Reaction of indium metal with R_3PI_2 (R = Ph, Pr^i, Pr^n); structural characterisation of the novel 'subvalent' indium(II) complex $In_2I_4(PPr^n_3)_2$ which contains an In–In bond, the four- and five-coordinate indium(III) complex $InI_3(PPh_3)_2 \cdot InI_3(PPh_3)$, and the tetrahedral indium(III) complex $InI_3(PPr^i_3)$

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Reaction of R_3PI_2 (R = Ph, Pr^n, Pr^i) with indium metal powder produces a variety of novel indium metal complexes: where R = Ph, the four- and five-coordinate metal(III) complex $InI_3(PPh_3)_2 \cdot InI_3(PPh_3)$ results; where R = Pr^n, the 'subvalent' indium(II) complex $In_2I_4(PPr^n_3)_2$ is formed, the first example of an indium tertiary phosphine complex containing an indium–indium bond; whereas for R = Pr^i, the monomeric tetrahedral indium(III) complex $InI_3(PPr^i_3)$ results; these complexes illustrate the subtle effect of the organic substituents on the phosphorus atom for the reaction of R_3PI_2 with indium metal powder and the novel indium complexes which are available.
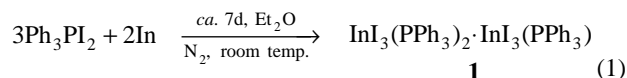
Virtually nothing was known about the coordination chemistry of indium with tertiary phosphines until the pioneering work of Carty and Tuck,[1–4] who produced tetrahedral $InX_3(PR_3)$, trigonal-bipyramidal $InX_3(PR_3)_2$, and the molecular octahedral species $InX_3(PR_3)_3$, although for this last stoichiometry it was found that one mole of tertiary phosphine was easily removed by the application of a vacuum. No complex of stoichiometry $InX_3(PR_3)$ containing a tertiary phosphine ligand has been crystallographically characterised, but the analogous complexes $InI_3(PHR_2)$ (R = Ph, Bu^t) containing secondary phosphines have recently been structurally characterised.[5] The trigonal-bipyramidal molecules $InX_3(PR_3)_2$ have received a little more attention: the first structurally characterised complex of this stoichiometry, $InCl_3(PPh_3)_2$, was reported in 1969,[6] and has the expected trigonal-bipyramidal geometry exhibiting very long axial indium–phosphorus bonds, 2.71(1) Å. The trimethylphosphine derivative $InCl_3(PMe_3)_2$ has been structurally characterised[7] as have $InBr_3(PPhMe_2)_2$ and $InI_3(PPh_2Me)_2$;[8] all these complexes exhibit regular trigonal-bipyramidal geometry.

We are engaged in a study of the oxidising power of a variety of R_3EX_2 compounds (E = P, As, Sb; X_2 = Br_2, I_2, IBr) with unactivated metal powders in diethyl ether solution. The strong oxidising power of some of these reagents, *e.g.* Me_3EI_2 (E = P, As), is illustrated by their ability to oxidise crude nickel, cobalt[9–14] and even gold[15] metal powders directly to the tripositive oxidation state in a simple one-step reaction.

We have now turned out attention to the reaction of these agents with indium metal powder, principally for three reasons: firstly, little is known concerning the coordination chemistry of indium halides with tertiary phosphine donor ligands; secondly, as we have already seen, novel complexes unobtainable from established synthetic techniques are available from our synthetic route, so there is the possibility of synthesising previously unavailable indium halide tertiary phosphine complexes; if such compounds are available they may have applications in the microelectronics industry as precursors for MOCVD. Finally, indium chemistry has been hampered by the difficulty of synthetic entries, *i.e.* the relatively low activity of the metal and

the insolubility of InX and of InX_3, and so the approach taken by us represents a significant advance.

Ph_3PI_2 reacts with indium metal powder in a 3:2 stoichiometric ratio, eqn. (1).

$$3Ph_3PI_2 + 2In \xrightarrow[\text{N}_2, \text{ room temp.}]{ca.\ 7d,\ Et_2O} InI_3(PPh_3)_2 \cdot InI_3(PPh_3) \quad \mathbf{1} \quad (1)$$
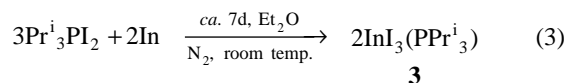
Recrystallisation of the pale yellow powder from diethyl ether produced yellow crystals, one of which was selected for analysis by single-crystal X-ray diffraction. The structure of the indium(III) complex was revealed to be $InI_3(PPh_3)_2 \cdot InI_3(PPh_3)$, **1**. Surprisingly, the structure contains both tetrahedral and trigonal-bipyramidal indium(III) centres within the unit cell. No complex of indium(III) of this stoichiometry has previously been identified.

$Pr^n_3PI_2$ reacts with indium metal powder according to eqn. (2).

