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The reaction of triorganophosphorus diiodides, R_3PI_2, with zinc metal powder; dependency of product on R; the X-ray crystal structures of dimeric $\{ZnI_2[P(NMe_2)_3]\}_2$ and monomeric $ZnI_2(PPh_2Me)_2$

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Abstract

Seventeen zinc(II) tertiary phosphine complexes have been synthesised directly from elemental zinc by reaction with the reagents R_3PI_2. The complexes have been characterised by elemental analysis and $^{31}P\{H\}$ NMR spectroscopy. The present work represents the first comprehensive study of a wide variety of zinc(II) tertiary phosphine complexes containing different parent tertiary phosphines and the majority of the complexes are reported for the first time. In most cases, reaction of R_3PI_2 with zinc metal powder in diethyl ether in a 1:1 stoichiometric ratio, produces the dimeric complexes $[ZnI_2(PR_3)]_2$, analogous to the previously reported $[ZnI_2(PEt_3)]_2$. In contrast, reaction of R_3PI_2 ($R = Ph_3$, Ph_2Et, Ph_2Me) with zinc metal powder produces the monomeric bis complexes $ZnI_2(PR_3)_2$ and an equimolar quantity of zinc(II) iodide, the latter product being identified by X-ray powder diffraction. The X-ray crystal structures of dimeric $\{ZnI_2[P(NMe_2)_3]\}_2$ and monomeric $ZnI_2(PPh_2Me)_2$ are also described. The formation of the bis complexes $ZnI_2(PR_3)_2$ ($R_3 = Ph_3$, Ph_2Me, Ph_2Et) is surprising and cannot be due to steric factors since complexes containing less bulky tertiary phosphines are shown to be dimeric and the adoption of a monomeric zinc(II) centre increases steric crowding at the metal atom. The existence of the bis complexes is therefore reasoned to be due to favourable Π–Π interactions on the ligands and crystal packing forces. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Zinc complexes; Phosphine complexes

1. Introduction

In contrast to that of divalent cadmium and mercury, very little work has been carried out into the coordination chemistry of zinc(II) with Group 15 donors. Although such complexes containing tertiary phosphine ligands have been known for nearly 50 years [1,2], their precise nature remains uncertain and has proved controversial [3,4]. Nonetheless, in the case of the coordination compounds formed between zinc(II) halides and tertiary phosphines, two structural types have been identified, viz. the bis-phosphine complexes, ZnX_2L_2, and the mono-ligand complexes, $[ZnX_2L]_2$. It has been believed that the steric demands of the tertiary phosphine may be fundamental in determining which structure is formed, i.e. with less sterically demanding tertiary phosphine ligands, the bis-phosphine complex would be favoured, whereas bulky tertiary phosphines would prefer the mono-ligand complex, thus relieving steric crowding at the zinc(II) centre. Such a theory seems reasonable and is in agreement with the cone-angle theory first expounded by Tolman [5].

Thus, Fergusson and Heveldt [6] prepared the bis-phosphine complexes $ZnX_2(R_3P)_2$ ($R_3 = Et_3$ or Et_2Ph; $X = Cl$, Br or I) and spectroscopically characterised them as monomeric tetrahedral species. With the bulky tricyclohexylphosphine, Moers and Langhout [7] reported both $ZnX_2(Cy_3P)_2$ and $ZnX_2(Cy_3P)$ ($X = Cl$, Br, I or NCS), concluding that the latter were dimeric. However, whilst Goel and Ogini [8] were able to pre-

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pare $ZnX_2(Cy_3P)$, attempts to prepare the bis-phosphine complex $ZnX_2(Cy_3P)_2$ claimed by Moers and Langhout [7] resulted in the isolation of the mixed phosphine–phosphine oxide complex $ZnX_2(Cy_3P)(Cy_3PO)$. These results seem to confirm Goel and Ogini's earlier conclusion [9] that bulky phosphines such as tri(tertiarybutyl)phosphine will only form mono-ligand complexes with zinc(II) halides.

