longest I-I bond, which is consistent with electronic arguments whereby a more electron-donating R group will result in a shortened P-I bond and lengthened I-I bond. The bond length data for 2, 3 and 5 suggests that the order of electron-donating ability of the three phosphines towards iodine is $(p-OCH_3C_6H_4)_3P > (m OCH_3C_6H_4)_3P > (p-SCH_3C_6H_4)_3P$, although the differences are fairly small between the three, (see Table 2). The I-I bonds in 2 and 3 are among the longest seen for aryl-substituted R₃Pl₂ adducts, but are still noticeably shorter than those of tri-alkyl R₃PI₂ adducts [2,10], and $\{2,4,6-(MeO)_3C_6H_2\}_3PI_2$ [9], where the I–I bond is 3.3394(5) Å. This adduct displays a unusually long P-I bond of 2.482(1) Å for such an electron rich phosphine, and is significantly longer than the P–I bond in either 2 or 3. This suggests that the long P–I bond in $\{2,4,6-(MeO)_3C_6H_2\}_3PI_2$ is due to a steric affect arising from the presence of methoxy groups in both *o*-positions on each the rings. This double substitution greatly increases the steric bulk, as illustrated by the very large crystallographic cone angle of 211.6°, significantly larger than 2 or 3.

We have previously shown that the crystal packing of Ph₃Pl₂ and the $(o/m/p-CH_3C_6H_4)_3PI_2$ series of adducts are dominated by edge-to-face (EF) embraces between phenyl or tolyl rings, and weak, non-classical, hydrogen bonding between the iodine spoke and C-H proton atoms on the aryl rings [15,16]. The conformations preferred by the aryl rings in these structures appear to be those which facilitate the aryl embraces, which often results in an a specific conformation being favoured for a particular aryl group. This has been illustrated by a comparison of Ar₃PI-I spoke adducts with linear [(Ar₃P)AuX] gold(I) complexes with the same aryl group, where the same conformations are often observed between the two systems [15,16]. Where differences are observed between the two systems it is often a consequence of the enhanced ability of the P-I...I iodide atom to participate in hydrogen bonding compared to the metal bound halide in the gold(I) complexes. These differences in hydrogen bonding can also result in different polymorphs being observed for these systems [16].

Whilst a number of conformational studies of tri-phenyl [15,23,42–44] and tri-tolyl phosphine systems [16,45–48] have been undertaken, systems involving other substituted tri-aryl phosphine systems have been less comprehensively examined [46], although some reports have appeared concerning anisyl/thio-anisyl systems [49,50], fluoro/trifluoromethyl substituted aryl compounds [51], and those containing bulky aryl groups on the aryl rings [52,53]. The conformations of the aryl rings in the structures of **2**, **3** and **5** have been assigned by an examination of the I– $P-C_{ipso}-C_{ortho}$ torsion angles, as shown in Table 3, along with cone angle data for comparison.

The conformation of the aryl rings in (m-OCH₃C₆H₄)₃Pl₂ **2**, shows that all three rings are twisted in the same direction (staggered propeller conformation) with I–P–C(*ipso*)–C(*ortho*) torsions falling in a narrow range between -44° and -54° . However, in one of the rings the methoxy group points upwards towards the P–I bond, (*exo* group), whilst in the other two rings the methoxy groups point away (*endo* groups), so **2** can be termed as having an *exo*₁ conformation using the notation of Howell et al. [22]. The structure of **2** is the first reported structure containing a (*m*-OCH₃C₆H₄)₃P group, thus no previous conformational data is known for this phosphine.

Molecules of **2** pack side-to-side in an infinite chain of slightly offset parallel pairs, which stack down the *c* axis Fig. 6, with a P...P separation between adjacent molecules of 7.144 Å. The presence of the OCH₃ group in the *m*-position clearly prevents the

Torsion angles, cone angles and conformations of Ar ₃ PI ₂ adducts.	Table 3
	Torsion angles, cone angles and conformations of Ar_3Pl_2 adducts.

Compound	I-P-C-C torsions (°)	Conformation	Cone angle (°)
$(m-OCH_3C_6H_4)_3PI_2, (2)$	-44.4(6) exo, $-54.4(6)$ endo, $-51.9(6)$ endo	exo ₁	148.8
$(p-OCH_{3}C_{6}H_{4})_{3}PI_{2}, (3)$	-50.4(16), -53.1(14), -36.7(16)	Staggered propeller	152.5
$(p-SCH_3C_6H_4)_3PI_2, (5)$	63.6(7), 47.3(6), 47.6(7)	Staggered propeller	147.0
$(m-FC_6H_4)_3PI_2, (6)^a$	45.7(12) exo, 55.6(12) exo, 54.6(11) exo/endo	exo_3/exo_2	154.6/151.6
	45.8(12) exo, 58.3(13) exo/endo, 43.9(13) exo	exo_3/exo_2	152.3/151.7
$(p-FC_6H_4)_3PI_2, (7a)^b$	41.6(10), 53.4(10), 47.4(11)	Staggered propeller	145.7
$(p-FC_6H_4)_3PI_2, (7b)^c$	-42.2(10), -52.3(9), -60.2(10)	Staggered propeller	145.5
	-54.4(9), -52.3(10), -16.8(12)	Staggered, one parallel ring	149.3
$(p-{\rm ClC}_{6}{\rm H}_{4})_{3}{\rm PI}_{2},$ (8)	72.9(9), 26.7(8), 28.8(9)	Staggered, one orthogonal ring	145.0

^a Two independent molecules in the asymmetric unit.

^b Monoclinic form (olive-green) of (*p*-FC₆H₄)₃Pl₂.

^c Triclinic form (orange) of (*p*-FC₆H₄)₃Pl₂ with two independent molecules in the asymmetric unit.



Fig. 6. Packing of (m-OCH₃C₆H₄)₃Pl₂ (**2**) looking down the *c* axis, showing aggregation of offset-parallel pairs packing in a side-to-side fashion.

back-to-back association of molecules, which instead pack side-toside with methoxy C–H protons pointing towards anisyl rings of the neighbouring molecules. The I–P···P–I torsion angle between adjacent molecules is 2.9° , and chains of these pairs then build up in a zig-zag fashion (also showing methoxy C–H to ring contacts), with each pair the mirror image of the pairs either side. The terminal iodine atom participates in three non-classical hydrogen bonds to ring protons on anisyl rings, see Table S1 in supplementary material.

