The X-Ray Crystal Structure of [Zn(PEt$_3$)I$_2$]$_2$, the First 1 : 1 Zinc(II) Complex of a Tertiary Phosphine of Low Steric Requirements, prepared by the Reaction of Unactivated Zinc Metal with Diiodotriethylphosphorane

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Unactivated zinc powder reacts with R$_3$PI$_2$ (R=Me, Et, Pr^n, Bu^n) to yield the unexpected 1 : 1 adducts of zinc(II), Zn(R$_3$P)I$_2$; the X-ray crystal structure of triethylphosphine complex shows it to be dimeric [Zn(PEt$_3$)I$_2$]$_2$.

Although tertiary phosphine complexes of zinc(II) halides have been known for many years,[1,2] their precise nature remains uncertain and has proved controversial,[3,4] which contrasts with the available data on analogous cadmium(II) and mercury(II) complexes.[5–7]

Despite the paucity of available data it is nonetheless clear that two types of complex exist, *viz.* the bis(phosphine) complexes, ZnL$_2$X$_2$, formed by tertiary phosphines of low steric requirements, and the mono(ligand) complexes, ZnLX$_2$, which involve bulky phosphines.[8–11] This seems reasonable and fits well with the cone-angle theory first expounded by Tolman.[12]

We have recently discovered a new synthetic route for transition metal phosphine complexes: the reaction of dihalogenophosphoranes with coarse-grain unactivated metals can yield established complexes, novel isomers of known complexes, and complexes in rare oxidation states, *e.g.* $NiI_3(PMe_3)_2$.[13] Here, we report the reaction of R_3PI_2 (R = Me, Et, Pr^n, Bu^n) with zinc powder to yield the unexpected 1 : 1 phosphine complexes $[Zn(PR_3)I_2]_2$. Moreover, whilst one X-ray crystal structure has been reported for the $[Zn(PPh_3)Br_3]^-$ anion,[14] and for a few unusual complexes containing P, O donor ligands[15] or zinc/vanadium mixed-metal species,[16] the structure we report here for $[Zn(PEt_3)I_2]_2$ is the first simple zinc(II) tertiary phosphine to be crystallographically characterised.

Standard reagent grade zinc powder reacts very rapidly, *ca.* 1 h, to consume one equiv. of diiodophosphorane in diethyl ether at room temperature to yield quantitatively the zinc(II) complex† [eqn. (1)].

$$\begin{gathered} Zn + R_3PI_2 \rightarrow [Zn(PR_3)I_2]_2 \\ (R = Me, Et, Pr^n, Bu^n) \end{gathered} \qquad (1)$$

In the case of the Zn + Et_3PI_2 reaction, recrystallisation of the white powder from dry diethyl ether yielded moisture-sensitive colourless needles suitable for single crystal X-ray analysis. The structure‡ of $[Zn(PEt_3)I_2]_2$ is shown in Fig. 1. It is dimeric, containing both bridging and terminal iodide ligands.

The molecule has C_i symmetry. We tentatively suggest that this dimeric structure is maintained in $CDCl_3$, since $^{31}P\{H\}$ NMR spectra in this solvent exhibit chemical shifts of δ 58.4 (R = Me), 15.6 (R = Et), 44.8 (R = Pr^n) and 42.3 (R = Bu^n), similar to those reported by Goel for similar cadmium(II) complexes which do not ionise in this solvent.[10,11,17–19]

In conclusion, not only is the first X-ray crystal structure for a simple zinc(II) complex of a tertiary phosphine reported here, but this work has clearly established that the 1 : 1 zinc : phosphine stoichiometry is available for phosphines of modest steric requirements *via* this new synthetic route. Moreover, we show here that metal-activation by dihalogenophosphoranes is not restricted to transition metals such as manganese, iron and nickel,[13] but is available to non-transition metals such as zinc. The requirement for anhydrous zinc(II) salts, emphasised by workers employing normal synthetic methods,[8–11] is obviated by our new procedure and, moreover, reaction times are considerably faster.

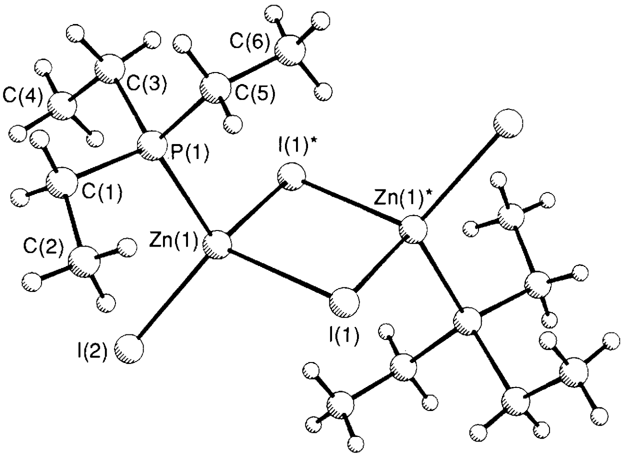

Fig. 1 Molecular structure of $Zn_2I_4(PEt_3)_2$. Selected bond lengths (Å) and angles (°); Zn(1)–I(1) 2.687(3), Zn(1)–I(1)* 2.690(3), Zn(1)–I(2) 2.532(3), Zn(1)–P(1) 2.361(5); Zn(1)–I(1)–Zn(1)* 80.67(9), I(1)–Zn(1)–I(1)* 99.33(9), I(1)–Zn(1)–I(2) 113.04(9), I(1)*–Zn(1)–I(2) 112.09(9), I(1)–Zn(1)–P(1) 109.0(1), I(1)*–Zn(1)–P(1) 108.2(1), I(2)–Zn(1)–P(1) 114.0(1). Where * denotes 1 − *x*, 1 − *y*, 1 − *z*.

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† Elemental analyses (found C, H, I) are in excellent agreement with the expected values.

‡ *Crystal data*: $C_{12}H_{30}I_4P_2Zn_2$, M = 874.69, T = 293 K, monoclinic, space group $P2_1/n$ (No. 14), a = 7.740(6), b = 11.671(9), c = 14.664(9) Å, β = 103.49(5)°, V = 1288 Å^3, Z = 2 (molecule has C_i symmetry), D_c = 2.255 mg m^{-3}, $F(000)$ = 808, Rigaku AFC6S diffractometer, Mo-Kα radiation, = 0.71069 Å, μ(Mo-Kα) = 6.773 mm^{-1}. Iodine located using Patterson techniques (SHELXS) with remaining non-hydrogen atoms found in difference Fourier maps. Hydrogen atoms placed in chemically reasonable positions. Full-matrix least-squares refinement (TEXSAN) with all non-hydrogen atoms treated anisotropically. $R = 0.048$, $R_\omega = 0.0643$, $\omega = 1/[\sigma^2[(F_o) + 0.03F_o^2]$ for 1269 unique reflections with $I > 3\sigma(I)$ and 91 refined parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.