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Preliminary communication

Preparation of some phosphidoindium compounds, and the crystal structures of $In(PBu^t_2)_3$ and $[Et_2InPBu^t_2]_2$

N.W. Alcock, I.A. Degnan, M.G.H. Wallbridge

Department of Chemistry, University of Warwick, Coventry, CV4 7AL (Great Britain)

H.R. Powell and M. McPartlin

School of Chemistry, The Polytechnic of North London, Holloway, London, N7 8DB (Great Britain)

and G.M. Sheldrick

Institut für Anorganische Chemie der Universität Gottingen, D-3400 Gottingen (F.R.G.)

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Abstract

The reaction of $LiPBu^t_2$ with InI_3 yields the monomeric compound $In(PBu^t_2)_3$, while the action of Bu^t_2PH on $InEt_3$ affords the dimeric phosphide $[Et_2InPBu^t_2]_2$. Both compounds have been fully characterised by analytical, spectroscopic, and X-ray diffraction methods.

In the course of our studies on compounds containing indium, together with a Lewis base from group 15, we thought it of interest to see whether the presence of bulky groups on the base could decrease the degree of association of the resulting indium compound. We have prepared, and obtained X-ray crystal structures of, two such compounds using the bulky phosphido group PBu^t_2. We find that if three such groups are attached to the indium, as in $In(PBu^t_2)_3$ (**1**), then the compound is monomeric, whereas if only one such group is present, as in $Et_2InPBu^t_2$ (**2**), then a dimer is obtained. It is noteworthy that **1** is the first reported structure of a monomeric tricoordinate compound of indium containing a bond between indium and a group 15 element, although the existence of such a species has been briefly alluded to previously [1].

The compound **1** can be obtained in good yield (~ 80%) by the reaction of $LiPBu^t_2$ (prepared by the action of $LiBu^n$ on Bu^t_2PH) with InI_3 in dry toluene at $-78\,^\circ C$ (eq. 1). The red crystalline air-sensitive solid product can be obtained by

$$3LiPBu^t_2 + InI_3 \rightarrow In(PBu^t_2)_3 + 3LiI \qquad (1)$$

cooling the concentrated toluene solution after filtering off the LiI. The presence of

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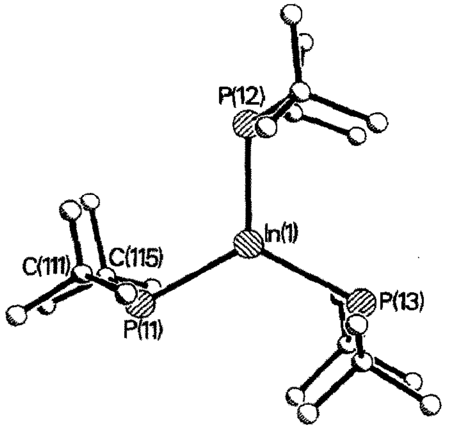

Fig. 1. The X-ray crystal structure of **1** (hydrogen atoms have been omitted for clarity). Selected bond distances (Å): In(1)–P(11) 2.588(14), In(1)–P(12) 2.574(11), In(1)–P(13) 2.613(12), P(11)–C(111) 1.954(44), P(11)–C(115) 1.744(65). Selected bond angles (deg): P(11)–In(1)–P(12) 120.7(4), P(12)–In(1)–P(13) 118.8(4), P(13)–In(1)–P(11) 120.4(4), C(111)–P(11)–C(115) 105.4(23), In(1)–P(11)–C(111) 103.6(16).

only one doublet in the ^{1}H NMR spectrum (δ 1.49 ppm, J(P–H) 11.1 Hz), and one singlet in the ^{31}P NMR spectrum (δ 71.8 ppm, rel. to H_3PO_4) shows that all the $\mathrm{PBu^t_2}$ groups are equivalent in solution (toluene-d_8). The monomeric nature of the compound is confirmed by the X-ray crystallographic structure determination * (Fig. 1), which shows the trigonal array of the three $\mathrm{PBu^t_2}$ groups around the central metal atom.

An essentially quantitative yield of **2** results from heating an equimolar mixture of $\mathrm{InEt_3}$ and $\mathrm{Bu^t_2PH}$ in refluxing dry hexane (eq. 2). The colourless solid product

$$\mathrm{InEt_3 + Bu^t_2PH \rightarrow \tfrac{1}{2}[Et_2InPBu^t_2]_2 + C_2H_6} \qquad (2)$$

was partly characterised by IR and NMR spectroscopy. In this case the ^{1}H NMR spectrum shows the expected triplet (δ 1.58 ppm) and quartet (δ 1.04 ppm) patterns for the ethyl groups, but unusually the resonance for the t-butyl groups appears as two doublets (J(P–H) 7 Hz) superimposed to give a triplet (δ 1.32 ppm). The two resonances from the t-butyl groups do not appear to arise from a monomer–dimer equilibrium in solution,since the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum consists of one singlet (δ 44.8 ppm, C_6D_6 solution). It is interesting that in $\mathrm{[Me_2GaPBu^t_2]_2}$ [1] and $\mathrm{[(Bu^tCH_2)_2InPPh_2]_2}$ [2], the resonances from the t-butyl protons appear as a triplet and doublet, respectively. The IR spectrum shows, in addition to the absence of the phosphine ν(PH) at 2280 cm^{-1}, bands typical of ν(PC) 728 cm^{-1}, ν(InC, rock) 641, 620 cm^{-1}, and ν(InC, stretch) 463 cm^{-1}.