The structures of (p-OCH₃C₆H₄)₃Pl₂ (**3**) and (p-SCH₃C₆H₄)₃Pl₂ (**5**) both exhibit slightly staggered propeller conformations. In **3** the I– P–C(*ipso*)–C(*ortho*) torsion angles are $-50.4(16)^{\circ}$, $-53.1(14)^{\circ}$, and $-36.7(16)^{\circ}$, and the OCH₃ groups on all three rings are oriented such that they point downwards with respect to the P–I–I portion of the molecule. In **5** the I–P–C(*ipso*)–C(*ortho*) torsion angles are $63.6(7)^{\circ}$, $47.3(6)^{\circ}$, and $47.6(7)^{\circ}$, with one ring somewhat flatter than the other two. In contrast to **3** only two of the SCH₃ groups are orientated so that they are pointing downwards relative to the P–I–I spoke, whereas in the flatter ring the SCH₃ is pointing slightly upwards. These differences in the ring conformations and orientation of the ECH_3 (E = O, S) groups result in slight differences in the crystal packing.

Molecules of **3** form anti-parallel pairs which then link into chains that propagate down the *c* axis, see Fig. 7. Pairs of molecules are linked by a single offset face-to-face (OFF) embrace [54] between anisyl rings, with a P···P separation of 6.944 Å between the pair of molecules. The propagation of the chains are reinforced by weak C–H···O hydrogen bonds from aryl C–H protons to methoxy oxygen atoms of neighbouring pairs, and P···P separations between pairs down the chain are 7.210 Å. Each chain is linked to neighbouring chains via a short C–H···I non-classical hydrogen bond from the terminal iodine atom, I(2), to an aryl C–H on a neighbouring chain, [I(2)···H(20): 3.00 Å]. Each I(2) atom also participates in two other hydrogen bonds to C–H atoms of neighbouring chains, see Table S1.

In the packing of 5 individual molecules pair in an anti-parallel, side-to-side fashion via two edge-to-face (EF)₂ embraces. In contrast to 2 and 3 there are no short I... H hydrogen bonds to the terminal iodine atom. However, there is a much closer $P \cdots P$ separation (6.038 Å) between embracing molecules than observed for **3**. This closer P · · · P distance may be a consequence of the presence of two (EF) aryl embraces rather than one (OFF) embrace in the case of **3**. These pairs stack diagonally down the cell parallel to the *b* axis, and further embrace with neighbouring pairs via an (OFF) interaction between thioanisyl rings, with a $P \cdots P$ separation of 7.088 Å between pairs. The packing is yet further extended as these stacks are linked by (OFF) embraces between thioanisyl rings in a back-to-back fashion down the *a* cell direction, with much longer P...P separations (9.076 Å). Finally, weak C-H...H-C contacts are observed between SCH₃ groups of molecules (also along the *a* cell direction). The network that is built up by these interactions is shown in Fig. 8.

2.3.2. Structures of halo-substituted Ar₃PI₂ adducts

The crystal structures of the halo-substituted aryl adducts (m-FC₆H₄)₃Pl₂ **6**, (p-FC₆H₄)₃Pl₂ **7**, and (p-ClC₆H₄)₃Pl₂ **8** were obtained via re-crystallization from dichloromethane solutions layered with diethyl ether. In the case of **7** a mixture of olive-green and orange crystals were formed. These were shown to be two different polymorphs (see below), the olive-green crystals being the monoclinic form **7a**, and the orange crystals the triclinic form **7b**. The molecular structures of **6**, **7a**, **7b** and **8** are shown in Figs. 9–12 below, along with selected bond lengths and angles. Both **6** and **7b** contain two independent molecules in the asymmetric unit. The conformations of **6**, **7a**, **7b** and **8** have been assigned by an examination of the I–P–C_{*ipso*}–C_{*ortho*} torsion angles, as shown in Table 3, along with cone angle data.

The P–I and I–I bond lengths in the structure of **6** are 2.475(4)/ 2.474(4) Å (P–I), and 3.1347(13)/3.1500(14) Å (I–I). These values



Fig. 7. Crystal packing of (*p*-OCH₃C₆H₄)₃Pl₂ (**3**) looking down the *a* axis, showing chains of anti-parallel molecules, and chains linked by weak C-H···I non-classical hydrogen bonds.



Fig. 8. Crystal packing of (p-SCH₃C₆H₄)₃Pl₂ (**5**) looking down the *c* axis, showing the formation of a network via propagation of anti-parallel pairs via a combination of (OFF) and (EF)₂ embraces, and weak C-H···H-C contacts.

are fairly similar to those of Ph₃PI₂ [3], suggesting that the change in electronic properties upon substitution of a fluorine atom in the *m*-position has little effect on the P–I–I CT system. The structure of **6** shows disorder in that in each of the independent molecules there are two partially occupied sites for the *m*-fluorine atoms on one of the (m-FC₆H₄) rings, viz atoms F(3) 0.65(2) occupancy/ F(3b) 0.35(2) occupancy, and F(5) 0.56(3) occupancy/F(5b) 0.44(3) occupancy. This partial occupancy results in two slightly different cone angles being calculated, one where all three fluorine atoms are pointing upwards (*exo*₃ conformation), or alternatively when one fluorine atom points down (exo₂ conformation). For the molecule based on P(1) the cone angle is 154.6° (exo₃) or 151.6° (*exo*₂), whilst for molecule P(2) the differences are smaller, 152.3° (exo₃) versus 151.7° (exo₂), and in each case the exo₃ conformation results in a slightly larger cone angle. The exo₂/exo₃ conformation observed for **6** contrasts with the exo_1 conformations observed for (m-CH₃C₆H₄)₃PI₂ and (m-OCH₃C₆H₄)₃PI₂. Recent reports on ruthenium complexes containing the $(m-FC_6H_4)_3P$ ligand also show partial occupancy of some of the *m*-fluorine atoms [55], in some cases on all three rings on each ligand. This results in all four possible conformations (exo_0-exo_3) being observed, and no particular conformation seems to be preferred for the $(m-FC_6H_4)_3P$ ligand.

The two different polymorphs of $(p-FC_6H_4)_3PI_2$, **7**, show noticeable variations in their P–I and I–I bond lengths. For this adduct we can compare three independent $(p-FC_6H_4)_3PI_2$ molecules, the monoclinic form **7a**, and the two molecules of the triclinic form **7b**. A comparison of P–I and I–I bond lengths again shows a relationship between the two bond lengths, however there are considerable variations within the different independent molecules in the same structure.