$$2Pr^n_3PI_2 + 2In \xrightarrow[\text{N}_2, \text{ room temp.}]{ca.\ 2d,\ Et_2O} [InI_2(PPr^n_3)]_2 \quad \mathbf{2} \quad (2)$$
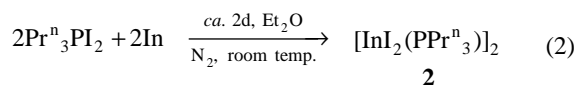
Recrystallisation of the white powder from diethyl ether solution at 60 °C and subsequent cooling to room temp. produced a large quantity of colourless crystals, from which one was selected for analysis by single-crystal X-ray diffraction,† revealing the dinuclear indium(II) complex $[InI_2(PPr^n_3)]_2$, **2**‡ Fig. 1. This is an unusual result, since we had anticipated a monomeric tetrahedral or a trigonal-bipyramidal indium(III) complex, in agreement with all previous studies of the conventional reaction of indium(III) halides with tertiary phosphines; **2** therefore represents a new, previously unconsidered, indium(II) halide complex containing tertiary phosphine ligands, and the first example of such a complex containing an indium–indium bond; d(In–In) in **2** is 2.745(3) Å. Our new synthesis may offer a route to 'subvalent' group 13 metal complexes. Although there are no examples of tertiary phosphine complexes containing an indium–indium bond, the organometallic species $In_2[CH(SiMe_3)_2]_4$ has been characterised by Uhl *et al.*[16] and $In_2IBr_3(C_6H_{16}N_2)_2$ by Tuck and coworkers.[17] The In–In bond distances for these complexes are 2.828(5) and 2.775(2) Å, respectively; both complexes were prepared from the conventional reaction of an indium(II) halide with the appropriate ligand(s).
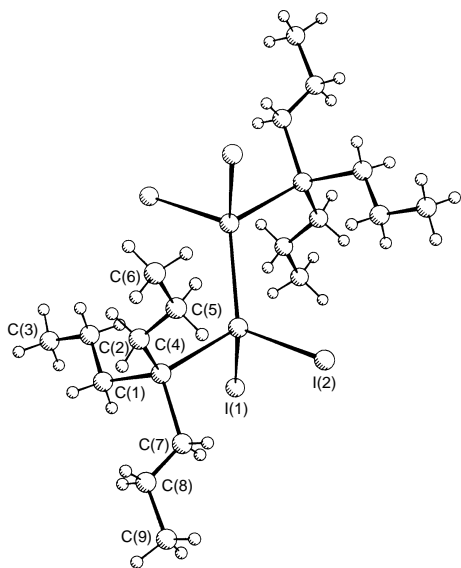
$Pr^i_3PI_2$ reacts with indium metal powder according to eqn. (3).

$$3Pr^i_3PI_2 + 2In \xrightarrow[\text{N}_2, \text{ room temp.}]{ca.\ 7d,\ Et_2O} 2InI_3(PPr^i_3) \quad \mathbf{3} \quad (3)$$

Recrystallisation of the white powder from diethyl ether produced colourless crystals. One of these was selected for

analysis by single-crystal X-ray diffraction.† The structure of **3**,§ Fig. 2, was revealed to be the tetrahedral monomeric $InI_3(PPr^i_3)$. Although the existence of complexes of this stoichiometry has previously been postulated by Carty and Tuck,[4] this complex nevertheless represents the first indium(III) complex of this stoichiometry containing a tertiary phosphine ligand to be crystallographically characterised. The indium–iodine distances are 2.689(3), 2.701(3) and 2.705(3) Å and the indium–phosphorus distance is 2.569(7) Å.

In conclusion, these new results clearly indicate that subtle changes in the nature of our oxidising agents result in the production of different complexes of indium in different oxidation states, *viz.* reaction of Ph_3PI_2 with indium metal powder produces the indium(III) complex $InI_3(PPh_3)_2 \cdot InI_3(PPh_3)$, containing the indium(III) centres in trigonal-bipyramidal and tetrahedral geometry, and the reaction of $Pr^n_3PI_2$ with indium metal powder produces the unique indium(II) tertiary phosphine complex, $In_2I_4(PPr^n_3)_2$, which contains an indium–indium bond. On the other hand, the reaction of $Pr^i_3PI_2$ with indium metal powder produces the monomeric tetrahedral indium(III) complex $InI_3(PPr^i_3)$. The compound $In_2I_4(PPr^n_3)_2$ represents the first example of a dimeric complex containing tertiary phosphine donor ligands, and since a complex of this type has never previously been observed, its synthesis may be attributed to our synthetic method and it may not be available from conventional techniques.

Fig. 1 Perspective view of the molecular structure of $In_2I_4(PPr^n_3)_2$: selected bond lengths (Å) and angles (°): In(1)–I(1) 2.750(2), In(2)–I(1) 2.745(3), In(1)–P(1) 2.585(6), I(1)–In(1)–I(2) 107.75(7), I(1)–In(1)–In(1) 115.36(8), I(1)–In(1)–P(1) 97.1(1), I(2)–In(1)–In(1) 116.57(8), I(2)–In(1)–P(1) 99.8(1), In(1)–In(1)–P(1) 117.5(2)
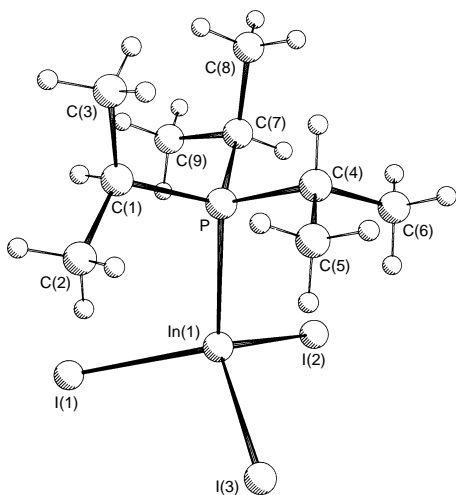
Fig. 2 Perspective view of the molecular structure of $InI_3(PPr^i_3)$: selected bond lengths (Å) and angles (°): I(1)–In 2.705(3), I(2)–In 2.701(3), I(3)–In 2.689(3), In–P(1) 2.569(7), I(1)–In–I(2) 109.7(1), I(1)–In–I(3) 106.87(9), I(1)–In–P(1) 108.9(2); I(2)–In–I(3) 112.4(1); I(2)–In–P(1) 106.1(2), I(3)–In–P(1) 112.9(2)

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