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* Crystal data for **1**: $\mathrm{C_{24}H_{54}InP_3}$, $M = 550.4$. Monoclinic, Å^3, space group Cc, a 17.855(5), b 30.873(8), c 17.617(5) Å, β 111.66(2)°, U 9025(4) Å^3, μ(Mo-K_α) 9.3 cm^{-1}, $Z = 12$, D_c 1.22 g cm^{-3}. The data were collected on a Nicolet P2$_1$ diffractometer in the θ range 3–25°, scan width 1.0. The structure was determined by heavy atom method. Refinement with considerable difficulty because of pseudo-symmetry (heavy atoms in $C2/c$), resolved by use of distance constraints. $R = 0.1005$, $R_w = 0.0841$ ($w = 1/\sigma^2(F) + 0.0008F^2$) for 3346 reflections with $I/\sigma(I) \geq 2.5$. Coordinates and dimensions have been deposited with Cambridge Crystallographic Data Centre.

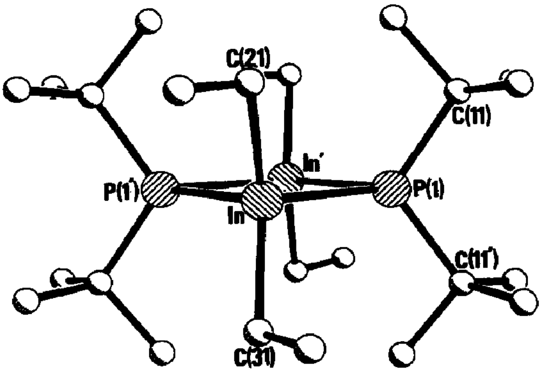

Fig. 2. The X-ray crystal structure of 2 (hydrogen atoms have been omitted for clarity). Selected bond distances (Å): In–P(1) 2.635(2), In–C(21) 2.170(13), In–C(31) 2.176(12), P(1)–C(11) 1.879(8). Selected bond angles (deg.): In–P(1)–In' 94.4(1), P(1)–In–P(1') 85.6(1), C(11)–P(1)–C(11') 112.7(6), C(11)–P(1)–In 112.2(3).

An X-ray structural study [*] of 2 showed that the compound consists of discrete dimers with a distorted tetrahedral distribution of groups around the indium atoms. A similar compound $[Me_2InPBu^t_2]$ [3], has been referred to as being dimeric, but has not been fully reported, while other related derivatives $[Et_2InPEt_2]$ and $[Me_2InPR_2]$ (R = Me, Et) have been reported as being trimeric in solution, but their structures in the solid state were not determined [4,5].

We have so far been unsuccessful in our attempts to prepare other intermediate compounds which have two phosphido groups attached to each indium atom. Thus, the action of 2 moles of Bu^t_2PH on one mole of $InEt_3$ in refluxing petroleum ether (b.p. 100–120 °C) produced only $[Et_2InPBu^t_2]_2$ and free phosphine, and other reaction mixtures such as $2LiPR_2/1InI_3$ or $2In(PBu^t_2)_3/1InI_3$ in toluene yielded intractable solids which we have been unable to identify. However, even in the absence of these derivatives, the above results demonstrate the ability of bulky groups on the Lewis base to influence significantly the degree of association of compounds of indium.

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References

1 A.M. Arif, B.L. Benac, A.H. Cowley, R. Geerts, R.A. Jones, K.B. Kidd, J.M. Power, and S.T. Schwab, J. Chem. Soc., Chem. Commun., (1986) 1543.

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[*] Crystal data for 2: $C_{24}H_{56}In_2P_2$, $M = 636.30$. Monoclinic, space group I_2/m (alternative setting of C_2/m No. 12), a 14.869(3), b 11.605(2), c 9.003(1) Å, β 91.38(2)°, U 1553.06 Å^3, μ(Mo-K_α) 14.66 cm^{-1}, $Z = 2$, D_c 1.361 g cm^{-3}. The data were collected on a Philips PW1100 diffractometer in the θ-range 3–25° with a scan width of 0.70°. Structure was determined by the heavy atom method. All non-H atoms anisotropic; H-atoms in ideal positions. $R = 0.0432$, $R_w = 0.0346$ ($w = 1/\sigma^2(F)$) for 858 observed reflections. Coordinates and dimensions have been deposited with Cambridge Crystallographic Data Centre.

2 O.T. Beachley, Jr, J.P. Kopasz, H. Zhang, W.E. Hunter, and J.L. Atwood, J. Organomet. Chem., 325 (1987) 69.

3 C.J. Carrano, A.H. Cowley, D.M. Giolando, R.A. Jones, C.M. Nunn, and J.M. Power, Inorg. Chem., 27 (1988) 2709.

4 O.T. Beachley and G.E. Coates, J. Chem. Soc., (1965) 3241.

5 F. Maury and G. Constant, Polyhedron, 3 (1984) 581.