For example, in **7a** the $(p-FC_6H_4)_3PI_2$ molecule has a P–I bond of 2.460(3) Å and an I–I bond of 3.1985(11) Å. These values are essentially the same as those in **3** suggesting that replacement of an SCH₃ group by a fluorine atom in the *p*-position on the ring has had essentially no impact on the P–I and I–I bond lengths, despite the different electronic properties. In contrast, in **7b** the molecule based on P(1) has a P–I bond of 2.461(3) Å and an I–I bond of 3.1529(11) Å, whereas the second molecule has a P–I bond of 2.507(3) Å and a I–I bond of 3.0807(12) Å. Therefore, while the P–I bond in **7a** and one of the molecules in **7b** are essentially identical, the I–I bonds vary considerably between the two, and the second molecule in **7b** has a significantly longer P–I bond and shorter I–I bond than the other two.

These differences in bond lengths may be due to a different orientation of the $(p-FC_6H_4)$ rings in each of the three $(p-FC_6H_4)_3Pl_2$ molecules. The I–P–C(*ipso*)–C(*ortho*) torsion angles have been measured, (see Table 3), and in all three cases the rings do not adopt the ideal C_3 symmetric "propeller" conformation for a tri-aryl phosphine system, but are staggered to varying degrees, as observed for the other *p*-substituted Ar₃Pl₂ adducts **3** and **5**. In the second molecule of **7b** one of the rings is twisted so that it is much more parallel with respect to the P–I bond, with a I–P–C–C torsion angle of $-16.8(12)^\circ$, compared to torsions of $-54.4(9)^\circ$ and $-52.3(10)^\circ$ for the other two rings. This appears to result in steric hindrance around the P–I bond with a resulting elongation of this bond and a concomitant shortening of the I–I bond. A comparison of cone angles shows that this molecule exhibits a slightly larger



Fig. 9. ORTEP representation of the molecular structure of $(m-FC_6H_4)_3Pl_2$ (**6**). Thermal ellipsoids are shown at the 30% probability level, with hydrogen atoms omitted for clarity. Atoms F(3)/F(3b) and F(5)/F(5b) are partially occupied. Selected bond lengths [Å] and angles [°]: P(1)–I(1): 2.476(4), I(1)–I(2): 3.1347(13), P(2)–I(3): 2.475(4), I(3)–I(4): 3.1500(14), P(1)–C(1): 1.814(14), P(1)–C(7): 1.799(14), P(1)–C(13): 1.795(15), P(2)–C(19): 1.788(14), P(2)–C(25): 1.812(14), P(2)–C(31): 1.772(14), C(3)–F(1): 1.33(2), C(9)–F(2): 1.332(17), C(15)–F(3): 1.38(2), C(18)–F(3b): 1.42(3), C(21)–F(4): 1.338(18), C(27)–F(5): 1.34(3), C(29)–F(5b): 1.30(3), C(33)–F(6): 1.373(16), P(1)–I(1)–I(2): 177.58(10), P(2)–I(3)–I(4): 174.10(10), I(1)–P(1)–C(1): 109.4(5), I(1)–P(1)–C(7): 108.1(5), I(1)–P(1)–C(13): 109.7(5), I(3)–P(2)–C(19): 112.2(4), I(3)–P(2)–C(25): 106.6(5), I(3)–P(2)–C(31): 109.8(5), C(1)–P(1)–C(13): 107.3(6), C(7)–P(1)–C(13): 112.3(6), C(19)–P(2)–C(25): 111.7(6), C(19)–P(2)–C(31): 106.5(6), C(25)–P(2)–C(31): 110.2(6).



Fig. 10. ORTEP representation of the molecular structure of $(p-FC_6H_4)_3Pl_2$ (monoclinic form) (**7a**). Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: P(1)–I(1): 2.460(3), I(1)–I(2): 3.1985(11), P(1)–C(1): 1.805(11), P(1)–C(7): 1.794(12), P(1)–C(13): 1.789(12), C(4)–F(1): 1.332(14), C(10)–F(2): 1.349(15), C(16)–F(3): 1.364(15), P(1)–I(1)–I(2): 171.91(8), I(1)–P(1)–C(1): 109.9(4), I(1)–P(1)–C(7): 113.3(4), I(1)–P(1)–C(13): 108.6(4), C(1)–P(1)–C(7): 110.3(5), C(1)–P(1)–C(13): 105.4(5), C(7)–P(1)–C(13): 109.2(5).

cone angle (149.3°) than the other molecule of **7b** (145.5°) and that of **7a** (145.7°). The cone angles are all somewhat smaller than those of $(m-FC_6H_4)_3Pl_2$ **6**.

The chloro-substituted analogue $(p-ClC_6H_4)_3Pl_2$, **8**, displays a P–I bond of 2.488(2) Å, again similar to that of Ph₃Pl₂ [3], whereas the I–I bond is somewhat shorter, at 3.1332(9) Å. The conformation of the aryl rings is different to both **7a** and either molecule in **7b**, with one of the rings twisted so that it is orthogonal to the P–I bond, with an I–P–C–C torsion angle of 72.9(9)°. As a consequence the other two rings are more upright, which may result in a lengthening of the P–I bond. The I–I bond is shorter than in two of the three

independent molecules of **7**, but is close in magnitude to the value observed for one of the molecules of **6**. The cone angle of **8** is 145.0°, which is very similar to the values observed for **7**.

The crystal packing of **6**, **7a**, **7b** and **8** have also been examined. In the structure of **6** each of the crystallographically independent molecules, based on atoms P(1) and P(2), stack in the *b* cell direction, see Fig. 13. The stack of P(1) molecules is staggered with a long P \cdots P separation of 7.874 Å, and is linked by distant (OFF) embraces, and a short F(3) \cdots H(18) contact of 2.60 Å (sum of the van der Waals radii of hydrogen and fluorine is 2.67 Å). The stack of P(2) molecules is also staggered and linked in a similar fashion,



Fig. 11. ORTEP representation of the molecular structure of $(p-FC_6H_4)_3Pl_2$ (triclinic form) (**7b**). Thermal ellipsoids are shown at the 30% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)–I(1): 2.461(3), I(1)–I(2): 3.1529(11), P(2)–I(3): 2.507(3), I(3)–I(4): 3.0807(12), P(1)–C(1): 1.793(11), P(1)–C(7): 1.794(11), P(1)–C(13): 1.785(11), P(2)–C(19): 1.801(11), P(2)–C(25): 1.798(12), P(2)–C(31): 1.792(11), C(4)–F(1): 1.361(13), C(10)–F(2): 1.368(14), C(16)–F(3): 1.340(14), C(22)–F(4): 1.359(15), C(28)–F(5): 1.372(14), C(34)–F(6): 1.346(15), P(1)–I(1)–I(2): 173.07(7), P(2)–I(3)–I(4): 177.76(7), I(1)–P(1)–C(1): 112.9(4), I(1)–P(1)–C(7): 110.1(4), I(1)–P(1)–C(13): 106.4(4), I(3)–P(2)–C(19): 107.2(4), I(3)–P(2)–C(25): 107.5(4), I(3)–P(2)–C(31): 113.4(4), C(1)–P(1)–C(7): 109.2(5), C(1)–P(1)–C(13): 107.7(5), C(7)–P(1)–C(13): 110.5(5), C(19)–P(2)–C(23): 110.5(5), C(25)–P(2)–C(31): 108.1(5).



