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Dimethylindium dialkylamides and organylphosphides, X-ray crystal structure of $(Me_2InNR_2)_2$ (R = Et, Pr^i, $SiMe_3$) and $(Me_2InPBu^t{}_2)_2$

Kenneth A. Aitchison, J.D. Julius Backer-Dirks, Donald C. Bradley *, Marc M. Faktor †, Dario M. Frigo, Michael B. Hursthouse *, Bilquis Hussain and Richard L. Short

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS (Great Britain)

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Abstract

The compounds $(Me_2InNR_2)_2$ (R = Et, Pr^i, $SiMe_3$) and $(Me_2InPR_2)_2$ (R = Bu^t, Ph) have been prepared. The X-ray crystal structures of all but the diphenylphosphide have been determined, and show them to be pnictido-bridged dimers; the mass spectra of all the compounds indicate that they are dimeric in the vapour phase. The stability of the dialkylamide dimers in the vapour as determined from the mass spectra appears to be in the order $NMe_2 > NEt_2 > NPr_2{}^i > N(SiMe_3)_2$, in line with steric effects; the crystal structures showed a slight lengthening of the In–N bond in the same order, but the most marked structural variation was shown to be the C–In–C angle which had values of 131, 126, 119 and 109°, respectively. The corresponding value for $(Me_2InPBu_2{}^t)_2$ was 109°.

Introduction

The chemistry of organo-indium compounds has recently received renewed attention because of their use as precursors for the Metal-organic Chemical Vapour Deposition (MOCVD) of single-crystal indium pnictides, materials that are of particular interest in the opto-electronics industry [1]. The currently used indium precursors are the trialkyls, or to a lesser extent their adducts with tertiary amines and phosphines; however, there is need for new precursors which present reduced fire and toxicity hazards whilst retaining the high volatility required for the MOCVD process. One approach to this may be by the use of bulky ligands that shield the metal centres from attack by atmospheric oxygen and water, and also reduce the tendency of the compounds to oligomerize, thus enhancing volatility.

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* Authors to whom correspondence should be addressed.

† Deceased.

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The dialkylindium pnictides were thought to be suitable systems in which to study these steric effects systematically. However, recent work has suggested that these systems may, in addition, prove to be useful precursors per se, as some have been shown to undergo thermolysis to the desired III–V material in the absence of any other Group V precursor [2]. Thus, the even greater hazards associated with the currently used Group V precursors (the hydrides) may be avoided at the same line as improvements in safety arising from use of Group III precursors.

The first dialkylindium dialkylamides [3] and dialkylphosphides [4], prepared by Coates et al., were generally found to be dimers and trimers in solution, respectively. The dimeric nature of $(Me_2InNMe_2)_2$ in the solid was subsequently confirmed by X-ray crystallography [5]. Further work on the dialkylamide system $Me_2In\overline{N(CH_2)_nC}H_2$ ($n = 1$–4) showed that in solution the first member ($n = 1$) was trimeric, but others in the series were dimers [6]. There remains, however, a dearth of X-ray structural data for amido compounds in the solid, but the structure of $[Me_2In\overline{N(CH_2)_2NMeCH_2C}H_2]_2$ is known [7]. There are even fewer data for the phosphides: the early work by Coates et al. showed them to be trimeric in solution [4], and more recent work on similar compounds has detected trimers in the mass spectra [8].

Coates attributed the degree of association in these compounds to a balance of steric effects, valency-angle strain, entropy, and the nature of reaction intermediates [9]. In order to explore the steric effects of the pnictide ligand we have synthesized and characterized a series of dimethylindium dialkylamides of varying alkyl size, as well as some fairly bulky diorganylphosphides.

