DALTON
FULL PAPER

The reaction of tertiary aryl phosphites with diiodine at ambient temperatures; structural characterisation of the tertiary phosphite tetraiodides $(PhO)_3PI_4$, $(4\text{-}MeC_6H_4O)_3PI_4$ and $(2,4\text{-}Bu^t_2C_6H_3O)_3PI_4$

Stephen M. Godfrey, Charles A. McAuliffe, Andrew T. Peaker and Robin G. Pritchard

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester, UK M60 1QD. E-mail: stephen.m.godfrey@umist.ac.uk

Received 16th November 1999, Accepted 25th February 2000
Published on the Web 30th March 2000

The reaction of the tertiary phosphites $(RO)_3P$ (R = Ph, $4\text{-}MeC_6H_4$, $4\text{-}Bu^tC_6H_4$, $2,4\text{-}Bu^t_2C_6H_3$, $2,6\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$ or $2\text{-}PhC_6H_4$) with one and two mole equivalents of diiodine has been investigated. In all cases the tetraiodide compounds $(RO)_3PI_4$ were isolated regardless of the stoichiometry employed. The three compounds $(RO)_3PI_4$ (R = Ph, $4\text{-}MeC_6H_4$ or $2,4\text{-}Bu^t_2C_6H_3$) have been crystallographically characterised for comparative purposes and represent the first examples of crystal structures for compounds of this formula. The structural characterisation of these compounds illustrates the structural dependence of $(RO)_3PI_4$ compounds on R. For $(RO)_3PI_4$ (R = Ph or $2,4\text{-}Bu^t_2C_6H_3$) the compounds exist as discrete molecular species whereas, for R = $4\text{-}MeC_6H_4$ the triiodide fragments of discrete molecules link *via* long-range I–I interactions to form a dimer. Additionally, *d*(I–I) for the $(RO)_3PI$ and I_3 fragments is sensitive to R, being 3.227(1) Å for $(2,4\text{-}Bu^t_2C_6H_3O)_3PI_4$ and 3.3888(7) Å for $(PhO)_3PI_4$. In contrast to the analogous R_3PI_4 compounds, which show great variation in δ in their $^{31}P\text{-}\{^1H\}$ NMR spectra depending on R, the $(RO)_3PI_4$ compounds described all exhibit quite similar δ values irrespective of R.

Introduction

The reaction of tertiary phosphites with diiodine has received only very limited attention; indeed, there have been no literature citations for the past forty years. In 1956 Rydon and Tonge[1] reported the formation of two triaryl phosphite diiodides, $(ArO)_3PI_2$, which were used as iodination compounds for alcohols. From conductimetric titrations the reaction of these triaryl phosphites with diiodine in light petroleum (bp 60–80 °C) at RT appeared to proceed *via* two steps, eqns. (1) and (2) (where

$$2\,(RO)_3P + I_2 \longrightarrow (RO)_4PI + (RO)_2PI \qquad (1)$$

$$(RO)_4PI + (RO)_2PI + I_2 \longrightarrow 2\,(RO)_3PI_2 \qquad (2)$$

R = Ph or $2,6\text{-}Me_2C_6H_3$). The same workers also investigated the reaction of triphenyl phosphite with diiodine at elevated temperatures (60 °C).[1] At this temperature, reaction (3) was

$$2\,(PhO)_3PI_2 \longrightarrow [(PhO)_3PI]I_3 + (PhO)_3P \qquad (3)$$

postulated to occur, *i.e.* 'free' triphenyl phosphite and the tetraiodide $[(PhO)_3PI]I_3$ were produced; the latter was assigned an ionic structure. The existence of this tetraiodide had previously been reported by Forsman and Lipkin[2] in 1953 along with the enneaiodide, $(PhO)_3PI_9$. Both species were assumed to contain identical cations, $[(PhO)_3PI]^+$, with the tetraiodide containing a triiodide anion and $(PhO)_3PI_9$ containing equal quantities of heptaiodide and enneaiodide anions, I_7^- and I_9^-.