Fig. 12. ORTEP representation of the molecular structure of (*p*-ClC₆H₄)₃Pl₂ (**8**). Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: P(1)–I(1): 2.488(2), I(1)–I(2): 3.1332(9), P(1)–C(1): 1.797(10), P(1)–C(7): 1.805(9), P(1)–C(13): 1.796(11), C(4)–Cl(1): 1.731(10), C(10)–Cl(2): 1.737(9), C(16)–Cl(3): 1.741(11), P(1)–I(1)–I(2): 178.86(6), I(1)–P(1)–C(1): 110.0(3), I(1)–P(1)–C(7): 112.5(3), I(1)–P(1)–C(13): 110.4(3), C(1)–P(1)–C(7): 108.7(4), C(1)–P(1)–C(13): 106.2(4), C(7)–P(1)–C(13): 108.9(4).

but has an even longer $P \cdots P$ separation of 8.006 Å, although the paired molecules are liked by two short $F \cdots H$ contacts, $F(4) \cdots H(24)$: 2.58 Å, and $F(4) \cdots H(36)$: 2.63 Å. The closest $P \cdots P$

separation between molecules in the entire structure is however between the stacks, i.e. between a P(1) molecule and a P(2) molecule, where the separation is 6.715 Å. These molecules are



Fig. 13. Crystal packing of (*m*-FC₆H₄)₃Pl₂ (**6**) looking down the *b* axis, showing alternating stacks based on P(1) molecules and P(2) molecules, linked by short F···H contacts, and weak I···H contacts.

orientated anti-parallel to each other, and display three $F \cdots H$ contacts between P(1) and P(2) molecules, viz. $F(1) \cdots H(23)$: 2.47 Å, $F(5) \cdots H(8)$: 2.32 Å and $F(6) \cdots H(14)$: 2.45 Å. The terminal iodine atoms of both molecules also show weak $I \cdots H$ hydrogen bonds, Table S1.

The extended structures of the two polymorphs of **7** show much closer $P \cdots P$ separations than seen for **6**. The monoclinic form of **7a** shows anti-parallel pairs of molecules stacking in the *a* direction, with a $P \cdots P$ separation of 6.044 Å and two (EF) interactions between pairing molecules. These pairs form a chain, as shown in Fig. 14, with each pair linked to the next by a short $F(2) \cdots F(2)$ contact of 2.867(14) Å, shorter than twice the van der Waals radii of fluorine (2.94 Å). This chain of pairing molecules is linked to an adjacent chain by a non-classical hydrogen bond of 3.15 Å from the terminal iodine atom I(2) to a H(6) proton on the next chain. In the second chain the $P \cdots P$ separation between anti-parallel pairs is slightly longer, (6.259 Å).

The packing of the triclinic form **7b** is very similar to that of **7a**, see Fig. 15. Anti-parallel pairs of P(1) molecules stack in the a direction, as do anti-parallel pairs of P(2) molecules. Whilst the $P \cdots P$ separation of the pairs of P(1) molecules is of a similar magnitude (5.996 Å) to **7a**, the separation between pairs of P(2) molecules is significantly shorter (5.844 Å). This closer approach may be linked to the different conformation observed for the P(2) molecule (with one ring much more parallel to the P-I bond). The main difference to the packing of 7a is that pairs of molecules are linked into a chain by F...H contacts, rather than F...F contacts. Each pair of P(1) molecules is linked to the next by an F(2)...H(5) contact of 2.53 Å, whilst each pair of P(2) molecules is linked to the next by two F···H contacts, F(4)···H(35): 2.52 Å, and F(5)···H(24): 2.50 Å, (all shorter than the sum of the van der Waals radii of hydrogen and fluorine at 2.67 Å). Additionally, the two sets of chains are linked to each both by I...H contacts (see Table S1), and also by two further short $F \cdots H$ contacts, $F(1) \cdots H(27)$: 2.52 Å and





Fig. 15. Crystal packing of the triclinic form of (*p*-FC₆H₄)₃Pl₂ (**7b**) looking down the *a* axis, showing chains of anti-parallel pairs of molecules. The chain of stacks of P(1) molecules is at the top, and P(2) molecules at the bottom.

 $F(5) \cdots H(3)$: 2.62 Å. The large number of $F \cdots H$ contacts in the structure of **7b** clearly contrasts with **7a** where the only short $F \cdots H$ contact (2.51 Å) is between stacking molecules down the *a* axis. The competition between the linking of stacks either by $F \cdots H$ contacts or $F \cdots F$ contacts may have resulted in the formation of different polymorphs.

The packing of **8** again shows a number of similarities to the polymorphs of **7** as molecules pair in an anti-parallel fashion (P \cdots P separation of 6.311 Å) and stack in the *b* cell direction, see Fig. 16. These stacks are linked by short C-H \cdots Cl-C contacts between the *p*-chlorophenyl rings, Cl(1) \cdots H(11): 2.75 Å and Cl(1) \cdots H(11): 2.83 Å, (compared to the sum of the van der Waals radii of chlorine and hydrogen, 2.95 Å). Weak I \cdots H hydrogen bonding between the stacks is also observed, see Table S1.

2.3.3. Comparison of conformations and crystal packing features of Ar_3PI_2 adducts

This study of the crystal packing of the Ar_3Pl_2 adducts **2**, **3**, **5**, **6**, **7a**, **7b** and **8** has shown that substitution of the aryl rings in different positions can result in changes in the preferred conformation of the aryl rings. All the Ar_3Pl_2 structures display conformations where all three rings are twisted in the same direction (based on a propeller conformation), but substitution in the *m*- or *p*-positions on the aryl rings results in disruption of the (EF)₆ embrace observed for (o-CH₃C₆H₄)₃Pl₂, where molecules are able to pack in a

back-to-back fashion [16]. Prediction of a conformation for the *m*-substituted adducts **2** and **6** is much less reliable than for *o*-substituted analogues, (which have an *exo*₃ conformation). Whilst (*m*-OCH₃C₆H₄)₃Pl₂ **2** exhibits an *exo*₁ conformation, as also observed previously for (*m*-CH₃C₆H₄)₃Pl₂ [16], (*m*-FC₆H₄)₃Pl₂ **6** exhibits disorder of the fluorine atoms, which results in either an *exo*₂ or *exo*₃ conformation being observed. The *p*-substituted derivatives **3**, **5**, **7a**, **7b** and **8** all exhibit staggered propeller conformations, with distortions from an ideal propeller being most noticeable for **7b** (where one ring is much more parallel to the P–I bond than the other two).

