Structure of diiodine adducts of some di- and tri-tertiaryphosphines in the solid state and in solution

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A series of ditertiaryphosphine–tetraiodine adducts $R_2P(I_2)(CH_2)_nP(I_2)R_2$ (R = Ph, n = 1–4; R = PhCH$_2$ or o-CH$_3$C$_6$H$_4$, n = 2) and two tritertiaryphosphine–hexaiodine adducts, PhP(CH$_2$CH$_2$PPh$_2$)$_2$I$_6$ and CH$_3$C(CH$_2$-PPh$_2$)$_3$I$_6$ have been prepared and characterised by ^{31}P-{H} solution NMR and Raman spectroscopy. In the case of Ph$_2$P(I$_2$)(CH$_2$)$_n$P(I$_2$)Ph$_2$ (n = 2 or 4), ^{31}P-{H} NMR magic angle spinning NMR spectroscopy has been used to investigate the nature of the compounds in the solid state. In agreement with our previous extensive studies on the monophosphine derivatives, R$_3$PI$_2$, the tetraiododiphosphine compounds Ph$_2$P(I$_2$)(CH$_2$)$_n$P(I$_2$)Ph$_2$ (n = 2 or 4) isolated from diethyl ether contain molecular four-co-ordinate phosphorus centres onto which the diiodine is bound as a linear spoke, as indicated by their ^{31}P-{H} NMR shifts obtained in CDCl$_3$ solution. Again, in agreement with our previous solution studies of the monophosphine derivatives R$_3$PI$_2$, the diphosphine–tetraiodine adducts completely ionise in CDCl$_3$ solution to produce the ionic compounds [R$_2$P(I)(CH$_2$)$_n$P(I)R$_2$]2I; the solution ^{31}P-{H} NMR shifts are very similar to analogous solution shifts previously assigned to [R$_3$PI]I. The Raman band assignable to ν(P–I) has been identified for the compounds and a further band at lower frequency has been observed and assigned to ν(I–I). Although the solid-state NMR spectra of the triphosphine–hexaiodine adducts were not recorded, a band assignable to ν(I–I) was observed in the Raman spectrum, suggesting the molecular four-co-ordinate spoke structure also prevails for these hexaiodotritertiaryphosphine compounds in the solid state. From solution ^{31}P-{H} NMR shifts these adducts also appear to ionise in CDCl$_3$ solution.

Reports concerning the reaction of di- or poly-tertiaryphosphines with dihalogens are extremely scarce and, in the few examples available, the products formed have not been well characterised. The tetrachloro adduct of bis(dimethylphosphino)ethane, Me$_2$P(Cl$_2$)CH$_2$CH$_2$P(Cl$_2$)Me$_2$[1] and the tetrabromo and tetraiodo adducts of bis(diphenylphosphino)ethane, Ph$_2$P(X$_2$)CH$_2$CH$_2$P(X$_2$)Ph$_2$ (X = Br or I)[2] have been reported. No attempt was made to isolate or characterise the products formed, which were assigned an ionic structure, [R$_2$P(X)CH$_2$-CH$_2$P(X)R$_2$]$^{2+}$2[X]$^-$ (R = Me, X = Cl; R = Ph, X = Br or I) in the solid state. Similarly, the dihalogen adducts of the polydentate phosphine C(CH$_2$PPh$_2$)$_4$ have been prepared and characterised.[3] It was concluded that these were also phosphonium salts [C{CH$_2$P(X)Ph$_2$}$_4$]$^{4+}$4[X]$^-$ (X = Cl, Br or I). The only interhalogen adduct which has been reported is the BrCl adduct of bis(dimethylphosphino)ethane[1] which was postulated to be Me$_2$P(Cl, Br)CH$_2$CH$_2$P(Cl, Br)Me$_2$ but again no characterisation of this product was reported. Clearly, the nature of di- and poly-tertiaryphosphine dihalogen adducts is very poorly understood.