We have reported the reaction of tertiary phosphines with diiodine and have found that, in the case of the 1 : 1 reaction, the CT complexes $R_3PI\text{–}I$ result.[3] The *d*(I–I) for such complexes is dependent on R; for example, *d*(I–I) for Ph_3PI_2 is 3.142(2) Å whereas for $PhMe_2PI_2$ *d*(I–I) is 3.409(2) Å. The reaction of tertiary phosphines with two mole equivalents of diiodine has also been investigated, being first reported by Gridunova *et al.*[4] These workers described the structure of R_3PI_4 (R = ferrocenyl) and found a weak cation–anion interaction between the iodine atom of the cation and an iodine atom of the triiodide anion [3.736(1) Å]. In 1987, Cotton and Kibala[5] described the products obtained from the reaction of two mole equivalents of diiodine with triphenylphosphine and crystallographically characterised two products. The first, $[(Ph_3PI)_2I_3]I_3$, reveals parallel zigzag chains of $[(Ph_3PI)_2I_3]^+$ cations sandwiched between layers of I_3^- anions. The second, $[Ph_3PI]I_3$, reveals a strong interaction between the $[Ph_3PI]^+$ cation and the triiodide anion [*d*(I–I) = 3.551(1) Å]. The triiodide anions further link into a polymeric ribbon *via* weak I–I interactions [*d*(I–I) = 3.741(1) Å]. Very recently, we have reported[6] two further crystallographically characterised compounds of formula R_3PI_4, $Pr^i_3PI_4$ and $(Pr^n_2N)_3PI_4$, and have found that these display subtly different structural arrangements compared to those of the R_3PI_4 compounds described previously: $Pr^i_3PI_4$ exists as a single $[Pr^i_3PI]^+$ cation interacting with both the terminal iodine atoms of an I_3^- anion to produce the cation $[(Pr^i_3PI)_2I_3]^+$, the charge being balanced by a discrete I_3^- anion; in contrast, $(Pr^n_2N)_3PI_4$ is essentially ionic, $[(Pr^n_2N)_3PI]I_3$.

In view of the structural diversity exhibited by tertiary phosphine di- and tetra-iodide compounds and the fact that there is a paucity of data concerning the analogous tertiary phosphite di- and tetra-iodide compounds, we decided to undertake a comprehensive study of the reaction of a variety of tertiary phosphites with one and two mole equivalents of diiodine. The aim of the present study was therefore to synthesize and characterise structurally new and existing triaryl phosphite di- and tetra-iodide compounds and to investigate whether the compounds formed are R group dependent. Such a study will enable a comparison to be drawn between the products formed from the reaction of diiodine with triaryl phosphites and their tertiary phosphine analogues.

DOI: 10.1039/a909057f

Table 1 Analytical and spectroscopic data for the compounds $(RO)_3PI_4$ (R = Ph, 4-MeC_6H_4, 4-$Bu^tC_6H_4$, 2,4-$Bu^t_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$ or 2-PhC_6H_4)

Compound	Colour	mp/°C	Found (% Calc.)[a] C	H	I	^{31}P-{^1H} NMR, δ[b]
$(PhO)_3PI_4$	Red/brown	79(1)	26.4 (26.5)	1.8 (1.9)	62.1 (62.2)	−4.8
$(4\text{-}MeC_6H_4O)_3PI_4$	Brown	86(1)	29.3 (29.2)	2.5 (2.5)	59.4 (59.0)	−4.4
$(4\text{-}Bu^tC_6H_4O)_3PI_4$	Dark red	89(1)	36.5 (34.8)	4.0 (3.6)	51.5 (52.7)	−4.0
$(2,4\text{-}Bu^t_2C_6H_3O)_3PI_4$	Brown	76(1)	43.6 (44.3)	5.5 (5.5)	43.9 (42.1)	−9.2
$(2,6\text{-}Me_2C_6H_3O)_3PI_4$	Red/brown	93(1)	32.0 (33.5)	3.0 (3.0)	56.3 (55.4)	1.8
$(2,4,6\text{-}Me_3C_6H_2O)_3PI_4$	Red/brown	117(1)	34.3 (33.0)	3.5 (3.2)	53.8 (54.9)	3.0
$(2\text{-}PhC_6H_4O)_3PI_4$	Dark red	98(1)	41.3 (39.5)	2.6 (2.4)	48.5 (48.2)	−5.4