Results and discussion

Reaction of trimethylindium with an excess of $NHMe_2$ followed by thermal elimination of methane [3] gave $(Me_2InNMe_2)_2$. Reaction of Me_2InCl with the *N*-lithiated derivatives of NHR_2($R = Et$, Pr^i, $SiMe_3$) in 1/1 molar ratio gave the corresponding $(Me_2InNR_2)_2$ compounds. Reaction of $Me_3In \cdot OEt_2$ with $PHBu_2{}^t$ gave $Me_3In \cdot PHBu_2{}^t$, which when heated at 170 °C for several hours liberated methane and gave $(Me_2InPBu_2{}^t)_2$. Similarly, a solution of $Me_3In \cdot OEt_2$ in diethyl ether was treated with $PHPh_2$, and began to liberate methane at ca. 0 °C, with precipitation of $(Me_2InPPh_2)_2$.

The compounds were obtained as white crystalline solids and all but $(Me_2InPPh_2)_2$ could be readily sublimed in vacuo. The diphenylphosphide began to decompose at 140 °C to a grey solid, and liberated a pyrophoric colourless liquid with a smell of a phosphine (and is tentatively suggested to contain Ph_2PPPh_2 on the basis of mass spectral evidence; vide infra). All the compounds were very sensitive to oxygen and water vapour except $(Me_2InPBu_2{}^t)_2$, which appeared to be unusually stable: crystals of ca. 1 mm dimensions showed only superficial decomposition after 24 h exposure to the air. Analytical and physical data for the compounds are given in Table 1. Selected IR and NMR spectral data are presented in Table 2.

The X-ray crystal structures of $(Me_2InL)_2$ where $L = NEt_2$, $NPr_2{}^i$, $N(SiMe_3)_2$ and $PBu_2{}^t$, are shown in Figs. 1–4, with selected structural parameters for these compounds and for $(Me_2InNMe_2)_2$ [5] in Table 3. As was found for other dimethylindium dialkylamides [5,7], the amido compounds are dimeric with a

Table 1

Analytical and physical data for the compounds prepared

Compound	M.p.(° C)	Accurate mass [a]	Analysis (%) [a]			
			C	H	N/P	In
$(Me_2InNMe_2)_2$	170–171 [b]	Monomer 189.0014 (189.0008)	25.4	6.2	7.3	60.7
		Dimer 378.0023 (378.0017)	(25.6)	(6.4)	(7.4)	(60.8)
$(Me_2InNEt_2)_2$	80– 90	Monomer 217.0430 (217.0321)	32.9	7.5	6.4	52.7
		Dimer 434.0584 (434.0643)	(33.2)	(7.4)	(6.5)	(52.9)
$(Me_2InNPr^i_2)_2$	110–112	Monomer 245.0643 (245.0634)	39.1	8.1	5.6	46.7
		Dimer 490.1293 (490.1269) [c]	(39.2)	(8.2)	(5.7)	(46.9)
$[Me_2InN(SiMe_3)_2]_2$	37– 38	Monomer 305.0497 (305.0486) [d]	– [e]	– [e]	– [e]	37.9
						(37.6)
$(Me_2InPBu^t_2)_2$	240 [f]	Dimer-Me565.1055 (565.1079)	40.7	8.1	Not obtained	Not obtained
			(41.4)	(8.3)		
$(Me_2InPPh_2)_2$	245 [g]		50.7	4.8	9.6	34.7
			(50.9)	(4.9)	(9.4)	(34.8)

[a] Required values are in parentheses. [b] Cf. 174–175 ° C, ref. 1. [c] Also, for dimer containing $^{115}In + ^{113}In$: $m/z = 488.1284$ (488.1271). [d] Also, for monomer containing ^{113}In: $m/z = 303.0510$ (303.0488). [e] Satisfactory C, H and N analyses could not be obtained. [f] Decomp. without melting. [g] Sample darkened slightly at 185 ° C.