Our interest in this area stems from our discovery that, when prepared in diethyl ether monophosphine–diiodine adducts, R$_3$PI$_2$, do not exhibit trigonal-bipyramidal geometry or an ionic formulation, [R$_3$PI]I, but rather than a molecular charge-transfer structure, R$_3$P–I–I, where the diiodine binds to the phosphorus centre as a linear 'spoke'.[4–6] Such an observation was unexpected and contrasts with conventional wisdom which, for example, from vibrational spectroscopic studies,[7,8] did not consider this structural modification. We have since shown that this charge-transfer structure is the norm for almost all compounds of stoichiometry R$_3$PI$_2$ prepared in diethyl ether, although we have also isolated a few compounds which, as indicated from solid-state magic angle spinning (MAS) ^{31}P-{H} NMR results, adopt the ionic structure [R$_3$PI]I [R$_3$ = (Me$_2$N)$_3$

or (CH$_2$=CHCH$_2$)$_2$Ph].[6] Additionally, we have also identified some R$_3$PI$_2$ compounds which, whilst being predominantly molecular R$_3$P–I–I, also contain a small but significant proportion of the ionic species, [R$_3$Pl]I, [R$_3$ = (p-FC$_6$H$_4$)$_2$Ph, (C$_6$H$_{11}$)-Ph$_2$, (PhCH$_2$CH$_2$)$_3$, (o-CH$_3$OC$_6$H$_4$)Ph$_2$ or (CH$_2$CHCH$_2$)Ph$_2$], again from solid-state MAS ^{31}P-{H} NMR results.[6] Considering the renewed interest in triorganophosphorus dihalogen compounds, and the fact that virtually nothing is known regarding the products formed from the reaction of diphosphine or polyphosphine compounds with dihalogens, we felt that an investigation into the diiodine adducts of these species was worthwhile. Specifically, we were interested to know if these di- and poly-tertiaryphosphine–diiodine adducts adopted the four-co-ordinate molecular spoke structure exhibited by the majority of our monophosphine diiodine compounds, R$_3$P–I–I. Additionally, we have already demonstrated the ability of R$_3$PI$_2$ compounds to oxidise crude metals at ambient temperatures to produce, in some cases, unpredictable products, e.g. AuI$_3$-(PMe$_3$)$_2$.[9] Here we report the characterisation of some diiodine adducts of di- and tri-tertiary phosphines and we will describe their utilisation as reagents for metal activation in due course. It is thus likely that the reaction of these species with metal powders will result in novel products (analogous to the reaction of R$_3$PI$_2$ with metal powders) which, considering the ubiquitous use of diphosphine ligands in co-ordination chemistry, is clearly of importance. We therefore report a comprehensive study of di- and poly-phosphine–diiodine adducts isolated from diethyl ether and have characterised these compounds by elemental analysis, ^{31}P-{H} NMR solution spectroscopy and solid-state Raman spectroscopy. In the case of the compounds Ph$_2$-P(I$_2$)(CH$_2$)$_n$P(I$_2$)Ph$_2$ (n = 2 or 4), the solid-state MAS ^{31}P-{H} NMR spectra are also reported. Previous workers have concluded that di- and poly-phosphine dihalogen compounds are ionic in both the solid state and in solution.[3]

Table 1 Analytical and spectroscopic data for the di- and tri-tertiaryphosphine diiodine adducts