In 1992, we reported, in a preliminary communication [10], the reaction of R_3PI_2 ($R = Me, Et, Pr^n, Bu^n$) with zinc metal powder in diethyl ether solution to yield the unexpected mono-ligand complexes $[ZnI_2(R_3P)]_2$ (Eq. (1)) [10].

$$R_3PI_2 + Zn \xrightarrow[\text{ca. 1 h, r.t.}]{\text{EtO}_2,\ N_2} [ZnI_2(R_3P)]_2 \qquad (1)$$

($R = Me, Et, Pr^n, Bu^n$)

The mono-ligand complex $[ZnI_2(PEt_3)]_2$ was structurally characterised by single crystal X-ray diffraction, and was the first simple zinc(II) tertiary phosphine complex to be crystallographically characterised. The fact that this complex contains a tertiary phosphine ligand of low steric requirements and has a mono-ligand stoichiometry casts further doubt on the existence of the bis-phosphine complexes $ZnX_2(R_3P)_2$, and suggests that previous reports of such complexes are incorrect, and may represent the mixed ligand species $ZnX_2(R_3P)(R_3PO)$ as originally proposed by Goel and Ogini [8]. However, in 1996 Cotton and Schmidt [11] characterised the monomeric tetrahedral complex $ZnCl_2(PMe_3)_2$, clearly establishing that monomeric zinc(II) complexes can be prepared if ligands of sufficiently small steric requirements are employed. In addition, the same workers also crystallographically characterised $Zn_2Cl_4(Me_3P)_3$, in which a cationic $(Me_3P)_3Zn^{2+}$ moiety is linked via a Cl bridge to an anionic $ZnCl_3^-$ moiety.

We have investigated the reaction of R_3PI_2 compounds with a number of unactivated course grain metal powders and have produced a variety of unanticipated metal complexes. The tremendous oxidising powder of our R_3PI_2 reagents is illustrated by the ability of Me_3PI_2 to oxidise cobalt [12–14], nickel [15] and even gold [16] powders directly to the +3 oxidation state in a single reaction step.

Additionally, our new synthetic procedure of reacting R_3PI_2 with metal powders has led to unusual and, in some cases, previously unobtainable metal complexes: for example, $CoI_3(SbPh_3)_2$ [17], $In_2I_4(PPr^n_3)_2$ [18] and $AuI_3(PMe_3)_2$ [16]. Recently we have investigated [19] the reaction of the related arsenic-containing reagents R_3AsI_2 ($R = Et, Me$) with zinc metal powder and found that where $R = Et$, a dimeric complex, $[ZnI_2(AsEt_3)]_2$, results, whereas, where $R = Me$, a monomeric complex results, $ZnI_2(AsMe_3)_2$. The reasons for this are assumed to be steric [19].

We now report a comprehensive study of the reaction of R_3PI_2 ($R_3 = Ph_3$, substituted triaryl, mixed aryl/alkyl, trialkyl) with zinc metal powder. The motivation for the present study is for the following reasons: firstly, no comprehensive study of zinc(II) complexes containing a wide variety of tertiary phosphine ligands has so far been reported; secondly, the use of a variety of tertiary phosphine ligands may shed further light on which structure (monomeric or dimeric) a given zinc(II) phosphine complex adopts. Finally, we have already reported the synthesis of novel products from the reaction of our reagents R_3PI_2 with other metal powders and there remains, therefore, the possibility that unexpected zinc complexes may be formed via this reaction route.

2. Results and discussion

Equimolar quantities of triorganophosphorus diiodide and zinc metal powder were reacted under anaerobic and anhydrous conditions in diethyl ether solution. For the majority of R_3PI_2 compounds, a dimeric complex results in quantitative yield (Eq. (2)):

$$2R_3PI_3 + 2Zn \xrightarrow[\text{r.t., 1–20 days}]{\text{Et}_2\text{O},\ N_2} [ZnI_2(PR_3)]_2 \qquad (2)$$

The reaction times vary considerably and are dependent upon R. In the case of trialkylphosphorus diiodides, all the zinc metal is consumed within a matter of hours; whereas, for substituted aryl derivatives reaction times were in the region of 18–20 days. Additionally, the reaction of R_3PI_2 ($R_3 = Ph_3, Ph_2Et, Ph_2Me$) with zinc metal powder does not produce a dimeric complex (Eq. (2)), and this will be discussed later.