A consistent feature of the packing of these Ar_3PI_2 adducts is formation of close packed pairs of Ar_3PI_2 molecules, with $P \cdots P$ separations between neighbouring molecules ranging between 5.844 Å (for **7b**), and 7.144 (for **2**), see Table S2 in supplementary data. All the *p*-substituted derivatives feature molecules packing in an anti parallel, side-to-side fashion, whilst the *m*-substituted adducts show some variation, e.g. in **2** molecules pack parallel and side-to-side, whereas in **6** molecules pack offset and back-toback. Of all the structures studied here molecules of (*p*-FC₆H₄)₃PI₂ **7** are able to pack the closest, with $P \cdots P$ separations between 5.844 and 6.259 Å. The shortest of these is between two P(2) molecules in the triclinic polymorph **7b**. This is the molecule which has one parallel ring, and it appears that a conformation with a parallel ring



Fig. 16. Crystal packing of (*p*-ClC₆H₄)₃Pl₂ (8) looking down the *b* axis, showing stacks of paired molecules linked by Cl…H and I…H contacts.

Table 4

Crystallographic parameters for compounds **2**, **3**, **5**, **6**, **7a**, **7b** and **8**.

	$(m-OCH_3C_6H_4)_3Pl_2, 2$	(<i>p</i> -OCH ₃ C ₆ H ₄) ₃ Pl ₂ , 3
Empirical formula	$C_{21}H_{21}I_2O_3P$	$C_{21}H_{21}I_2O_3P$
Formula weight	605.98	605.98
Colour, habit	Yellow, prism	Yellow, prism
Crystal system	monoclinic	triclinic
Space group	PZ_{1}/C (No. 14)	P1 (No. 2)
Unit coll dimensions	$0.15 \times 0.17 \times 0.17$	$0.12 \times 0.15 \times 0.17$ mm ⁻³
$a(\hat{\lambda})$	12 1092(5)	10 1802(4)
$h(\mathbf{A})$	13.8366(7)	10.1805(4)
$c(\hat{A})$	13 9951(7)	11 4234(7)
α (°)	10,000 (/)	80.074(3)
β (°)	106.386(3)	67.751(3)
γ(°)		84.443(4)
Volume (Å ⁻³)	2249.45(19)	1138.59(11)
T (K)	100(2)	150(2)
Z	4	2
D_{calc} (mg/m ³)	1.790	1.768
λ (A)	0.71073	0.71073
μ (Mo K α) (mm ⁻¹)	2.885	2.850
F(000)	1168	584
θ range (*)	2.94-27.50 21400 (5152 unique)	2.93-25.50 2028 (2028 unique)
	0.082	0 124
$R_{\rm int}$	0.083	0.124
R_1/wR_2 (all data)	0.0870/0.1292	0.1656/0.2473
Largest diff. peak and hole $(e^{A^{-3}})$	1.639 and -1.365	3.643 and -1.555
Goodness-of-fit	1.077	1.172
Functional formerals	$(p-5Cn_3C_6n_4)_3P_2, 5$	$(m-rC_6\pi_4)_3r_{12}$, o
Empirical formula	$C_{21}H_{21}I_2S_3P$	C ₁₈ H ₁₂ I ₂ F ₃ P
Formula Weight	054.33 vollow rod	569.95 vellow plate
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
Crystal size (mm^{-3})	$0.14 \times 0.08 \times 0.08$	$0.12 \times 0.15 \times 0.17$
Unit cell dimensions	0.14 × 0.00 × 0.00	0.12 × 0.13 × 0.17
a (Å)	10.5524(2)	18,5533(6)
$b(\mathbf{A})$	10.5565(2)	10.1852(3)
c (Å)	12.0515(3)	19.8241(9)
α (°)	71.361(1)	
β (°)	67.644(1)	91.0760(10)
γ (°)	82.370(1)	
Volume (Å ⁻³)	1176.37(4)	3745.5(2)
<i>T</i> (K)	293(2)	100(2)
Z	2	8
D_{calc} (mg/m ³)	1.847	2.022
λ (A)	0.71073	0.71073
μ (Mo K α) (mm ⁻¹)	3.013	3.468
F(000)	b32 2.02.27.50	2144
e range (*)	2.93-27.50 22702 (5287 unique)	3.04-25.50 20052 (6621 upique)
P.	0.071	0.088
R_1/wR_2	0.0547/0.1227	0.088
R_1/wR_2 (all data)	0.0847/0.1227	0.1261/0.2007
Largest diff. peak and hole $(e^{A^{-3}})$	1.837 and -1.906	2.062 and -1.395
Goodness-of-fit	1.048	1.179
Empirical formula		$(p-rC_6\pi_4)_3r_{12}, 70$
Formula weight	C ₂₁ Π ₁₂ I ₂ Γ ₃ P 570 05	C ₁₈ n ₁₂ i ₂ r ₃ r 570 05
Colour, habit	olive green, prism	orange, needle
Crystal system	monoclinic	triclinic
Space group	$P2_{1}/c$ (No. 14)	<i>P</i> 1 (No. 2)
Crystal size (mm ⁻³)	0.17 imes 0.17 imes 0.19	0.08 imes 0.08 imes 0.20
Unit cell dimensions		
a (Å)	9.8484(3)	9.4690(1)
b (Å)	9.6638(3)	11.6950(2)
<i>c</i> (Å)	20.1127(6)	18.4350(3)
α (°)		79.733
β (°)	94.279(2)	86.213(1)
γ (°)		68.624(1)
Volume (A ⁻³)	1908.85(10)	1870.61(5)
Т(К)	150(2)	150(2)
		(continued on next page)

Table 4 (continued)

