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

Neil Bricklebank,[a] Stephen M. Godfrey,*[,a] Charles A. McAuliffe,*[,a] Paula Deplano,[b] Marie L. Mercuri[b] and Joanne M. Sheffield[a]

[a] *Department of Chemistry University of Manchester, Institute of Science and Technology, PO Box 88, Manchester, UK M60 1QD*
[b] *Dipartimento di Chimica Inorganische, University of Cagliari, Via Ospedale 72, 09124 Cagliari, Italy*

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-$CH_3C_6H_4$, n = 2) and two tritertiaryphosphine–hexaiodine adducts, $PhP(CH_2CH_2PPh_2)_2I_6$ and $CH_3C(CH_2PPh_2)_3I_6$ have been prepared and characterised by ^{31}P-{H} solution NMR and Raman spectroscopy. In the case of $Ph_2P(I_2)(CH_2)_nP(I_2)Ph_2$ (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_3PI_2, the tetraiododiphosphine compounds $Ph_2P(I_2)(CH_2)_nP(I_2)Ph_2$ (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_3PI_2, the diphosphine–tetraiodine adducts completely ionise in $CDCl_3$ solution to produce the ionic compounds $[R_2P(I)(CH_2)_nP(I)R_2]2I$; the solution ^{31}P-{H} NMR shifts are very similar to analogous solution shifts previously assigned to $[R_3PI]I$. 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, $Me_2P(Cl_2)CH_2CH_2P(Cl_2)Me_2$[1] and the tetrabromo and tetraiodo adducts of bis(diphenylphosphino)ethane, $Ph_2P(X_2)CH_2CH_2P(X_2)Ph_2$ (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, $[R_2P(X)CH_2CH_2P(X)R_2]^{2+}2[X]^-$ (R = Me, X = Cl; R = Ph, X = Br or I) in the solid state. Similarly, the dihalogen adducts of the polydentate phosphine $C(CH_2PPh_2)_4$ have been prepared and characterised.[3] It was concluded that these were also phosphonium salts $[C\{CH_2P(X)Ph_2\}_4]^{4+}4[X]^-$ (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 $Me_2P(Cl, Br)CH_2CH_2P(Cl, Br)Me_2$ 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_3PI_2, do not exhibit trigonal-bipyramidal geometry or an ionic formulation, $[R_3PI]I$, but rather than a molecular charge-transfer structure, $R_3P–I–I$, 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_3PI_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 $[R_3PI]I$ [$R_3 = (Me_2N)_3$ or $(CH_2{=}CHCH_2)_2Ph$].[6] Additionally, we have also identified some R_3PI_2 compounds which, whilst being predominantly molecular $R_3P–I–I$, also contain a small but significant proportion of the ionic species, $[R_3PI]I$, [$R_3 = (p\text{-}FC_6H_4)_2Ph$, $(C_6H_{11})Ph_2$, $(PhCH_2CH_2)_3$, $(o\text{-}CH_3OC_6H_4)Ph_2$ or $(CH_2CHCH_2)Ph_2$], 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, $R_3P–I–I$. Additionally, we have already demonstrated the ability of R_3PI_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_3PI_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 $Ph_2P(I_2)(CH_2)_nP(I_2)Ph_2$ (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] (%) C	H	I	$\delta(^{31}P-\{H\})$[c]	Raman/cm^{-1} ν(P–X)	ν(I–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_2pe·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
$PhP(CH_2CH_2PPh_2)_2\cdot I_6$	Mustard	31.2 (31.5)	2.9 (2.5)	56.1 (58.0)	56.0, 55.6	148	110
$CH_3C(CH_2PPh_2)_3\cdot I_6$	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[(diphenylphosphino)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)%.