[a] For some of the compounds the values are a little out with respect to the theoretical values due to the extreme moisture sensitivity, which meant that perfect analyses were difficult to obtain despite numerous attempts. [b] All shifts recorded in $CDCl_3$ solution relative to concentrated phosphoric acid as standard.

Results and discussion

All attempts to synthesize tertiary phosphite diiodine compounds, $(RO)_3PI_2$, in diethyl ether solution at RT were unsuccessful; equimolar quantities of the tetraiodide, $(RO)_3PI_4$, and free tertiary phosphite being observed in each case, eqn. (4)

$$2\,(RO)_3P + 2\,I_2 \longrightarrow (RO)_3PI_4 + (RO)_3P \qquad (4)$$

(R = Ph, 4-MeC_6H_4, 4-$Bu^tC_6H_4$, 2,4-$Bu^t_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$ or 2-PhC_6H_4).

Analytical data of the dark red solids produced from each reaction indicated the formation of the tetraiodides, $(RO)_3PI_4$. The existence of free triaryl phosphite was confirmed using ^{31}P-{^1H} NMR spectroscopy. These observations would appear to mirror the results of Rydon and Tonge at 60 °C.[1] However, in contrast to Rydon's observation at RT (*i.e.* the proposed formation of $(PhO)_3PI_2$), in our hands no evidence for the formation of a diiodide $(RO)_3PI_2$ was noted in any of the reactions performed during this study. The same reactions were also performed in a 2 : 1 diiodine : triaryl phosphite stoichiometric ratio. As expected, the same tertiary phosphite tetraiodide compounds, $(RO)_3PI_4$, were obtained in quantitative yield. All of the tertiary phosphite tetraiodide compounds described are acutely air and moisture sensitive (far more so than the analogous R_3PI_4), decomposing to black oils in a matter of minutes upon exposure to the atmosphere; consequently, strictly anaerobic and anhydrous conditions were adhered to. Only one of the compounds described in Table 1, $(PhO)_3PI_4$, has been reported previously.[1,2]

No compound containing a tertiary phosphite and iodine has previously been crystallographically characterised. We were therefore interested in crystallographically characterising $(PhO)_3PI_4$, to compare to the two polymorphs of Ph_3PI_4 described by Cotton and Kibala[5] and other $(RO)_3PI_4$ compounds to determine the effect of R on the solid state structure.

Crystals of $(PhO)_3PI_4$ were prepared by recrystallisation of the bulk solid in diethyl ether, appearing in the reaction vessel on standing in a refrigerator at *ca.* 2 °C after 5 d. They were plunged into an inert oil and a suitable one was chosen for single crystal X-ray diffraction after examination under the microscope. The crystal structure of $(PhO)_3PI_4$ **1** is illustrated in Fig. 1 and selected bond lengths and angles are displayed in Table 2. Compound **1** was previously assigned an ionic structure, $[(PhO)_3PI]I_3$; however, Fig. 1 shows that it is actually a molecular species in the solid state and is similar in structure to one polymorph of Ph_3PI_4 previously described.[5] The *d*(I–I) **1**, 3.3888(7) Å, is significantly shorter than that exhibited by Ph_3PI_4, 3.55(1) Å. Unlike that molecule, which exhibits long range I–I interactions [*d*(I–I) = 3.741(1) Å] between individual I_3^- anions linking the structure into a polymer, **1** is a discrete molecular entity with no long I–I contacts. The triiodide fragment of **1** has distinctly different I–I distances, 3.0485(7) and 2.7992(7) Å. The difference between these bond lengths, 0.2493(7) Å, is large but shorter than the largest known: 0.322(6) Å in NH_4I_3.[7] The asymmetry in I–I bond lengths exhibited by **1** is easily explained by the close approach of the $(PhO)_3PI$ fragment to one iodine atom in the triiodide fragment. This causes polarisation of the triiodide leading to one short and one long iodine–iodine bond. The triiodide fragment is virtually linear, 177.52(2)°, and is very similar to that exhibited by Ph_3PI_4, 177.23(4)°.[5]