	(<i>p</i> -FC ₆ H ₄) ₃ PI ₂ , 7a	(<i>p</i> -FC ₆ H ₄) ₃ PI ₂ , 7b
Z $D_{calc} (mg/m^3)$ $\lambda (\dot{A})$ μ (Mo K α) (mm ⁻¹) $F(000)$ θ range (°) No. of reflections R_{int} R_1/wR_2 R_1/wR_2 (all data) Largest diff. peak and hole (eÅ ⁻³) Goodness-of-fit	4 1.984 0.7107 3.403 1072 3.01–25.50 3495 (3495 unique) 0.092 0.0752/0.1974 0.1107/0.2426 4.438 and -2.125 1.094	4 2.024 0.71073 3.472 1072 3.07-25.50 6914 (6914 unique) 0.048 0.0697/0.1774 0.0954/0.2045 2.968 and -1.388 1.104
		(<i>p</i> -ClC ₆ H ₄) ₃ Pl ₂ , 8
Empirical formula Formula weight Colour, habit Crystal system Space group Crystal size (mm ⁻³) Unit cell dimensions a (Å) b (Å) c (Å) β (°) Volume (Å ⁻³) T (K) Z D_{calc} (mg/m ³) λ (Å) μ (Mo Kα) (mm ⁻¹) F(000) θ range (°) No. of reflections R_{int}		$\begin{array}{c} C_{21}H_{12}I_2CI_3P\\ 619.30\\ Yellow, rod\\ Monoclinic\\ P2_1/n (No. 14)\\ 0.10 \times 0.10 \times 0.16\\ 10.8892(4)\\ 12.4480(5)\\ 14.8186(7)\\ 91.135(2)\\ 2008.25(14)\\ 100(2)\\ 4\\ 2.049\\ 0.71073\\ 3.609\\ 1168\\ 3.20-25.50\\ 20745 (3725 unique)\\ 0.090\\ \end{array}$
$\frac{\kappa_1/w\kappa_2}{R_1/wR_2}$ (all data) Largest diff. peak and hole (eÅ ⁻³) Goodness-of-fit		0.0534/0.0945 0.1103/0.1315 1.373 and -1.278 1.047

allows the closest approach of pairing molecules. However, the presence of a parallel ring results in an increase in steric congestion, as the cone angle rises from 145° to 149°. This results in a longer P–I and shorter I–I bond length than observed for the other molecule in **7b**, and for the monoclinic form **7a**.

The cone angles for all of the Ar_3PI_2 structures reported in this paper fall over a relatively small region, varying between 145.0° and 154.6°, suggesting that whilst the P–I bond may be affected by a ring which becomes too close to parallel with it, the overall steric "footprint" of the Ar_3P group is moderated by the other rings twisting such that the overall steric repulsion does not become too great. However, the case of **7b** shows that changes in the conformation of the aryl rings can affect the P–I and I–I bond lengths.

3. Conclusion

A series of Ar_3PI_2 adducts have been synthesized via the 1:1 reactions of Ar_3P with di-iodine in anhydrous diethyl ether. The ${}^{31}P{}^{1}H{}$ NMR spectra of these adducts has been examined to resolve the conflicting data previously reported. We find no evidence for ionization of Ar_3PI_2 adducts in CDCI₃ solution (in contrast to related tri-alkyl adducts), and resonances previously assigned as $[Ar_3PI]I$ are have been shown in most cases to be due to hydrolyzed species such as $[Ar_3POH]^+$ or $[{Ar_3PO}_2H]^+$. In many cases the Ar_3PI_2 adducts show reasonable stability towards hydrolysis (although this is highly dependent on the nature of R), with slow hydrolysis often producing $[Ar_3PH]I$ species.

The structures of most of these adducts have been obtained, and shown to be R_3PI_2 charge-transfer systems of the D–I···I type, with short P-I bonds and long I-I bonds. In contrast, the structure of (o- $SCH_3C_6H_4)_3PI_2$ (where suitable crystals could not be grown due to poor solubility) may be a (10-I-2) type of CT adduct, on the basis of the Raman spectrum and dark red colour of the adduct. An examination of P-I and I-I bond lengths in the structurally characterized adducts show that electronic effects are primarily responsible for differences in the bond lengths in *m*- and *p*-substituted Ar₃PI₂ adducts (unlike o-substituted adducts where steric effects are also important). The adduct $(p-FC_6H_4)_3PI_2$ forms two polymorphs 7a and **7b**, the presence of which may be a consequence of the possibility of either $F \cdots F$ contacts (as in **7a**) or $F \cdots H$ contacts (as in **7b**) being able to link pairs of molecules into chains. Between the two polymorphs there are a total of three crystallographically unique molecules. Differences are observed in the ring conformations between these molecules, with one exhibiting a ring which is close to parallel with respect to the P-I bond, resulting in steric congestion, a lengthening of the P-I bond and concomitant shortening of the I-I bond.

4. Experimental

4.1. Reagents and physical measurements

The synthesis of the di-iodide adducts described herein was undertaken using standard Schlenk techniques under anhydrous and anaerobic conditions with all solvents being rigorously dried before use. $(o-OCH_3C_6H_4)_3P$, $(m-OCH_3C_6H_4)_3P$ and $(p-OCH_3C_6H_4)_3P$ were purchased commercially (Alfa Aesar), as were $(m-FC_6H_4)_3P$ (Apollo Scientific), $(p-FC_6H_4)_3P$, $(p-ClC_6H_4)_3P$ and iodine (all Aldrich). $(o-SCH_3C_6H_4)_3P$ was synthesized as previously described [12], and $(p-SCH_3C_6H_4)_3P$ by a modification of the literature preparation [56], as outlined below. Elemental analyses were performed by the University of Manchester School of Chemistry Microanalytical service. Raman spectra were recorded as solid samples on a Nicolet–Nexus combined FT-IR/FT-Raman spectrometer. ¹H, ¹³C(¹H), ³¹P(¹H) and ¹⁹F NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer operating at 400.1 (¹H), 100.6 (¹³C), 162.0 (³¹P) and 376.5 (¹⁹F) MHz, respectively. Peak positions are quoted relative to TMS (¹H/¹³C), 85% H₃PO₄ (³¹P) or CFCl₃ (¹⁹F) using the high frequency positive convention throughout.