| Compound[a] | Colour | Analysis[b] (%) | | | $\delta(^{31}P\text{-}\{H\})^{c}$ | Raman/cm^{-1} | |
		C	H	I		$\nu(P\text{–}X)$	$\nu(I\text{–}I)$
dppm·I$_4$	Yellow	33.6 (33.6)	2.5 (2.5)	56.1 (56.9)	48.0	181	112
dppe·I$_4$	Yellow	34.7 (34.4)	2.8 (2.7)	55.8 (56.1)	59.9	150	109
dtpe·I$_4$	Mustard	37.2 (37.4)	3.1 (3.3)	53.1 (52.8)	48.4	d	d
db$_2$pe·I$_4$	Mustard	37.1 (37.4)	2.9 (3.3)	53.2 (52.8)	59.9	141	101
dppp·I$_4$	Mustard	35.5 (35.2)	2.8 (2.8)	54.7 (55.2)	54.7	146	105
dppb·I$_4$	Mustard	35.5 (35.7)	3.0 (3.0)	54.5 (54.0)	58.0	151	111
dpen·I$_4$	Mustard	43.0 (43.2)	3.2 (2.9)	44.5 (45.8)^e	54.3	151	111
PhP(CH$_2$CH$_2$PPh$_2$)$_2$·I$_6$	Mustard	31.2 (31.5)	2.9 (2.5)	56.1 (58.0)	56.0, 55.6	148	110
CH$_3$C(CH$_2$PPh$_2$)$_3$·I$_6$	Mustard	35.9 (35.5)	2.7 (2.8)	54.7 (55.0)	45.4	147	110

^{a} dppm = Bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dtpe = 1,2-bis(di-o-tolylphosphino)ethane, dbzpe = 1,2-bis-(dibenzylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane, dpen = N,N'-bis[(diphenyl-phosphino)benzylidene]ethylenediamine. ^{b} Required values given in parentheses. ^{c} All shifts are recorded relative to 85% phosphoric acid standard. ^{d} Sample decomposed in the Raman beam. ^{e} Found (calc.): N, 2.7 (2.5)%.
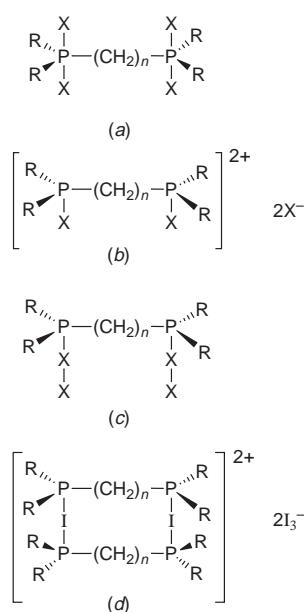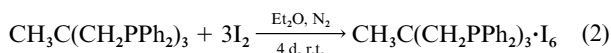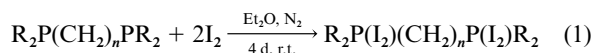

Fig. 1 Four possible structural modifications for the compounds R$_2$P(I$_2$)(CH$_2$)$_n$(I$_2$)PR$_2$; (a) trigonal bipyramidal, (b) ionic, (c) molecular charge transfer, (d) iodine-bridged dimer

Results and Discussions

The di- and tri-tertiaryphosphine–diiodine adducts were synthesised by the reaction of 1 mol of the di- or tri-phosphine species with either 2 or 3 mol of diiodine, respectively, in diethyl ether suspension, equations (1) and (2) (r.t. =

$$R_2P(CH_2)_nPR_2 + 2I_2 \xrightarrow[\text{4 d, r.t.}]{\text{Et}_2\text{O, N}_2} R_2P(I_2)(CH_2)_nP(I_2)R_2 \quad (1)$$

$$CH_3C(CH_2PPh_2)_3 + 3I_2 \xrightarrow[\text{4 d, r.t.}]{\text{Et}_2\text{O, N}_2} CH_3C(CH_2PPh_2)_3\cdot I_6 \quad (2)$$

room temperature). Analytical and spectroscopic data for the compounds are contained in Table 1.