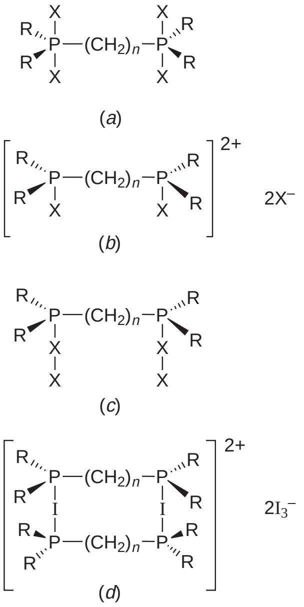

Fig. 1 Four possible structural modifications for the compounds $R_2P(I_2)(CH_2)_nP(I_2)PR_2$; (*a*) trigonal bipyramidal, (*b*) ionic, (*c*) molecular charge transfer, (*d*) iodine-bridged dimer

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

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

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

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 $PhP(CH_2CH_2PPh_2)_2\cdot I_6$, exhibit a single resonance, as expected, indicating that all the phosphorus centres in the compound are equivalent, Table 1. The spectrum of $PhP(CH_2CH_2PPh_2)_2\cdot I_6$ 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 $PhP(CH_2PPh_2)_2\cdot I_6$ 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, $[R_2P(I)(CH_2)_nP(I)R_2]2I^-$ 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, $[R_3PI]I_3$. For example addition of 2 mol equivalents of diiodine to $Ph_2PCH_2CH_2PPh_2\cdot I_4$ yields $[Ph_2P(I)CH_2CH_2P(I)Ph_2]^{2+}2I_3^-$. 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 tetraiododiphosphorus 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_3PI_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]

Compound	δ(^{31}P-{H}) Solid-state MAS[b]	Solution[c]	Ref.
Ph_3PI_2	−17.8	44.8	5
$PhMe_2PI_2$	−7.6	61.9	5
Me_3PI_2	−5.6	80.0	5
$(Me_2N)_3PI_2$	25.7, 26.6, 27.3	25.4	6
$(CH_2{=}CHCH_2)_2PhPI_2$	6.9	8.8	6
(p-$FC_6H_4)_2PhPI_2$	−22.2/42.8	44.3	6
$(C_6H_{11})PhPI_2$	10.3/52.1	52.7	6
$(PhCH_2CH_2)_3PI_2$	19.9/89.7	82.0	6
(o-$CH_3OC_6H_4)Ph_2PI_2$	−28.1/42.2	46.8	6
$(CH_2{=}CHCH_2)Ph_2PI_2$	−27.7/42.2	40.4	6
$Ph_2P(I_2)(CH_2)_2P(I_2)Ph_2$	−14.8	59.9	This work
$Ph_2P(I_2)(CH_2)_4P(I_2)Ph_2$	−0.88	58.0	This work

[a] All peaks recorded relative to 85% phosphoric acid standard. [b] Peaks assignable to both a molecular, R_3P–I–I and an ionic, $[R_3PI]I$ form, see text and ref. 6. [c] In $CDCl_3$.

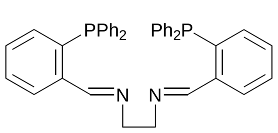

Fig. 2 Schematic representation of the structure of the ditertiary-phosphine N,N'-bis[o-(diphenylphosphino)benzylidene]ethylene-diamine (dpen)

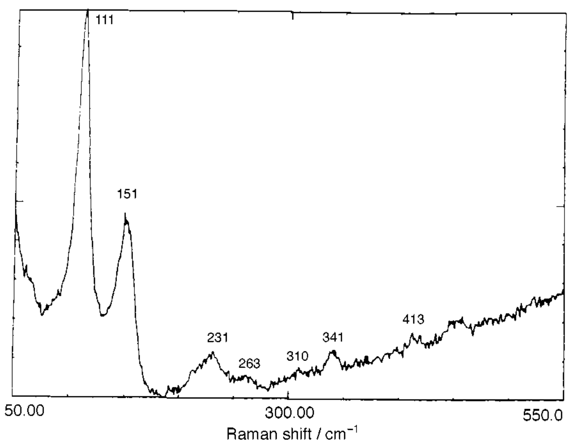

Fig. 3 Low frequency Raman spectrum of tetraiodo-N,N'-bis-[o-(diphenylphosphino)benzylidene]ethylenediamine (dpen·I_4)