Analytical data and $^{31}P\{H\}$ NMR shifts for the dimeric complexes, $[ZnI_2(PR_3)]_2$, are presented in Table 1. Clearly, from elemental analysis results in Table 1, this stoichiometry is favoured for the majority of tertiary phosphine complexes of zinc(II) iodide prepared by this route. Interestingly, the reaction of Me_3PI_2 with zinc metal powder also produces the dimeric complex $[ZnI_2(PMe_3)]_2$ which contrasts with the reaction of Me_3AsI_2 with zinc powder [19], which produces the monomeric complex $ZnI_2(AsMe_3)_2$ and ZnI_2. Clearly the production of the zinc(II) complex formed (dimeric/monomeric) results from a delicate balance of steric and electronic factors

Only one compound of formula $[ZnI_2(PR_3)]_2$ has been crystallographically characterised [10], $[ZnI_2(PEt_3)]_2$, which contains a tertiary phosphine of modest steric requirements. It was therefore decided to crystallographically characterise a second example of a complex of this stoichiometry which contains a bulky tertiary phosphine for comparative purposes. Recrystallisation of $\{ZnI_2[P(NMe_2)_3]\}_2$ from dichloromethane solution at room temperature yielded a large quantity

Table 1
Analytical and spectroscopic data for the complexes $[ZnI_2(PR_3)]_2$

Complex	Colour	Analysis % Found (Calc.)				$^{31}P\{H\}$ [a] (ppm)
		C	H	I	N	
$\{ZnI_2[P(NMe_2)_3]\}_2$	white	14.8(14.9)	4.0(3.7)	52.2(52.7)	8.5(8.7)	41.5[b]
$\{ZnI_2[P(NEt_2)_3]\}_2$	v. pale green	25.6(25.4)	5.6(5.3)	44.4(44.9)	7.2(7.4)	38.6
$[ZnI_2(PPr^i_3)]_2$	white	24.0(22.5)	5.2(4.4)	52.5(53.0)		42.8
$\{ZnI_2[P(CH_2CH_2CN)_3]\}_2$	v. pale green	21.6(21.1)	2.4(2.3)	48.4(49.6)	7.8(8.2)	11.8
$\{ZnI_2[P(CH_2CH_2Ph)_3]\}_2$	white	43.5(43.3)	4.0(4.1)	37.9(38.2)		40.0 [b]
$[ZnI_2(PCy_3)]_2$	white	35.9(36.1)	5.7(5.5)	42.9(42.4)		77.3
$[ZnI_2(PBz_3)]_2$	white	40.7(40.4)	3.6(3.4)	40.9(40.8)		24.0
$[ZnI_2(PPh_2Bz)]_2$	white	39.9(38.3)	3.3(2.9)	42.3(42.7)		10.1
$[ZnI_2(PPh_2Py)]_2$	off-white	34.9(35.1)	2.7(2.4)	43.4(43.6)	2.3(2.4)	−6.9
$\{ZnI_2[P(4\text{-}FC_6H_4)_3]\}_2$	white	35.0(34.0)	2.3(1.9)	39.9(40.0)		36.1
$\{ZnI_2[P(4\text{-}ClC_6H_4)_3]\}_2$	white	30.5(31.6)	1.9(1.8)	38.8(37.1)		38.4 [b]
$\{ZnI_2[P(4\text{-}CH_3OC_6H_4)_3]\}_2$	pale yellow	36.2(37.6)	3.4(3.1)	36.7(37.9)		−19.9
$\{ZnI_2[P(2,6\text{-}CH_3OC_6H_3)_3]\}_2$	v. pale yellow	36.3(37.8)	3.7(3.5)	32.1(33.4)		−59.4
$\{ZnI_2[P(2,4,6\text{-}CH_3OC_6H_2)_3]\}_2$	v. pale yellow	36.4(38.1)	3.8(3.9)	29.3(29.8)		−52.4

[a] All shifts are relative to 85% phosphoric acid standard.