central planar In_2N_2 unit. The effect on the molecular geometry of the increase in steric bulk along the series is interesting. The centrosymmetry on the methyl, ethyl, and trimethylsilyl derivatives is reflected in a narrow spread of values for chemically equivalent bond lengths and angles for each structure. The di-isopropylamide dimer, however, has an unsymmetrical structure, the most notable feature being the orientation of the isopropyl groups on the amide bridges (Fig. 2). In one bridge the two alkyl groups are disposed symmetrically in relation to the $N \cdots N$ vector, whilst in the other bridge one isopropyl group has swung round so as to lie over the In_2N_2 plane. The effect of this unsymmetrical configuration is to generate a considerable spread in the values of chemically-equivalent geometry parameters, both bond lengths and angles (see Table 3). However, except for an indication of an increase in the In–N bond length, variation in the geometry of the In_2N_2 ring

Table 2

Selected infrared and NMR data for the Me_2In moiety

Compound	Infrared bands (cm^{-1})				NMR signals (ppm)	
	Me deformation	Rocking mode	ν_{sym}	ν_{asym}	^1H	^{13}C
$(Me_2InNMe_2)_2$	1162 [a]	700 [a]	481 [a]	510 [a]	−0.16 [b]	Not obtained
$(Me_2InNEt_2)_2$	1159	699	475	507	−0.08 [c]	−10.8 [c]
$(Me_2InNPr^i_2)_2$	1165	70	471	492	0.09 [c]	−3.8 [c]
$[Me_2InN(SiMe_3)_2]_2$	1165	696 [d]	486	508	0.01 [b]	Not obtained
$(Me_2InPBu^t_2)_2$	1173	717, 690 [d]	478	503	Not obtained [e]	Not obtained [e]
$(Me_2InPPh_2)_2$	1160	695	472	508	0.18 [c]	−1.1 [c]

[a] In good agreement with refs. 1 and 3. [b] In $C_6D_5CD_3$. [c] In C_6D_6. [d] Assignment tentative. [e] Sample too insoluble.

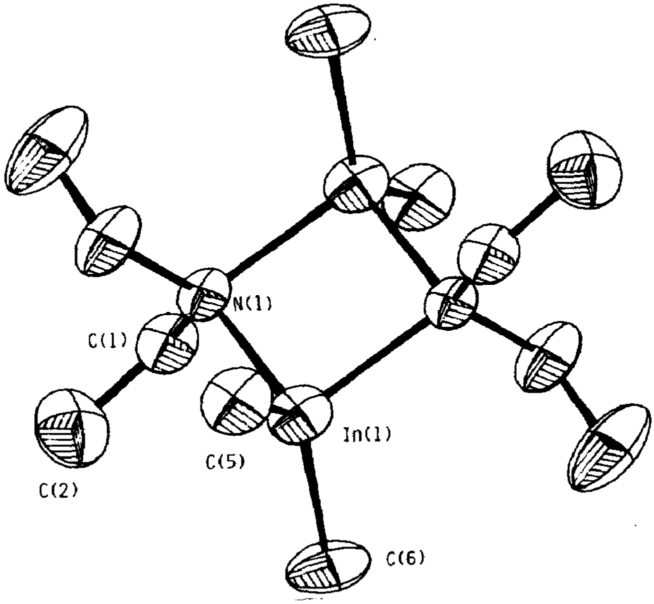

Fig. 1. Molecular structure of $(Me_2InNEt_2)_2$.

across the series is not generally systematic, and in fact the geometry of the ring is not strongly affected by steric factors. In contrast, the one parameter which does show a considerable change is the external C–In–C angle, which decreases along the series from 131° in the dimethylamide to 109° in the silylamide. It appears, therefore, that the increase in the steric bulk of the amido group along the series is accommodated in part by a small increase in the In–N distance and in part by a reduction in the C–In–C angle. It is of interest that where this reduction is not