Table 2 Selected bond lengths (Å) and angles (°) for $(RO)_3PI_4$ (R = Ph for **1**, 4-MeC_6H_4 for **2** and 2,4-$Bu^t_2C_6H_3$ for **3**)

	1	**2**	**3**
P(1)–I(1)	2.366(2)	2.361(3)	2.390(5)
I(1)–I(2)	3.3888(7)	3.345(1)	3.227(1)
I(2)–I(3)	3.0485(7)	2.9863(12)	3.033(2)
I(3)–I(4)	2.7992(7)	2.8726(13)	2.819(3)
P(1)–O(1)	1.550(6)	1.536(7)	1.530(12)
P(1)–O(2)	1.566(6)	1.536(8)	1.552(14)
P(1)–O(3)	1.578(5)	1.551(8)	1.552(12)
I(1)–I(2)–I(3)	170.5(3)	170.79(3)	170.77(8)
P(1)–I(1)–I(2)	125.10(3)	86.59(4)	80.77(6)
I(2)–I(3)–I(4)	177.52(2)	177.58(4)	176.14(8)
I(1)–P(1)–O(1)	111.3(2)	111.7(3)	107.0(5)

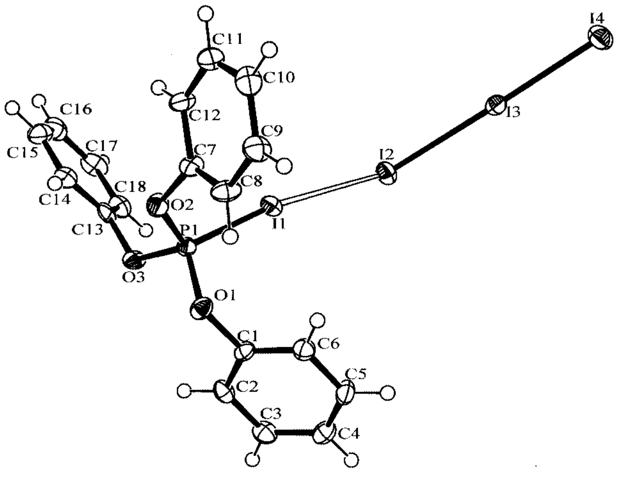

Fig. 1 The molecular structure of compound **1**.

In order to investigate the effect of R on $(RO)_3PI_4$ compounds, we decided crystallographically to characterise two further examples of compounds with this formula, where R = 4-MeC_6H_4 and 2,4-$Bu^t_2C_6H_3$. Crystals of both compounds were prepared in an identical manner to that described for $(PhO)_3PI_4$. The crystal structure of $(4\text{-}MeC_6H_4O)_3PI_4$ **2** is illustrated in Fig. 2. Selected bond lengths and angles are displayed in Table 2. As expected, **2** has a similar structure to that of **1**,

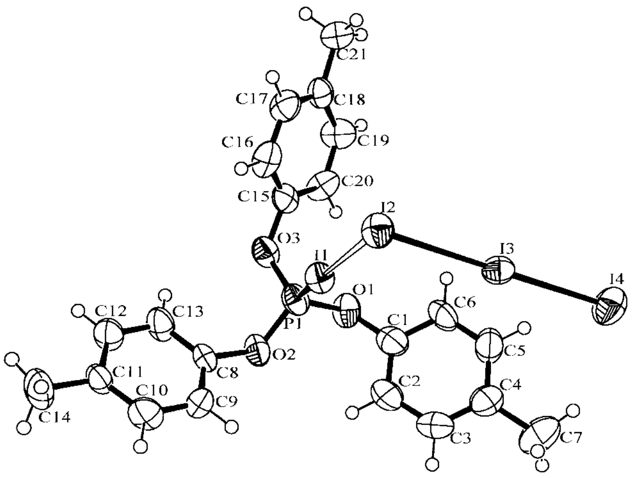

Fig. 2 The molecular structure of compound **2**.