4.2. Synthesis of $(p-SCH_3C_6H_4)_3P$

4-Bromothioanisole (12.55 g, 0.062 mol) was dissolved in anhydrous THF (80 mL) in a 500 mL three-necked round bottomed flask equipped with a stirrer bar and nitrogen inlet/outlet. To this was slowly added dried magnesium turnings (1.54 g, 0.063 mol) over 15 min. The reaction was initiated with two drops of 1,2-dibromoethane and heated gently with a heat gun until reaction commenced. A cloudy grey solution was formed after 30 min which was allowed to stir for 2 h until all the magnesium had been consumed. The reaction was then cooled to -78 °C (acetone slush bath) and a solution of phosphorus(III) chloride (1.80 mL, 2.83 g, 0.021 mmol) in 50 mL of THF was added dropwise over 2 h. The reaction was then allowed to warm up to room temperature overnight. Any residual Grignard was destroyed by careful shaking of the solution with an aqueous solution. The solution was then reduced in volume by half, and 50 mL each of dichloromethane and water were added. The layers were shaken and the organic layer separated off. The aqueous layer was then shaken with further 2×30 mL portions of dichloromethane. The organic extracts were combined, dried (MgSO₄), filtered and the solvent removed to yield $(p-SCH_3C_6H_4)_3P$ as a white solid, which was re-crystallized from dichloromethane/40:60 petroleum ether. Spectroscopic data is as follows: ¹H NMR (CDCl₃): 2.40 [s, SCH₃, 9H], 7.15-7.18 [m, aromatic]. ¹³C{¹H} NMR (CDCl₃): 15.3 [s, SCH₃], 126.0 [d, C_m, ${}^{3}J(PC) = 8.5 \text{ Hz}], 133.0 \text{ [d, } C_{i}, {}^{1}J(PC) = 10.3 \text{ Hz}], 133.9 \text{ [d, } C_{o}, {}^{2}J(PC) = 19.8 \text{ Hz}], 139.9 \text{ [s, } C_{p}]. {}^{3}P{}^{1}H} \text{NMR (CDCl_3): } -8.3 \text{ [s].}$

4.3. Synthesis of Ar₃PI₂ adducts 1-8

The series of Ar_3Pl_2 adducts were all prepared by reaction of the aryl phosphine with l_2 in anhydrous diethyl ether in a 1:1 ratio. The synthesis of **1** is typical: 40 mL of diethyl ether was freshly distilled into a pre-dried rotaflo tube. To this solution was added 0.650 g, (1.85 mmol) of (*o*-OCH₃C₆H₄)₃P, followed by 0.469 g, (1.85 mmol) of l_2 . A yellow solid rapidly formed and the reaction was left to stir for *ca*. 48 h. The solid was isolated using standard Schlenk techniques, and dried *in vacuo* for 2 h, before being transferred to pre-dried argon filled ampoules. Characterising data for **1** is given below, along with the other adducts **2–8** which were synthesised via the same method. Raman spectroscopic data for **7** and **8** has been previously reported [27].

4.3.1. $(0-OCH_3C_6H_4)_3PI_2$ (**1**)

Yield: 0.886 g (79.2%). Yellow solid. *Anal.* Calc. for $C_{21}H_{21}O_3PI_2$: C, 41.5; H, 3.4; P, 5.1; I, 41.8. Found: C, 42.0; H, 3.4; P, 5.1; I, 41.3%. ¹H NMR (CDCl₃): 3.75 [s, OCH₃, 9H], 6.89–7.40 [m, aromatic, 6H], 7.56–7.73 [m, aromatic, 6H]. ¹³C{¹H} NMR (CDCl₃): 55.0 [s, OCH₃], 108.8 [d, C_i, ¹J(PC) = 71.2 Hz], 112.5 [d, C_m, ³J(PC) = 6.5 Hz], 121.3 [d, C_o, ²J(PC) = 12.9 Hz], 134.9 [d, C_m, ³J(PC) = 7.4 Hz], 136.2 [s, C_p], 161.3 [s, C_{o(bound to methoxy)}]. ³¹P{¹H</sup> NMR (CDCl₃): -34.6 [s,

broad]. Raman: (cm⁻¹): 3051, 2920, 1587, 1565, 1203, 1047, 800, 661, 559, 516, 463, 400, 273, 213, 155.

4.3.2. $(m-OCH_3C_6H_4)_3PI_2$ (**2**)

Yield: 0.602 g (75.9%). Yellow solid. *Anal.* Calc. for $C_{21}H_{21}O_3PI_2$: C, 41.5; H, 3.4. Found: C, 41.4; H, 3.4%. ¹H NMR (CDCl₃): 3.85 [s, OCH₃, 9H], 6.98–7.39 [m, aromatic, 6H], 7.44–7.64 [m, aromatic, 6H]. ¹³C{¹H} NMR (CDCl₃): 55.8 [s, OCH₃], 118.9 [d, C_0 , ²*J*(PC) = 11.9 Hz], 119.7 [s, C_p], 125.5 [d, C_m , ³*J*(PC) = 9.9 Hz], 131.7 [d, C_0 , ²*J*(PC) = 13.7 Hz], 160.2 [d, $C_m(bound \ to \ methoxy)$, ³*J*(PC) = 13.8 Hz]. ³¹P{¹H} NMR (CDCl₃): -18.5 [s, broad]. Raman: (cm⁻¹): 3064, 2835, 1588, 1493, 1308, 1292, 1267, 1181, 1121, 795, 675, 572, 545, 512, 454, 272, 154.

4.3.3. $(p-OCH_3C_6H_4)_3PI_2$ (**3**)

Yield: 0.766 g (82.0%). Yellow solid. *Anal.* Calc. for $C_{21}H_{21}O_3PI_2$: C, 41.5; H, 3.4; P, 5.1. Found: C, 41.1; H, 3.2; P, 4.8%. ¹H NMR (CDCl₃): 3.85 [s, OCH₃, 9H], 6.96–7.04 [m, aromatic, 6H], 7.36–7.47 [m, aromatic, 6H]. ¹³C{¹H} NMR (CDCl₃): 56.0 [s, OCH₃], 113.1 [d, C_i , ¹J(PC) = 76.2 Hz], 115.7 [d, C_m , ³J(PC) = 14.5 Hz], 135.4 [d, C_o , ²J(PC) = 12.4 Hz], 164.5 [d, C_p , ⁴J(PC) = 2.8 Hz]. ³¹P{¹H</sup> NMR (CDCl₃): -12.7 [s, broad]. Raman: (cm⁻¹): 3063, 2829, 1589, 1103, 795, 613, 534, 503, 490, 463, 272, 207, 157.