Like their monophosphine analogues,[4–6] there are four possible structures which these compounds could adopt: the five-co-ordinate molecular species, Fig. 1(a), the ionic phosphonium species, Fig. 1(b), the molecular four-co-ordinate charge-transfer 'spoke' structure, Fig. 1(c), or a further example of an ionic species where one iodine atom is shared between each pair of phosphorus atoms, the charge being balanced by a triiodide anion, Fig. 1(d). Analogous structural behaviour exhibited in Fig. 1(d) has previously been observed in diiodine derivatives of cyclic compounds containing a nitrogen-donor atom.[10]

^{31}P-{H} NMR results in CDCl$_3$ solution

The ^{31}P-{H} NMR spectra of all the compounds in CDCl$_3$ solution, with the exception of PhP(CH$_2$CH$_2$PPh$_2$)$_2$·I$_6$, exhibit a single resonance, as expected, indicating that all the phosphorus centres in the compound are equivalent, Table 1. The spectrum of PhP(CH$_2$CH$_2$PPh$_2$)$_2$·I$_6$ contains two closely spaced peaks at δ 56.0 and 55.6 in approximately 2:1 ratio. The peak at δ 56.0 results from the two terminal phosphorus atoms, whereas the peak at δ 55.6 is due to the bridging phosphorus atom in PhP-(CH$_2$PPh$_2$)$_2$·I$_6$ and these occur in a 2:1 ratio, as expected.

None of these compounds reported here has previously been the subject of a ^{31}P-{H} NMR study. However, by comparison with their monophosphorus analogues, which have similar ^{31}P-{H} NMR values in CDCl$_3$ solution[5,6] it seems likely that all the compounds are ionic, [R$_2$P(I)(CH$_2$)$_n$P(I)R$_2$]2I$^-$ in solution. Confirmation of this was achieved by the addition of a further 2 or 3 mol equivalents of diiodine to the di- and tri-phosphine–diiodine adducts, respectively, which resulted in the formation of the corresponding ionic tetraiodo adducts, analogous to the monophosphine derivatives, [R$_3$PI]I$_3$. For example addition of 2 mol equivalents of diiodine to Ph$_2$PCH$_2$CH$_2$PPh$_2$·I$_4$ yields [Ph$_2$P(I)CH$_2$CH$_2$P(I)Ph$_2$]$^{2+}$2I$_3^-$. In all cases addition of the extra 2 or 3 mol equivalents of diiodine to the di- and tri-phosphine–diiodine adducts resulted in a pronounced darkening of the solution and bands appearing at 294 and 366 nm in the UV/VIS spectrum, diagnostic for the I$_3^-$ ion.[9] The ^{31}P-{H} NMR shifts for these ionic species containing the I$_3^-$ ion are identical to those of the parent compounds prior to the addition of extra diiodine, thus providing proof that the tetra-iododiphosphorus and hexaiodotriphosphorus compounds are ionic in CDCl$_3$ solution.

Raman spectroscopic studies

Assignment of the bands in the low frequency Raman spectra of the di- and tri-phosphine–diiodine compounds is more difficult than for their monophosphine–diiodine analogues. In each spectrum, Table 1, the dominant band appears at ca. 110 cm^{-1}, but several slightly weaker bands are also observed in the 140–185 cm^{-1} region. The analogous R$_3$PI$_2$ compounds[5,6] exhibit ν(P–I) over a wide range (132–222 cm^{-1}), the more basic tertiary phosphines exhibiting the highest ν(P–I), as expected. By comparison with the diiodomonophosphine compounds, the band appearing between 140 and 185 cm^{-1} for each compound is assigned to ν(P–I). The band appearing at ca. 110 cm^{-1} in each of the di- and tri-phosphine adducts of diiodine is tentatively assigned to ν(I–I), since bands appearing in this region for other reported[12–14] compounds which contain weak I–I bonds have also been assigned to ν(I–I). A list of the ν(P–I) and ν(I–I) stretching frequencies for the di- and tri-phosphine–diiodine compounds is given in Table 1. The structure of the

Table 2 Solid-state MAS and solution ^{31}P-{H} NMR data for mono- and di-phosphorus–diiodine adducts[a]