[b] These shifts were recorded in $CDCl_3$, the remainder were recorded in CD_3CN.

of colourless crystals on standing at r.t. for approximately 5 days. From these, one suitable for analysis by single crystal X-ray diffraction was chosen. The crystal structure of $\{ZnI_2[P(N\ Me_2)_3]\}_2$ is illustrated in Fig. 1, and selected bond lengths and angles are displayed in Table 2. Predictably, this complex is also dimeric, similar to the only other crystallographically characterised [10] simple zinc(II) iodide tertiary phosphine complex $[ZnI_2(PEt_3)]_2$. This result shows that the dimeric structure is available for zinc(II) iodide complexes containing tertiary phosphine ligands of both modest and rather greater steric requirements: d(Zn–P) for $\{ZnI_2[P(N\text{-}Me_2)_3]\}_2$, 2.372(3) Å, is slightly longer than that observed for $[ZnI_2(PEt_3)]_2$, 2.361(5) Å, whereas both the terminal and bridging d(Zn–I) are similar for both complexes, being 2.533(1) and 2.532(3), and 2.695(1) and 2.689(3) Å, for $\{ZnI_2[P(NMe_2)_3]\}_2$ and $[ZnI_2(PEt_3)]_2$, respectively. Both complexes exhibit close to regular tetrahedral geometries for the zinc(II) metal centres.

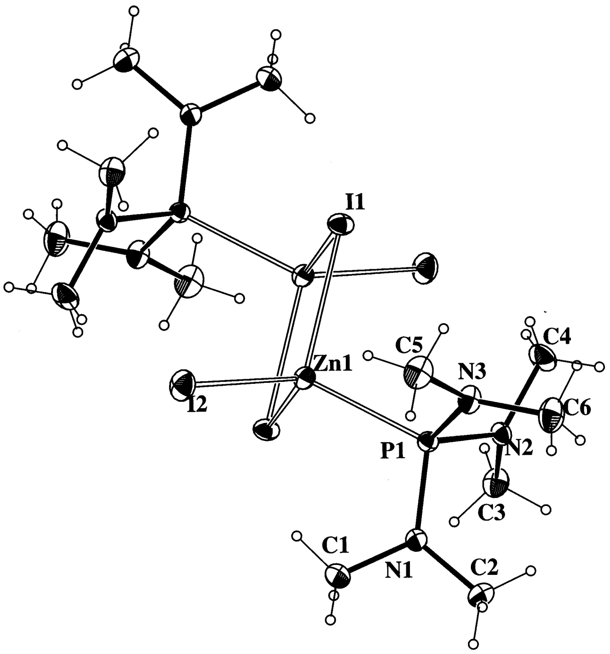

Fig. 1. The X-ray crystal structure of dimeric $\{ZnI_2[P(NMe_2)_3]\}_2$.

The $^{31}P\{H\}$ NMR shifts for the complexes $[ZnI_2(PR_3)]_2$ recorded in $CDCl_3$ solution are shown in Table 1. The spectra exhibit single chemical shifts, similar to the limited number of spectra previously recorded for other zinc complexes of formula $[ZnI_2(PR_3)]_2$, which have been shown not to ionise in solution [8,9]. It therefore seems likely, by analogy to these latter compounds, that the zinc(II) complexes reported here also retain their molecular dimeric structure in solution.

2.1. The reaction of R_3PI_2 ($R_3 = Ph_3$, Ph_2Et, Ph_2Me) with zinc metal powder

Surprisingly, reaction of 1 equiv. of R_3PI_2 ($R_3 = Ph_3$, Ph_2Et, Ph_2Me) with zinc powder does not produce the 1:1 dimeric complex $[ZnI_2(PR_3)]_2$. Instead, equimolar quantities of the bis-phosphine monomeric complexes $ZnI_2(PR_3)_2$ ($R_3 = Ph_3$, Ph_2Et, Ph_2Me) and zinc(II) iodide are produced, (Eq. (3)).

$$2R_3PI_2 + 2Zn \xrightarrow[\text{2 days, r.t.}]{Et_2O,\ N_2} ZnI_2(PR_3)_2 + ZnI_2 \quad (3)$$

($R_3 = Ph_3$, Ph_2Et, Ph_2Me)

The slightly lower solubility of $ZnI_2(PR_3)_2$ compared to ZnI_2 in diethyl ether solution means that separation of

Table 2
Selected bond lengths (Å) and angles (°) for $\{ZnI_2[P(NMe_2)_3]\}_2$

Zn(1)–P(1)	2.372(3)
Zn(1)–I(2)	2.5331(15)
Zn(1)–I(1)	2.6930(15)
Zn(1)–I(1) [a]	2.6968(14)
P(1)–Zn(1)–I(2)	123.55(8)
P(1)–Zn(1)–I(1)	105.79(7)
I(2)–Zn(1)–I(1) [a]	110.06(5)
P(1)–Zn(1)–I(1) [a]	104.83(7)
I(2)–Zn(1)–I(1) [a]	109.89(5)
I(1)–Zn(1)–I(1) [a]	100.13(4)
Zn(1)–I(1)–Zn(1) [a]	79.87(4)

[a] Symmetry transformations to generate equivalent atoms: $-x+1$, $-y$, $-z+1$.