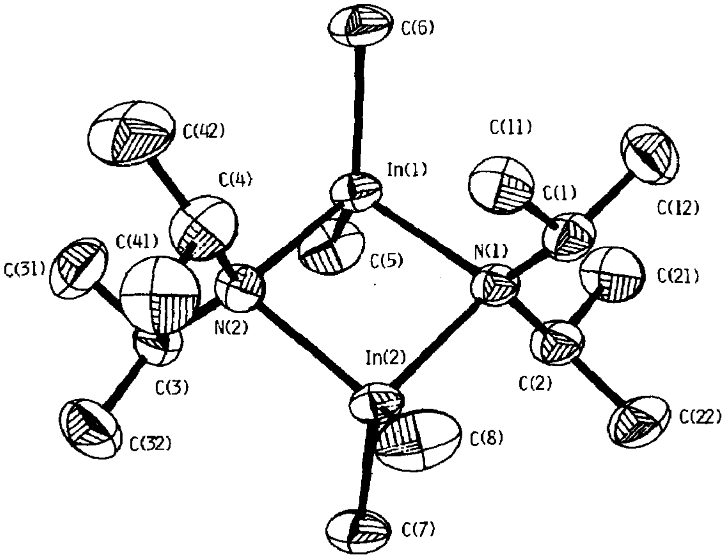

Fig. 2. Molecular structure of $(Me_2InNPr^i_2)_2$.

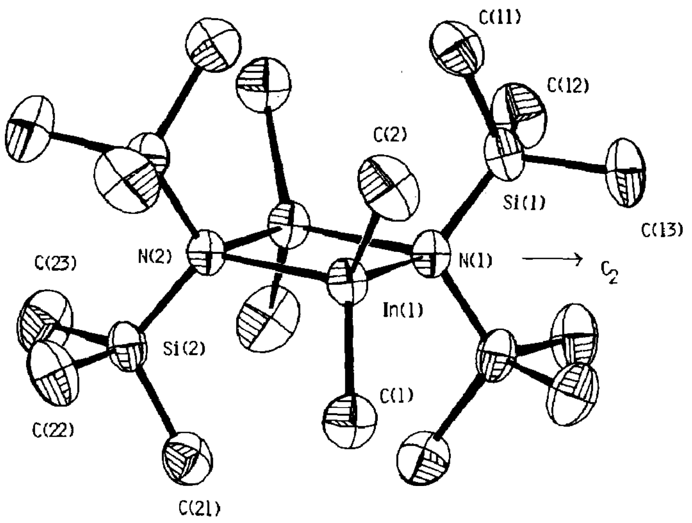

Fig. 3. Molecular structure of $[\mathrm{Me_2InN(SiMe_3)_2}]_2$.

feasible, viz. when the alkyl groups on the metal are also highly sterically demanding, then the dimeric structure cannot form, as shown by the monomeric $\mathrm{Bu_2^tIn\overline{NCMe_2(CH_2)_3CMe_2}}$ [10].

The dimerization of $(\mathrm{Me_2InPBu_2^t})_2$ is in contrast to the trimerization of analogous compounds with less bulky substituents, namely methyls and ethyls [4,8]. From the viewpoint of valency-angle strain, the cyclohexane-type trimer, with its almost tetrahedral angles, is optimal. Whether this structure is adopted, therefore, depends mainly upon the magnitude of the van der Waals repulsion between adjacent axial-equatorial and equatorial-equatorial substituents. Clearly, for small alkyl groups in conjunction with the comparatively long In–P covalent distance this repulsion is not large enough to override the advantages of negligible valency-angle