	$\delta(^{31}$P-{H}$)$		
Compound	Solid-state MAS[b]	Solution[c]	Ref.
Ph$_3$PI$_2$	−17.8	44.8	5
PhMe$_2$PI$_2$	−7.6	61.9	5
Me$_3$PI$_2$	−5.6	80.0	5
(Me$_2$N)$_3$PI$_2$	25.7, 26.6, 27.3	25.4	6
(CH$_2$=CHCH$_2$)$_2$PhPI$_2$	6.9	8.8	6
(p-FC$_6$H$_4$)$_2$PhPI$_2$	−22.2/42.8	44.3	6
(C$_6$H$_{11}$)PhPI$_2$	10.3/52.1	52.7	6
(PhCH$_2$CH$_2$)$_3$PI$_2$	19.9/89.7	82.0	6
(o-CH$_3$OC$_6$H$_4$)Ph$_2$PI$_2$	−28.1/42.2	46.8	6
(CH$_2$=CHCH$_2$)Ph$_2$PI$_2$	−27.7/42.2	40.4	6
Ph$_2$P(I$_2$)(CH$_2$)$_2$P(I$_2$)Ph$_2$	−14.8	59.9	This work
Ph$_2$P(I$_2$)(CH$_2$)$_4$P(I$_2$)Ph$_2$	−0.88	58.0	This work

[a] All peaks recorded relative to 85% phosphoric acid standard. [b] Peaks assignable to both a molecular, R$_3$P–I–I and an ionic, [R$_3$PI]I form, see text and ref. 6. [c] In CDCl$_3$.
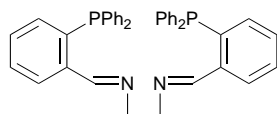

Fig. 2 Schematic representation of the structure of the ditertiaryphosphine N,N'-bis[o-(diphenylphosphino)benzylidene]ethylenediamine (dpen)
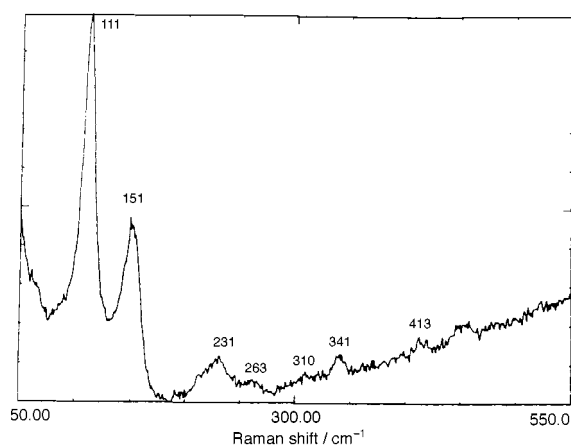

Fig. 3 Low frequency Raman spectrum of tetraiodo-N,N'-bis-[o-(diphenylphosphino)benzylidene]ethylenediamine (dpen·I$_4$)
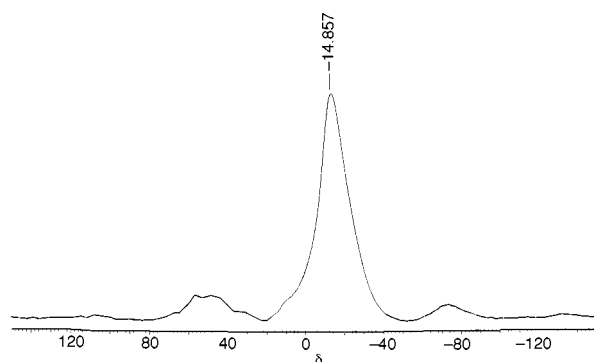

Fig. 4 Solid-state ^{31}P-{H} MAS NMR spectrum of tetraiodo-1,2-bis(diphenylphosphino)ethane (dppe·I$_4$)

ditertiaryphosphine N,N'-bis[o-(diphenylphosphino)benzylidene]ethylenediamine (dpen) is illustrated in Fig. 2. The low frequency Raman spectra of its diiodine adduct (dpen·I$_4$) is illustrated in Fig. 3.