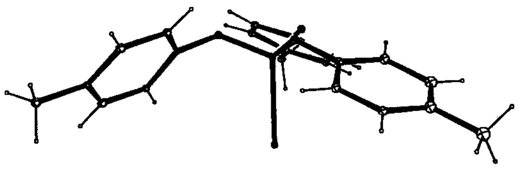

Fig. 3 The 'umbrella' configuration of the (4-$MeC_6H_4O)_3PI$ fragment (atoms are represented by ellipsoids at 5% probability level).

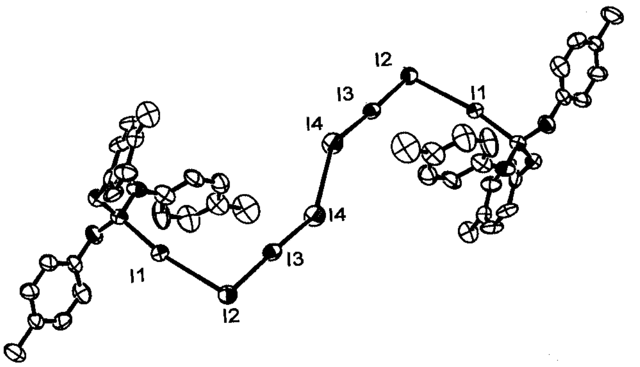

Fig. 4 The linking of two molecules of compound **2** through a weak I–I bond (3.521(2) Å) to form the dinuclear compound [(4-$MeC_6H_4O)_3PI_4]_2$ (non-iodine atoms are unlabelled and hydrogen atoms are omitted for clarity).

once again being a molecular species in the solid state. The I–I bond between the (4-$MeC_6H_4O)_3PI$ fragment and the I_3 fragment is 3.345(1) Å, very similar to that exhibited by **1** (3.3888(7) Å). The phosphorus atom adopts a near-perfect tetrahedral geometry with the aryl rings orientating to point towards the iodine atom in an umbrella configuration, Fig. 3. The reason for this is probably due to an electrostatic interaction between P–$I^{\delta+}$ and the π electrons of the aromatic rings. A major difference between **1** and **2** is the P–I–I bond angle: 125.10(3)° for the former and 86.59(4)° for the latter. The asymmetry in *d*(I–I) for the I_3 fragment of **2** is significantly smaller than that exhibited by **1**, the *d*(I–I) distances for **2** being 2.9863(12) and 2.8276(13) Å. This phenomenon would appear to suggest that the I_3 fragment in this molecule is less polarised than in **1**. However, in contrast to **1** (and in common with Ph_3PI_4) there is significant interaction between the I_3 fragments of adjacent molecules of **2**, *d*(I–I) = 3.521(2) Å, Fig. 4.

As previously mentioned, we also prepared crystals of (2,4-$Bu^t_2C_6H_3O)_3PI_4$ **3** for comparative purposes. The crystal structure of this compound is illustrated in Fig. 5. Selected bond lengths and angles are displayed in Table 2. The *d*(I–I) for the iodine atom of (2,4-$Bu^t_2C_6H_3O)_3PI$ and the I_3 moiety, 3.227(1) Å, is well within the range quoted for molecular CT complexes of formula R_3PI_4[3] and this indicates that the compound is best described as molecular rather than ionic. In common with **1**, but in contrast to **2**, **3** is a discrete molecule with no long-range iodine–iodine interactions. This is reflected in *d*(I–I) for the triiodide fragment, the bond lengths being distinctly asymmetric (3.033(2) and 2.819(3) Å).