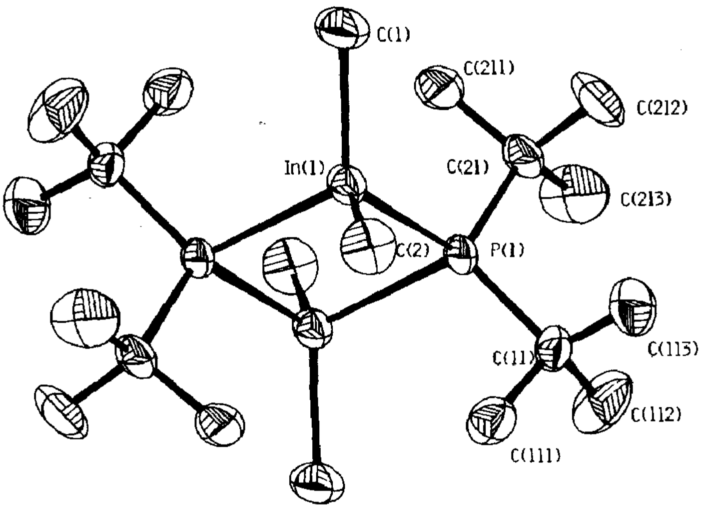

Fig. 4. Molecular structure of $(\mathrm{Me_2InPBu^t_2})_2$.

Table 3

Geometry of $[Me_2In(ER_2)]_2$ where E = N, P and R = Me, Et, Pr^i, $SiMe_3$, and Bu^t

Ligand	NMe_2 [a]	NEt_2	NPr^i_2	$N(SiMe_3)_2$	PBu^t_2
Bond lengths (Å)					
In–C	2.17(2)	2.147(3)	2.159(6)	2.161(6)	2.177(6)
	2.17(2)	2.171(4)	2.195(6)	2.163(6)	2.191(6)
In–E	2.22(2)	2.234(3)	2.242(6)	2.304(5)	2.637(4)
	2.22(2)	2.236(3)	2.284(6)	2.305(5)	2.656(4)
In···In	3.278(2)	3.269(1)	3.224(1)	3.270(1)	3.897(1)
Bond angles (°)					
C–In–C	131.3(4)	125.9(2)	118.1(3)	109.1(1)	108.6(3)
			119.9(3)		
E–In–E	85.7(4)	86.0(2)	87.7(2)	89.7(1)	85.2(3)
			87.9(2)		
C–In–E	106.9(6)	108.4(3)	106.3(2)	110.9(1)	116.3(2)
	107.6(6)	110.0(3)	120.0(3)	117.5(1)	116.1(2)
In–E–In	94.3(3)	94.0(2)	90.4(2)	90.3(1)	94.8(2)

[a] Data from reference 5.

strain. With the shorter In–N distances in the amide system, or with highly bulky t-butyl groups on the phosphorus in the phosphide system, then it appears energetically more favourable to form the dimer, thus leading to valency-angle strain in the inorganic nucleus (the internal angles reduce from 109.6 to ca. 90°) but reducing the van der Waals repulsion. It is most unlikely that the difference in entropy between a dimer and trimer will be very important in the solid state, but its effect will be larger in solution and may become a major factor in determining the degree of association in the vapour.

The ^1H NMR spectra confirmed the ratio of one pnictide ligand to two indium methyls for all but $(Me_2InPBu_2^t)_2$. This phosphide was so insoluble in the usual organic solvents (pentane, benzene, toluene, diethyl ether, tetrahydrofuran) that a reliable spectrum could not be obtained. A satisfactory spectrum was obtained of its precursor, $Me_3In \cdot PHBu_2^t$ (δ 0.96 (18H, d, J 12.3 Hz, Bu^t) 0.104 ppm (9H, s, Me–In)), but the corresponding phosphide showed no detectable solubility in boiling toluene after 2 h. A spectrum recorded for a deuteropyridine solution showed only what appeared to be peaks due to unchanged $Me_3In \cdot PHBu_2^t$ along with an excess of $PHBu_2^t$. There also appears to be nothing in the crystal structure of $(Me_2InPBu_2^t)_2$ (e.g. an indication of intermolecular interactions tending to give a quasi-polymeric structure) or in the enthalpy and entropy of vaporization [11], to account for this unusual behaviour.