Solid-state ^{31}P-{H} MAS NMR spectra of Ph$_2$P(I$_2$)(CH$_2$)$_n$-P(I$_2$)Ph$_2$ (n = 2 or 4)

In order to gain more information regarding the solid-state structures of diphosphine–diiodine adducts, the solid-state ^{31}P-{H} MAS NMR spectra of Ph$_2$P(I$_2$)(CH$_2$)$_n$P(I$_2$)Ph$_2$ (n = 2 or 4) were recorded and compared to the CDCl$_3$ solution values, Table 2. The solid-state ^{31}P-{H} MAS NMR spectrum of Ph$_2$P(I$_2$)CH$_2$CH$_2$P(I$_2$)Ph$_2$ is illustrated in Fig. 4. The solid-state values, δ −14.8 and −0.9 are markedly different from the solution values of δ 59.9 and 58.0 for dppe·I$_4$ and dppb·I$_4$, respectively. Moreover, the difference in these values, and the values themselves, are similar to the solid-state ^{31}P-{H} MAS NMR and solution shifts for Ph$_3$PI$_2$ of δ −17.8 and 44.8, respectively.[5] For this compound, single-crystal X-ray diffraction has unequivocally shown that it is molecular Ph$_3$P–I–I in the solid state, and we have shown that it may be considered as ionic, [Ph$_3$PI]I, in CDCl$_3$ solution. However, a recent study[15] of R$_3$PI$_2$ compounds has concluded from ^{31}P-{H} NMR and Raman spectroscopy, that these charge-transfer complexes, R$_3$P–I–I may also be considered as interaction of the strong nucleophilic I$^-$ and the electrophilic I atom in R$_3$PI$^+$. These results, therefore, overwhelmingly point to the diphosphorus–diiodine adducts as having the molecular four-co-ordinate 'spoke' structure in the solid state, Fig. 1(c), like Ph$_3$PI$_2$ and the majority of R$_3$PI$_2$ compounds. Additionally, unlike some R$_3$PI$_2$ compounds studied, the diphosphorus–diiodine adducts dppe·I$_4$ and dppb·I$_4$ are exclusively four-co-ordinate molecular species in the solid state, and no minor peak in the NMR spectrum of each is observed which could be assigned to an ionic component.

Conclusion

In agreement with previous studies on R$_3$PI$_2$ compounds, the di- and tri-phosphorus–diiodine adducts completely ionise in CDCl$_3$, as shown from solution ^{31}P-{H} NMR studies. The observation of a Raman band at $ca.$ 110 cm^{-1} for solid samples of the compounds, tentatively assigned to ν(I–I), and more importantly, the vastly different solid-state ^{31}P-{H} MAS NMR shift compared to the solution values for Ph$_2$P(I$_2$)CH$_2$CH$_2$-P(I$_2$)Ph$_2$ and Ph$_2$P(I$_2$)(CH$_2$)$_4$P(I$_2$)Ph$_2$, strongly indicate that these compounds are molecular four-co-ordinate species in the solid state. This statement is further strengthened by the fact that the solid-state ^{31}P-{H} NMR shift for Ph$_3$PI$_2$ is similar to that of the Ph$_2$P(I$_2$)(CH$_2$)$_2$P(I$_2$)Ph$_2$ and Ph$_2$P(I$_2$)(CH$_2$)$_4$P(I$_2$)Ph$_2$ adducts described here; Ph$_3$PI$_2$ has been shown to be a molecular four-co-ordinate species in the solid state by a single-crystal X-ray diffraction study. Additionally, the CDCl$_3$ solution ^{31}P-{H} NMR shift of Ph$_3$PI$_2$, known to be ionic, [Ph$_3$PI]I, is similar to the shifts of Ph$_2$P(I$_2$)(CH$_2$)$_2$P(I$_2$)Ph$_2$ and Ph$_2$P(I$_2$)-(CH$_2$)$_4$P(I$_2$)Ph$_2$ in CDCl$_3$ solution, thus indicating, in agreement with previous studies,[1–3] that ditertiaryphosphine diiodides ionise, [R$_2$P(I)(CH$_2$)$_n$P(I)R$_2$]2I, in CDCl$_3$ solution.