Table 4
Comparison of the X-ray powder diffraction patterns of experimentally derived ZnI_2 and the standard database entry

Experimentally derived [a] ZnI_2		ZnI_2 JCPDS card no. 10-72	
d (Å)	I_{rel}	d (Å)	I_{rel}
3.495	100	3.489	100
3.963	26	3.067	19
2.946	30	2.944	5
		2.441	3
2.171	38	2.169	19
2.128	45	2.125	39

[a] Differences observed between the two patterns are due to trace contamination of the experimentally derived ZnI_2 with the complex $ZnI_2(PR_3)_2$ (see text).

the two products is possible, although difficult. Analytical data and $^{31}P\{H\}$ NMR shifts for the complexes $ZnI_2(PR_3)_2$ ($R_3 = Ph_3$, Ph_2Et, Ph_2Me) are given in Table 3. In the case of the reaction of Ph_3PI_2 with zinc, gradual concentration of the filtrate from the reaction led eventually to a relatively pure sample of ZnI_2. This was studied using X-ray diffraction, and the *d*-spacings and relative intensities of experimentally derived ZnI_2 and the standard database entry for ZnI_2 are compared in Table 4. Although there are some unassigned peaks (which arise from trace contamination from the complex, $ZnI_2(PPh_2Me)_2$), the agreement unequivocally establishes zinc(II) iodide as a product from the reaction. Acceptable X-ray powder diffraction patterns recorded for experimentally derived ZnI_2 from the other two reactions were also obtained.

In the case of the reaction of Ph_2MePI_2 with zinc metal powder, a sample of the complex $ZnI_2(PPh_2Me)_2$ was carefully separated from ZnI_2 and recrystallised from diethyl ether solution at r.t. On standing for approximately 7 days at r.t. a large number of colourless crystals formed, one of which was selected for analysis by single crystal X-ray diffraction. The structural analysis confirms the monomeric structure of $ZnI_2(PPh_2Me)_2$ (Fig. 2). Selected bond lengths and angles are displayed in Table 5. The fact that this complex, which contains a tertiary phosphine of relatively high steric requirements, adopts a monomeric structure is very surprising and unequivocally shows that bisphosphine complexes of zinc(II) are not restricted to the lighter halides nor to PR_3 ligands with very small cone angles, e.g. $ZnCl_2(PMe_3)_2$, which had previously been claimed by Goel and coworkers [8,9]. Indeed, the formation of a mononuclear species from the reaction of Ph_2MePI_2 with zinc metal powder is particularly surprising since the reaction of Et_3PI_2, which contains a parent tertiary phosphine of lower steric requirements, produces the dimeric complex $[ZnI_2(PEt_3)]_2$. It is also interesting that, in the present study, the complexes which appear to favour a monomeric structure contain phenyl rings (but not substituted phenyl rings). It therefore occurred to us that the presence of these non-substituted aromatic rings may be responsible for this monomeric structure. A closer examination of the crystal structure of $ZnI_2(PPh_2Me)_2$ provides a possible explanation. The nature of the crystal packing allows for significant $\Pi-\Pi$ interactions of the phenyl rings of the tertiary phosphine ligands. This presumably imparts greater stability to the complex, and, since such interactions may not be possible in a dimeric complex, may explain why zinc(II) complexes containing tertiary phosphine ligands with phenyl rings prefer a monomeric structure. The $\Pi-\Pi$ interactions of the phenyl rings in $ZnI_2(PPh_2Me)_2$ is more clearly illustrated in its space-filling representation (Fig. 3). It is presumed that such interactions are also present in the monomeric complexes $ZnI_2(PR_3)_2$ ($R = Ph_3$, Ph_2Et),