4.3.4. $(o-SCH_3C_6H_4)_3PI_2$ (4)

Yield: 0.637 g (68.6%). Red solid. *Anal.* Calc. for $C_{21}H_{21}S_3PI_2$: C, 38.5; H, 3.2; P, 4.7; I, 38.8. Found: C, 38.1; H, 2.9; P, 4.6; I, 38.6%. ¹H NMR (CDCl₃): 2.38 [s, SCH₃, 9H], 6.76–7.15 [m, aromatic, 6H], 7.18–7.57 [m, aromatic, 6H]. ¹³C{¹H} NMR (CDCl₃): 17.8 [s, SCH₃], 125.9 [d, *J*(PC) = 13.6 Hz], 128.1 [d, *J*(PC) = 7.4 Hz], 130.5 [d, *J*(PC) = 12.9 Hz], 133.6 [s, C_p], 144.2 [d, C_{o(bound to SCH3)}, ²*J*(PC) = 23.2 Hz]. ³¹P{¹H</sup> NMR (CDCl₃): -31.4 [s, vbroad]. Raman: (cm⁻¹): 3048, 2984, 2915, 1569, 1268, 1103, 1036, 698, 365, 160.

4.3.5. $(p-SCH_3C_6H_4)_3PI_2$ (5)

Yield: 0.444 g (72.0%). Yellow solid. *Anal.* Calc. for $C_{21}H_{21}S_3PI_2$: C, 38.5; H, 3.2; S, 14.7. Found: C, 37.9; H, 2.9; S, 14.6%. ¹H NMR (CDCl₃): 2.59 [s, SCH₃, 9H], 7.27–7.58 [m, aromatic, 6H], 7.70– 7.81 [m, aromatic, 6H]. ¹³C{¹H} NMR (CDCl₃): 14.9 [s, SCH₃], 126.0 [d, *C_m*, ³*J*(PC) = 15.0 Hz], 133.1 [d, *C_o*, ²*J*(PC) = 12.8 Hz]. ³¹P{¹H} NMR (CDCl₃): -18.5 [s, broad]. Raman: (cm⁻¹): sample decomposes in the laser beam.

4.3.6. (m-FC₆H₄)₃PI₂ (**6**)

Yield: 0.493 g (83.8%). Yellow solid. *Anal.* Calc. for $C_{18}H_{12}F_3PI_2$: C, 37.9; H, 2.1; I, 44.5. Found: C, 37.8; H, 1.8; I, 45.0%. ¹H NMR (CDCl₃): 7.22–7.34 [m, aromatic, 3H], 7.39–7.54 [m, aromatic, 6H], 7.66–7.78 [m, aromatic, 3H]. ¹³C{¹H} NMR (CDCl₃): 120.2 [dd, C_o , ²*J*(CF) = 11.1 Hz, ²*J*(PC) = 23.1 Hz], 121.8 [dd, C_o , ⁴*J*(CF) = 3.0 Hz, ²*J*(PC) = 21.1 Hz], 124.6 [dd, C_i , ¹*J*(PC) = 53.3 Hz, ³*J*(CF) = 6.0 Hz], 129.5 [dd, C_p , ⁴*J*(PC) = 4.0 Hz, ²*J*(CF) = 10.1 Hz], 132.4 [dd, C_m , ³*J*(CF) = 8.0 Hz, ³*J*(PC) = 15.1 Hz], 162.8 [dd, C_m , ³*J*(PC) = 17.1 Hz, ¹*J*(CF) = 255.5 Hz]. ¹⁹F NMR (CDCl₃): -106.9 [m, broad]. ³¹P{¹H} NMR (CDCl₃): -29.8 [s, broad]. Raman: (cm⁻¹): sample decomposes in the laser beam.

4.3.7. $(p-FC_6H_4)_3PI_2$ (7)

Yield: 0.728 g (74.4%). Olive-green solid. *Anal.* Calc. for $C_{18}H_{12}F_{3}Pl_{2}$: C, 37.9; H, 2.1; I, 44.5. Found: C, 37.6; H, 2.2; I, 44.2%. ¹H NMR (CDCl₃): 7.31–7.46 [m, aromatic, 6H], 7.69–7.97 [m, aromatic, 6H]. ¹³C{¹H} NMR (CDCl₃): 118.1 [dd, *C_m*, ²*J*(CF) = 14.1 Hz, ³*J*(PC) = 22.1 Hz], 126.2 [d, *C_i*, ¹*J*(PC) = 73.4 Hz], 136.4 [dd, *C_o*, ³*J*(CF) = 9.1 Hz, ²*J*(PC) = 11.1 Hz], 166.4 [d, *C_p*, ¹*J*(CF) = 258.6 Hz]. ¹⁹F NMR (CDCl₃): -100.6 [m, broad]. ³¹P{¹H} NMR (CDCl₃): -20.2 [s, broad].

4.3.8. $(p-ClC_6H_4)_3Pl_2$ (8)

Yield: 0.686 g (78.4%). Yellow solid. Anal. Calc. for C₁₈H₁₂Cl₃Pl₂: C, 36.5; H, 2.0; I, 42.9. Found: C, 36.3; H, 1.9; I, 42.4%. ¹H NMR (CDCl₃): 7.18-7.50 [m, aromatic, 6H], 7.62-7.96 [m, aromatic, 6H]. ${}^{13}C{}^{1}H$ NMR (CDCl₃): 130.1 [d, C_m, ${}^{3}J(PC) = 11.1$ Hz], 135.0 [d, C_o , ²J(PC) = 16.1 Hz], 139.7 [d, C_p , ⁴J(PC) = 3.0 Hz]. ³¹P{¹H} NMR (CDCl₃): -14.1 [s, broad].

4.4. Crystallographic details

Details of the structural analysis for compounds 2. 3. 5. 6. 7a. 7b and 8 are summarized in Table 4. Diffraction data were recorded with a Nonius κ -CCD four-circle diffractometer at 100(2) K for 2, 6 and 8, 150(2) K for 3, 7a and 7b and 293(2) K for 5. Graphitemonochromated Mo K α radiation (λ = 0.71073 Å) was used in all cases. The structural data was solved by direct methods (SHELXS97) and refined by full-matrix least squares against F^2 using all data (SHELXL97) [57]. Absorption corrections were carried out on all structures via the multiscan method, and applied with the SORTAV program [58]. Non-hydrogen atoms were refined with anisotropic thermal parameters, whilst all hydrogen atoms were modeled in ideal positions. In the structure of 6 the fluorine atoms exhibit partial occupancy, F(3):F(3b) = 0.65(2):0.35(2) in one independent molecule, and F(5):F(5b) = 0.56(3):0.44(3) in the other. Problems with the crystal cooling systems prevented complete data-sets being collected for compounds **3** and **6**. As a result, completeness to theta is low (92.8% for 3 and 95.0% for 6). All thermal ellipsoid plots were generated using ORTEP-3 for Windows, [59] or MERCURY [60].

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Appendix A. Supplementary data

CCDC 843214-843220 contain the supplementary crystallographic data for compounds 2, 3, 5, 6, 7a, 7b and 8. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.12.023.

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