Experimental

All the di- and tri-tertiaryphosphine–diiodine adducts described are moisture sensitive. Therefore strictly anaerobic and anhydrous conditions must be observed for their successful synthesis. Any subsequent manipulation of the compounds was performed in a Vacuum Atmospheres HE-493 glove-box. The tritertiaryphosphines, bis(2-diphenylphosphinoethyl)phenylphosphine and tris(diphenylphosphinomethyl)ethane were obtained commercially (Aldrich) as was diiodine. All were used as received. The ditertiaryphosphines were all synthesised by the same method, the synthesis of bis(diphenylphosphino)ethane is typical. Small pieces of lithium metal (5.25 g, 0.75 mol) were added with stirring to a solution of triphenylphosphine (53.4 g, 0.2 mol) in tetrahydrofuran (THF) (300 cm^3) in a 1 1 three-necked flask equipped with a condenser. The resultant mixture was then refluxed until a deep red solution

formed and all of the lithium had been consumed. The resultant solution of lithium diphenylphosphide was cooled to 0 °C and a solution of 1,2-dichloroethane (5.94 g, 0.06 mol) in THF (20 cm³) was added dropwise. After stirring for *ca.* 30 min a change from red to straw coloured was observed. The mixture was allowed to slowly warm to room temperature and subsequently poured slowly into water (*ca.* 2 l). The organic layer was separated and dried over sodium sulfate. The THF was then removed and the resultant solid recrystallised from toluene–methanol. Yield *ca.* 70%.

Diethyl ether (BDH) was dried over sodium wire for *ca.* 1 d and subsequently distilled over CaH_2 in an inert atmosphere (N_2). All the diiodine adducts of the di- or tri-tertiaryphosphine compounds were synthesised by the direct reaction of the di- or tri-tertiaryphosphine with 2 or 3 mol equivalents of diiodine, respectively. The synthesis of $Ph_2P(I_2)CH_2CH_2P(I_2)Ph_2$ is typical: 1,2-bis(diphenylphosphino)ethane (dppe) (2.00 g, 5.02 mmol) was suspended in diethyl ether (*ca.* 100 cm³) in a rotaflo tube and subsequently diiodine (2.55 g, 10.05 mmol) was added. After *ca.* 4 d the resultant mustard coloured solid was isolated by standard Schlenk techniques and dried *in vacuo*. The reaction product was then transferred to pre-dried argon-filled ampoules which were flame sealed. Elemental analyses (Table 1) were performed by the analytical laboratory of this department. Electronic spectra were recorded on a Shimadzu UV-2101PC spectrophotometer. Raman spectra were recorded by the University of Manchester Raman service using a Coherent Innova 90 5W argon-ion laser and SPEX 1403 double monochromator (focal lengths 0.85 m) fitted with a BGCS microscope sampling attachment. The radiation was detected using a Hamamatsu R928 photomultiplier tube which was cooled to −30 °C in a Products for Research Inc. TE 177 RF-005 cooler housing. The data were processed on a SPEX DM1B data station. The ^{31}P-{H} NMR spectra for all the compounds were recorded as $CDCl_3$ solutions on a Bruker AC200 high-resolution multiprobe spectrometer relative to concentrated phosphoric acid as standard. The ^{31}P-{H} MAS solid-state NMR spectra for the compounds $Ph_2P(I_2)(CH_2)_nP(I)Ph_2$ ($n = 2$ or 4) were recorded on a Bruker ASL 500MHz high-resolution multiprobe MAS solid-state spectrometer relative to concentrated phosphoric acid as standard.

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