As can be seen from Table 2, the ^1H NMR chemical shift of the Me–In signal for all the compounds examined is downfield of that due to Me_3In at δ -0.18 (in C_6D_6 or $C_6D_5CD_3$). The protons on the α-carbon of the diethylamide and di-isopropylamide are both shifted downfield relative to those for the parent amine, whereas those on β-carbon are shifted upfield and downfield, respectively. There is a downfield shift for the silylamide protons relative to those for hexamethyldisilazane. Because of the complexity of the spectrum of the diphenylphosphide a similar comparison is not possible. It has previously been noted that, in contrast to the dialkylamides, the signals from organo-amines are generally shifted upfield upon complex formation with organo-indium [12].

The dimethylindium moiety exhibits a number of well-defined bands in the infrared [3,5,13], some of which are tentatively assigned in Table 2. There appear to be no significant trends in these data as the pnictide group is varied. This is not very surprising in view of the small variation in the mean In–C distance (for the amides these all fall in the range 2.16–2.17 Å; the distance in the phosphide is slightly longer, 2.18 Å) although, as has been mentioned, there is a marked variation in the C–In–C angle. Hausen et al. reported a correlation between the difference, $\delta\nu$, between ν_{sym} (InC_2) and ν_{asym} (InC_2) and the C–In–C angle for dimethylindium compounds, especially the halides Me_2InX for which the correlation was linear. However, there does not appear to be any significant correlation between $\delta\nu$ and the C–In–C angle for the structurally characterized amides and phosphides.

As has been found with other similar compounds [7], the mass spectra of all the dialkylamides showed the presence of significant concentrations of the molecular ions due to both the dimer and the monomer, as well as predicted fragmentation products therefrom. The ratio of [dimer] : [monomer] at constant ionization energy (70 eV) was found to decrease as the steric bulk of the amide ligand increased: NMe_2, 2.74; NEt_2, 0.48; NPr_2^i, 0.28. Indeed the silylamide compound was so unstable that it gave a spectrum which contained peaks close to the dimer only when the ionization energy was reduced to 23 eV. The relationship between steric factors and the stability of the dimer is further indicated by the tendency of the less bulky NMe_2 and NEt_2 compounds to fragment via loss of methyl groups (thus maintaining the In_2N_2 core), whereas the NPr_2^i and $N(SiMe_3)_2$ show a greater tendency to lose NR_2.

These data also indicate that, at least for dialkylamides, the dimeric nature persists in the vapour at moderate temperature (as has been already observed for similar compounds from volatility measurements [14]); for the silylamide the data are inconclusive.

Similarly, the mass spectrum of $(Me_2InPBu_2^t)_2$ showed dimer and monomer peaks plus predicted fragments therefrom, but in addition these was a cluster of peaks we were unable to assign, at 151–155 mass units higher than the dimer. Only the peak at $(D + 153)$, i.e. m/z 733, has any substantial abundance, and this peak increases in abundance as the temperature is raised, possibly indicating that it is a decomposition product produced in the source.

The mass spectrum of $(Me_2InPPh_2)_2$ at 165 °C shows a low abundance protonated dimer $(M_2 + H)$ as well as readily assignable fragments. At all temperatures above 50 °C the spectrum was dominated by a peak at m/z 370, corresponding to Ph_2PPPh_2; in the spectrum at 165 °C this is the base peak together with that due to Ph_2P. It is possible that this diphosphine is a major product in the thermolysis of $(Me_2InPPh_2)_2$.

Metastable ions were observed for the amido compounds in order to throw light on possible decomposition pathways. Dimer → monomer metastable peaks were observed for $(Me_2InNEt_2)_2^+$ and $(Me_2InNPr_2^i)_2^+$ at m/z 108.6 (calc. 108.5) and 122.2 (122.5), respectively, but were absent for $(Me_2InNMe_2)_2^+$ and $[Me_2InN(SiMe_3)_2]_2^+$. For the dimethylamide, peaks were observed (inter alia) for the loss of CH_2 from the monomer at 111.9 (111.2). Although the dimer was not observed in the mass spectrum of the silylamide, its initial presence may be inferred from the observation of a metastable ion corresponding to the process (dimer) → (monomer $- CH_3 - CH_4$) at 123.2 (123.1).