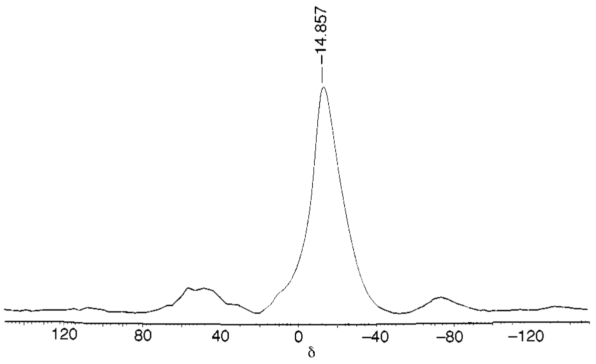

Fig. 4 Solid-state ^{31}P-{H} MAS NMR spectrum of tetraiodo-1,2-bis(diphenylphosphino)ethane (dppe·I_4)

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 $Ph_2P(I_2)(CH_2)_nP(I_2)Ph_2$ (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 $Ph_2P(I_2)(CH_2)_nP(I_2)Ph_2$ (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 $Ph_2P(I_2)CH_2CH_2P(I_2)Ph_2$ 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_3PI_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_3P–I–I in the solid state, and we have shown that it may be considered as ionic, $[Ph_3PI]I$, in $CDCl_3$ solution. However, a recent study[15] of R_3PI_2 compounds has concluded from ^{31}P-{H} NMR and Raman spectroscopy, that these charge-transfer complexes, R_3P–I–I may also be considered as interaction of the strong nucleophilic I^- and the electrophilic I atom in R_3PI^+. 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_3PI_2 and the majority of R_3PI_2 compounds. Additionally, unlike some R_3PI_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_3PI_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 $Ph_2P(I_2)CH_2CH_2P(I_2)Ph_2$ and $Ph_2P(I_2)(CH_2)_4P(I_2)Ph_2$, 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_3PI_2 is similar to that of the $Ph_2P(I_2)(CH_2)_2P(I_2)Ph_2$ and $Ph_2P(I_2)(CH_2)_4P(I_2)Ph_2$ adducts described here; Ph_3PI_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_3PI_2, known to be ionic, $[Ph_3PI]I$, is similar to the shifts of $Ph_2P(I_2)(CH_2)_2P(I_2)Ph_2$ and $Ph_2P(I_2)(CH_2)_4P(I_2)Ph_2$ in $CDCl_3$ solution, thus indicating, in agreement with previous studies,[1–3] that ditertiaryphosphine diiodides ionise, $[R_2P(I)(CH_2)_nP(I)R_2]2I$, 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 l 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 cm^3) 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 cm^3) 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 $^{31}P\text{-}\{H\}$ 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 $^{31}P\text{-}\{H\}$ 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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References

1 B. M. Gladstein, V. G. Noskov and L. Z. Soborovskii, *Zh. Obshch. Khim.*, 1967, **37**, 2513.
2 S. P. Schmidt and D. W. Brooks, *Tetrahedron Lett.*, 1987, **28**, 767.
3 J. Ellermann and D. Schirmacher, *Chem. Ber.*, 1969, **102**, 289.
4 S. M. Godfrey, D. G. Kelly, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and S. M. Watson, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 1163.
5 N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and P. J. Kobryn, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 101.
6 N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe, R. G. Pritchard and J. M. Moreno, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2421.
7 J. Goubeau and R. Baumigartner, *Z. Elektrochem.*, 1960, **64**, 598.
8 F. W. Parrett, *Spectrochim. Acta*, *Part A*, 1969, **26**, 1271.
9 S. M. Godfrey, N. Ho, C. A. McAuliffe and R. G. Pritchard, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 2343.
10 H. Pritzkow, *Acta Crystallogr.*, *Sect. B*, 1975, **31**, 1505.
11 A. I. Popov and R. F. Svenson, *J. Am. Chem. Soc.*, 1955, **77**, 3724.
12 F. W. Parrett and N. J. Naylor, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2458.
13 E. M. Nour, L. H. Chen and J. Lane, *J. Phys. Chem.*, 1986, **90**, 2481.
14 R. Poli, J. C. Gordon, R. K. Khanna and P. E. Fanwich, *Inorg. Chem.*, 1992, **31**, 3165.
15 P. Deplano, S. M. Godfrey, F. Isaia, C. A. McAuliffe, M. L. Mercuri and E. F. Trogu, *Chem. Ber.*, 1997, **130**, 299.

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