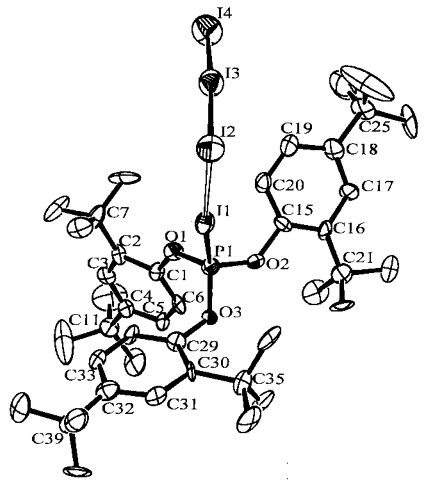

Fig. 5 The molecular structure of compound **3** (hydrogen atoms are omitted for clarity).

$^{31}P-\{^1H\}$ NMR studies

In contrast to the analogous R_3PI_2 and R_3PI_4 compounds, which show a significant difference in δ depending on the R groups present on the tertiary phosphine (*e.g.* δ 9.1 for $Bu^i_3PI_4$, 87.9 for $Pr^n_3PI_4$), little variation is seen in the $^{31}P-\{^1H\}$ NMR spectra of $(RO)_3PI_4$ compounds. The δ values for compounds of that formula (described within) range from −9.2 to 3.0. This is as expected since the R groups are not bound directly to the phosphorus atom in $(RO)_3PI_4$ but are in R_3PI_4.

Conclusion

The first comprehensive study of the reaction of tertiary phosphites with diiodine is described. In contrast to earlier reports, in our hands no evidence was noted for the formation of the diiodide compound $(RO)_3PI_2$. In all cases the tetraiodides resulted, *i.e.* $(RO)_3PI_4$. In common with the analogous compounds R_3PI_4,[3] the solid state structures of $(RO)_3PI_4$ are sensitive to R. For example, **1** and **3** are discrete molecular species whereas **2** is linked *via* long-range I–I contacts into a dimeric species, similar to one polymorph of Ph_3PI_4. Although all of the compounds described are molecular, *d*(I–I) for the $(RO)_3PI$ and I_3 fragments is sensitive to R, being 3.227(1) Å for **3** and 3.3888(7) Å for **1**. In other words, *d*(I–I) increases with increasing basicity of the tertiary phosphite. A concurrent decrease in *d*(P–I) is also noted. These observations mirror those seen for analogous R_3PI_4 compounds. Also observed with the increasing basicity of the tertiary phosphite is a decrease in the angle between the two linear sections of the molecule, *i.e.* the P–I bond of the $(RO)_3PI$ fragment and the triiodide fragment at the apex, Table 2.

Experimental

All of the compounds reported are very moisture sensitive, consequently strictly anaerobic and anhydrous conditions were employed for their synthesis. Any subsequent manipulations were carried out inside a Vacuum Atmospheres HE-493 glove box. Diethyl ether (BDH) was dried by standing over sodium wire for *ca.* 1 d, subsequently refluxed over CaH_2 in an inert atmosphere and distilled directly into the reaction vessel. Tertiary phosphites were either obtained commercially

Table 3 Crystal data and details of refinement for compounds **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{18}H_{15}I_4O_3P$	$C_{42}H_{42}I_8O_6P_2$	$C_{42}H_{63}I_4O_3P$
Formula weight	817.87	1719.90	1154.49
T/K	146(2)	203(2)	203(2)
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$C2/c$	$P2_12_12_1$
a/Å	9.3386(10)	10.594(5)	11.763(10)
b/Å	10.000(2)	18.425(6)	19.565(2)
c/Å	24.168(2)	28.120(5)	21.003(2)
β/°		98.65(3)	
V/Å^3	2257.0(3)	5427(3)	4833.9(8)
Z	4	4	4
D_c/Mg m^{-3}	2.407	2.105	1.586
No. reflections	2244	5073	4704
No. observations	2244	5073	4704
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0214, 0.0848	0.0533, 0.0683	0.0646, 0.1379
(all data)	0.0224, 0.0874	0.1366, 0.0880	0.1247, 0.1681