Experimental

All operations were performed under purified nitrogen or argon by use of modified Schlenk-type all-glass apparatus. Solvents were distilled under nitrogen from the sodium ketyl of benzophenone. Amines and phosphines were dried over calcium hydride and distilled under nitrogen as required. Methyllithium (in diethyl ether) and n-butyllithium (in hexane) were obtained from commercial sources, and were filtered and standardized by a Gilman titration [15] immediately prior to use. Hexamethyldisilazane $(Me_3Si)_2NH$ was prepared by the reaction of chlorotrimethylsilane with liquid ammonia.

Chlorodimethylindium was prepared by a published method involving reactions of indium trichloride with methyllithium in 1/2 molar ratio [16]. Analysis for indium was performed by a modification of Beachley and Coates' method involving EDTA titration [4]. Analyses for C,H,N and P were carried out by the Micro-analytical Laboratory of University College, London. Infrared spectra were recorded as Nujol mulls between CsI plates with a Perkin–Elmer 577 spectrophotometer over the range 4000–200 cm^{-1}. NMR spectra were recorded on Bruker WP80 FT and WH400 FT spectrometers, with solutions in solvents distilled from sodium wire or 3A molecular sieves. Proton chemical shifts are quoted relative to TMS with the signals due to incomplete solvent deuteration used as internal standard. Mass spectra were obtained with an AEI MS902 instrument fitted with a variable temperature direct insertion probe, a device for handling air-sensitive compounds developed by Cook and Copperthwaite being used [17]. In general, only principal peaks are reported; m/z values for ions being used containing In refer to the ^{115}In isotope.

Bis(μ-dimethylamido)-tetramethyldi-indium(III)

This was prepared in a manner similar to that used by Coates et al. [3]; the product was sublimed at 60 °C/10^{-2} mmHg. δ(H) (80 MHz, $C_6D_5CD_3$): −0.16(12H, s, Me–In) 2.41 ppm (12H, s, N–Me); m/z (21 °C, 70 eV): 378 (18%, M_2), 363 (94, $M_2 - Me$) 334 (40, $M_2 - NMe_2$) 320 (23, $M_2 - NMe_2 - CH_2$) 233 (12, $M + NMe_2$) 189 (7, M) 188 (100, $M - H$) 174 (14, $M - Me$) 158 (22, $M - 2Me - H$) 145 (92, Me_2In) 115 (77, In).

Bis(μ-diethylamido)-tetramethyldi-indium(III)

A slight excess of diethylamine was added at 0 °C to a stirred solution of n-butyllithium (3.1 cm^3 of 1.56 *M* solution, 4.8 mmol) diluted with diethyl ether (20 cm^3). The mixture was allowed to warm to room temperature and solvent and excess amine were removed in vacuo. The residue was redissolved in ether (20 cm^3) and the solution added to a stirred suspension of Me_2InCl (0.9 g, 5 mmol) in ether (20 cm^3) at −80 °C. The mixture was allowed to warm to room temperature, at which a white precipitate was present (LiCl). The ether was removed in vacuo and replaced by pentane, and after 30 min stirring at room temperature the mixture was filtered. The residue was washed with more pentane nd the combined filtrates were concentrated in vacuo then kept at −25 °C to give colourless crystals. These sublimed at 70 °C/10^{-2} mmHg; 0.9 g, 83% yield based upon Me_2InCl. IR (below 1500 cm^{-1}): 1357s, 1342m, 1282m, 1166w sh, 1159m, 1140s, 1105m br, 1039m, 1000s, 895w, 847m, 790s, 699s br, 663m br, 559s, 540m, 507s, 475s, 455w, 450w, 317w br, 270w, 265w, 220m cm^{-1}; δ(H) (80 MHz, C_6D_6): −0.08 (12H, s, Me–In) 0.82 (12H, t, *J* 6.8 Hz,CH_2–$C\mathit{H}_3$) 2.87 (8H, q, *J* 6.8 Hz,CH_2); δ(C) (100.6 MHz, C_6D_6): −10.8 (C–In), 12.6 (CH_3–C) 42.7 ppm (CH_2); *m/z* (21 °C, 70 eV); 434 (4%, M_2) 419 (46, $M_2 - Me$) 362 (30, $M_2 - NEt_2$) 348 (9, $M_2 - CH_2NEt_2$) 217 (9, *M*) 216 (100, $M - H$) 202 (29, $M - Me$) 172 (11, $M - Et - CH_4$) 145 (61, Me_2In) 115 (71, In).