Table 3
Analytical and spectroscopic data for the complexes $ZnI_2(PR_3)_2$

Complex	Colour	Analysis % Found (Calc.)			$^{31}P\{H\}$ [a] (ppm)
		C	H	I	
$ZnI_2(PPh_2Me)_2$	white	42.1(43.4)	3.5(3.6)	36.5(35.3)	−4.5
$ZnI_2(PPh_2Et)_2$	white	42.4(45.0)	4.1(4.0)	36.6(34.0)	2.7
$ZnI_2(PPh_3)_2$	white	49.7(51.2)	3.5(3.6)	29.0(30.1)	−3.3

[a] All shifts are relative to 85% phosphoric acid standard.

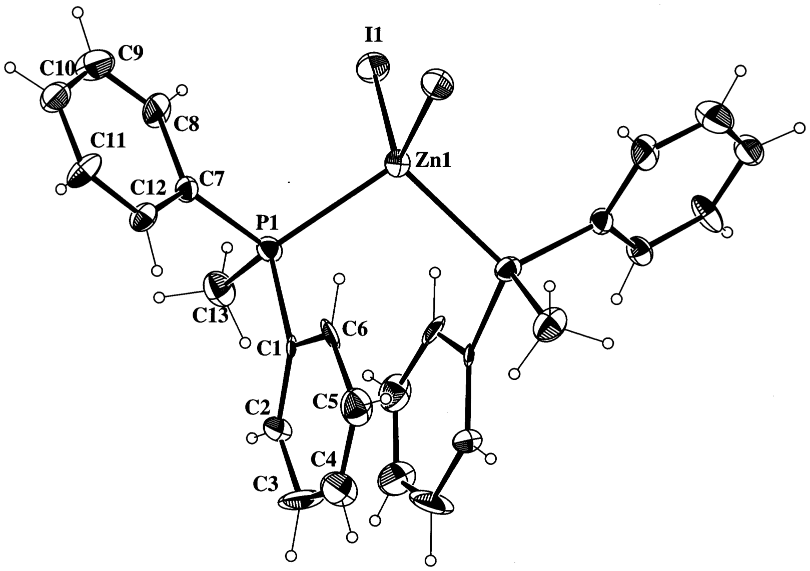

Fig. 2. The X-ray crystal structure of monomeric $ZnI_2(PPh_2Me)_2$.

thus providing a possible explanation why this structure is favoured rather than the dimeric structure, $[ZnI_2(PR_3)]_2$, exhibited by the majority of zinc(II) tertiary phosphine complexes. For $ZnI_2(PPh_2Me)_2$, both d(Zn–I), 2.570(2) Å and d(Zn–P), 2.4165(5) Å are significantly longer than $d(Zn–I_t)$, and d(Zn–P) in $\{ZnI_2[P(NMe_2)_3]\}_2$ which are 2.533(1) and 2.372(3) Å, respectively. A likely explanation for this is the greater basicity of $P(NMe)_3$ compared to PPh_2Me, and the greater steric crowding around the mono-ligand, compared to the bis-ligand, zinc(II) metal centre.

The $^{31}P\{H\}$ NMR solution shifts for the complexes $ZnI_2(PR_3)_2$ recorded in $CDCl_3$ solution are shown in Table 3. The spectra exhibit single chemical shifts similar to those previously recorded for the analogous cadmium(II) complexes $CdI_2(PR_3)_2$ ($R_3 = Ph_3$ [20], Ph_2Et [21], Ph_2Me [22]). These cadmium(II) complexes have been shown not to dissociate in $CDCl_3$ solution and, due to the similarity of the $^{31}P\{H\}$ NMR values for these complexes and the analogous zinc complexes $ZnI_2(PR_3)_2$, described herein, it is tentatively concluded that these complexes also retain their molecular structure and do not dissociate in this solvent.