[$(PhO)_3P$, $(4\text{-}MeC_6H_4O)_3P$, $(2\text{-}PhC_6H_4O)_3P$ and $(2,4\text{-}Bu^t{}_2\text{-}C_6H_3O)_3P$ (Lancaster)] or synthesized according to the method published elsewhere.[8] Diiodine was obtained commercially (Aldrich) and used as received. All of the reactions performed resulted in the isolation of $(RO)_3PI_4$ regardless of the stoichiometry (either 1 : 1 or 1 : 2 $(RO)_3P : I_2$). The synthesis of $(PhO)_3PI_4$ **1** is typical. Triphenyl phosphite (2.00 g, 6.45 mmol) was dissolved in Et_2O (*ca.* 75 cm^3) and subsequently diiodine (3.28 g, 12.9 mmol) added. After *ca.* 2 d the resultant red-brown solid was isolated using standard Schlenk techniques. The material was then transferred to pre-dried argon-filled ampoules, which were flame-sealed.

Elemental analyses were performed by the analytical laboratory of this department and the results are presented in Table 1. The $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AC200 high-resolution multiprobe spectrometer relative to concentrated phosphoric acid as standard.

Crystallography

Crystals of $(RO)_3PI_4$ (R = Ph in **1**, $4\text{-}MeC_6H_4$ in **2** and $2,4\text{-}Bu^t{}_2C_6H_3$ in **3**) were submerged in an inert oil under anaerobic conditions and suitable ones were chosen by examination under a microscope. Each crystal, with its protective coating of oil, was then mounted on a glass fibre, transferred to the diffractometer and cooled to *ca.* 203(2) K in the cold gas stream derived from liquid nitrogen. All measurements were performed on a Nonius MAC3 CAD4 diffractometer employing graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and ω–2θ scans. All three structures were solved by direct methods. Unit cell dimensions were derived from the setting angles of 25 accurately centred reflections. Lorentz-polarisation corrections were applied. Details of the X-ray measurements and subsequent structure determinations are presented in Table 3. Hydrogen atoms were confined to chemically reasonable positions. Neutral atom scattering factors were taken from ref. 9, anomalous dispersion effects from ref. 10. All calculations were performed using SHELXS 86[11] and SHELXL 93[12] crystallographic software packages.

CCDC reference number 186/1875.

See http://www.rsc.org/suppdata/dt/a9/a909057f/ for crystallographic files in .cif format.

Acknowledgements

We are grateful to the EPSRC for a research studentship to A. T. P.

References

1 H. N. Rydon and B. C. Tonge, *J. Chem. Soc.*, 1956, 3043.
2 J. P. Forsman and D. Lipkin, *J. Am. Chem. Soc.*, 1953, **75**, 3145.
3 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; 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; 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.
4 G. V. Gridunova, V. E. Shklover, Y. T. Struchkov, V. D. Vil'Chevskaya, N. L. Podobedova and A. J. Krylova, *J. Organomet. Chem.*, 1982, **238**, 297.
5 F. A. Cotton and P. A. Kibala, *J. Am. Chem. Soc.*, 1987, **109**, 3308.
6 W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, J. M. Sheffield and G. M. Thompson, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2795.
7 G. H. Cheeseman and A. I. T. Finney, *Acta Crystallogr., Sect. B*, 1972, **28**, 1331.
8 S. M. Godfrey, A. T. Peaker and R. G. Pritchard, *Acta Crystallogr., Sect. C*, submitted for publication.
9 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2A.
10 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.3.1.
11 G. M. Sheldrick, SHELXS 86, in *Crystallographic Computing 3*, ed. G. M. Sheldrick, Oxford University Press, 1985, p. 175.
12 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.