In conclusion, we would like to emphasise that the complex $\{ZnI_2[P(NMe_2)_3]\}_2$ represents only the second example of a simple zinc(II) compound containing tertiary phosphine ligands to be characterised by single crystal X-ray diffraction. Both this complex and $[ZnI_2(PEt_3)]_2$, the first crystallographically characterised example of the mono-ligand complex, have been prepared from the novel reaction of the reagents R_3PI_2 ($R = NMe_2$, Et) with zinc metal powder. It has thus been established that the dimeric 1:1 zinc:tertiary phosphine stoichiometry is available for zinc(II) complexes regardless of the steric requirements of the tertiary

Table 5
Selected bond lengths (Å) and angles (°) for $ZnI_2(PPh_2Me)_2$

Zn(1)–P(1)	2.416(5)
Zn(1)–I(1)	2.5702(2)
P(1)–Zn(1)–P(1) [a]	103.9(3)
P(1)–Zn(1)–I(1)	108.83(11)
P(1) [a]–Zn(1)–I(1)	109.05(11)
I(1)–Zn(1)–I(1) [a]	116.44(12)

[a] Symmetry transformations to generate equivalent atoms: $-x+1$, y, $-z+2/3$.

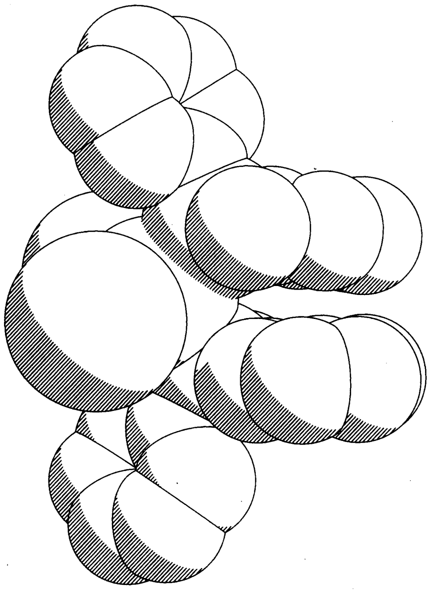

Fig. 3. A space-filling representation of the crystal structure of $ZnI_2(PPh_2Me)_2$.

phosphine. The crystallographic characterisation of $ZnI_2(PPh_2Me)_2$ is important since it represents the first crystal structure of a bis-phosphine complex of zinc(II) iodide to be reported and, more importantly, illustrates that the nature of the zinc(II) complexes formed from the reaction of R_3PI_2 reagents with zinc metal powder is dependent on R, a phenomenon we have previously observed in the reaction of R_3PI_2 with manganese [23–25], cobalt [12–14], nickel [15], gallium [26], and indium [18] metal powders. The reason why the monomeric $[ZnI_2(PR_3)]$, rather than the dimeric $[ZnI_2(PR_3)]_2$, complexes result from the reaction of R_3PI_2 (R_3 = Ph_3, Ph_2Et, Ph_2Me) with zinc metal powder may be due to favourable $\Pi-\Pi$ interactions in the ligand phenyl rings, illustrating the subtle structural balance between mono- and bis-ligand complexes for zinc(II) halide tertiary phosphine complexes. Synthesis of the dimeric complexes, $[ZnI_2(PR_3)]_2$, by the direct reaction of zinc metal powder and the appropriate R_3PI_2 reagent provides an excellent, even favourable synthetic route, compared to conventional techniques using ZnI_2. Reaction times are fast (being only a few hours in many cases) and the need for rigorous drying of ZnI_2 is obviated; additionally, yields are quantitative in all cases. In contrast, however, synthesis of the bis-ligand complexes, $ZnI_2(PR_3)_2$, is, in fact, problematic. Separation of the complex $ZnI_2(PR_3)_2$ from an equimolar quantity of ZnI_2 in diethyl ether is difficult and complete separation of the two products can be rather time-consuming. The principal reason for this is the similar solubilities of the two products. Nevertheless, isolation of a sufficient quantity of the pure complex $ZnI_2(PR_3)_2$ for characterisation is easily achieved by removal of approximately half of the solvent from which uncontaminated $ZnI_2(PR_3)_2$ can then be obtained. Removal of more solvent tends to lead to the precipitation of some ZnI_2. More importantly, since previous workers [8,9] have claimed that the monomeric complexes $ZnI_2(PR_3)_2$ are only available from conventional synthetic techniques (using ZnI_2 as starting material) when small tertiary phosphine ligands are employed, the synthesis of the complexes $ZnI_2(PR_3)_2$ ($R = Ph_3$, Ph_2Et, Ph_2Me) which contain tertiary phosphine ligands of relatively large steric requirements could possibly be attributed to our new synthetic methodology starting from zinc metal powder.

3. Experimental

All of the zinc(II) tertiary phosphine complexes described herein are moisture sensitive, as are the reagents R_3PI_2; therefore, strictly anaerobic and anhydrous conditions were adhered to during their synthesis. The synthesis of the triorganophosphorus diiodide reagents, R_3PI_2, has been described elsewhere [27,28]. Diethyl ether (BDH) was dried over sodium wire for approximately 1 day and then distilled over CaH_2 in an inert atmosphere prior to use. The dry diethyl ether was then distilled directly into the reaction vessel. Standard reagent grade zinc metal powder was found in the laboratory, crudely labelled, and was used without further purification. After isolation, any subsequent manipulation of the complexes was carried out inside a Vacuum Atmospheres HE-493 glovebox.

3.1. Synthesis of the complexes $[ZnI_2(PR_3)]_2$

All the complexes $[ZnI_2(PR_3)]_2$ were synthesised in quantitative yield from the direct stoichiometric 1:1 reaction of R_3PI_2 and zinc metal powder. The synthesis of $\{ZnI_2[P(NMe_2)_3]\}_2$ is typical: $I_2P(NMe_2)_3$ (0.895 g, 2.15 mmol) was suspended in diethyl ether (ca. 70 cm^3) and subsequently zinc metal powder (0.142 g, 2.15 mmol) was added. After approximately 3 days, the resultant white solid was isolated by standard Schlenk techniques and dried in vacuo. The solid 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 displayed in Tables 1 and 3. $^{31}P\{H\}$ NMR spectra were recorded as $CDCl_3$ solutions on a Brucker AC200 high-resolution multiprobe spectrometer relative to concentrated phosphoric acid as standard. X-ray powder diffraction patterns were recorded on a Scintag XRD2000 powder diffractometer using copper Kα radiation of $\lambda = 1.5418$ Å.

3.2. Crystallography

Crystals of $\{ZnI_2[P(NMe_2)_3]\}_2$ and $ZnI_2(PPh_2Me)_2$ were independently mounted in Lindemann tubes under an atmosphere of dry argon. All measurements were performed on a Rigaku AFC 6S four-circle diffractometer employing graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) and ω–2θ scans. Both 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 6. Hydrogen atoms were confined to chemically reasonable positions. Neutral atom scattering factors were taken from Ref. [29]. Anomalous dispersion effects were taken from Ref. [30]. All calculations were performed using the TEXSAN suite of computer programs [31].

Table 6
Crystal data and details of refinement for $\{ZnI_2[P(NMe_2)_3]\}_2$ and $ZnI_2(PPh_2Me)_2$

	$\{ZnI_2[P(NMe_2)_3]\}_2$	$ZnI_2(PPh_2Me)_2$
Empirical formula	$C_6H_{18}I_2N_3PZn$	$C_{26}H_{26}I_2P_2Zn$
Formula weight	482.37	359.79
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$C2/c$
Unit cell dimensions		
a (Å)	10.910(3)	14.872(4)
b (Å)	10.094(3)	13.130(9)
c (Å)	13.552(4)	15.259(4)
β (°)	95.08(2)	109.32(3)
Volume (Å^3)	1486.6(7)	2812(2)
Z	4	8
D_{calc} (Mg m^{-3})	2.155	1.700
Absorption coefficient (mm^{-1})	58.84	31.95
$F(000)$	904	1392
Crystal size (mm)	0.30 × 0.20 × 0.20	0.25 × 0.15 × 0.10
Reflections collected	2746	2408
Observed reflections	2602	2408
Parameters	124	142
Goodness-of-fit on F^2	1.021	0.803
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0417$, $wR_2 = 0.1055$	$R_1 = 0.0448$, $wR_2 = 0.1024$
R indices (all data)	$R_1 = 0.0935$, $wR_2 = 0.1288$	$R_1 = 0.3471$, $wR_2 = 0.1734$
Largest difference peak and hole (e Å^{-3})	0.589 and −1.193	0.908 and −1.434

4. Supplementary material

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre (CCDC). See instructions for Authors, J. Chem. Soc., Dalton Trans. 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number.

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