Bis(μ-di-isopropylamido)-tetramethyldi-indium(III)

This was prepared in a similar manner to $(Me_2InNEt_2)_2$ from Me_2InCl (1.4 g, 7.8 mmol), n-butyllithium (5 cm^3 of 1.56 *M* solution, 7.8 mmol), ether (30 cm^3) and a slight excess of di-isopropylamine. The colourless crystals thus obtained sublimed at 100 °C/10^{-2} mmHg; 1.4 g, 73% based upon Me_2InCl.

IR (below 1500 cm^{-1}): 1365s, 1330m, 1259w, 1165s, 1145s, 1128m, 1105m, 1022w br, 1014w br, 969m, 961m sh, 909m, 835w, 825vw, 779m, 740s, 715s sh, 700 vs br, 650w, 622w, 605m, 561m, 492s, 471s, 455m, 415m br, 320w, 312w, 298w, 288w, 270w, 262w, 240w, 219m cm^{-1}. δ(H) (80 MHz, C_6D_6): 0.09(12H, s, Me–In) 1.13(24H, d, *J* 7.0 Hz, CH–$C\mathit{H}_3$) 3.55(4H, sept, *J* 7.0 Hz, CH); δ(C)(100.6 MHz, C_6D_6): −3.8(C–In) 26.3(C–CH_3) 50.8 ppm (CH): *m/z* (56 °C, 70 eV): 490 (1%, M_2) 475(16, $M_2 - Me$) 390(21, $M_2 - NPr_2^i$) 245(4, *M*) 244(20, $M - H$) 230(51, $M - Me$) 215(7, $M - 2Me$) 200(14, $M - 3Me$) 145(55, Me_2In) 130(5, MeIn) 115(51, In).

Bis[μ-bis(trimethylsilyl)amido]-tetramethyldi-indium(III)

This was prepared in a similar manner to $(Me_2In \cdot NEt_2)_2$ using Me_2InCl (0.3 g, 1.7 mmol), n-butyllithium (0.9 cm^3 of 1.86 *M* solution, 1.7 ether mmol), (20 cm^3) and hexamethyldisilazane (0.3 cm^3, 2.4 mmol). The colourless crystals obtained sublimed at 50 °C/10^{-2} mmHg.

IR (below 1500 cm^{-1}): 1396w, 1368w sh, 1341vw sh, 1285w sh, 1257s, 1248s, 1182w, 1165w, 1010s, 965s br, 940m sh, 879s, 864s, 848s sh, 835s, 825sh, 789m, 752s, 741m sh, 696m, 672s, 615m, 569w sh, 519m, 508m, 486m, 463m br, 391w, 357s, 329w, 299w sh, 281w, 245m cm^{-1}; δ(H) (80 MHz, $C_6D_5CD_3$): 0.01(12H, s, Me–In) 0.20 ppm (36H, s, Si–Me); *m/z* (40 °C, 23 eV): 524(6%, $M_2 - NSiMe_2CH_2$) 435[9, $M_2 - N(SiMe_3)_2 - Me$] 305(31, *M*) 291 (100, $M - CH_2$) 274(18, $M - CH_3 - CH_4$) 260(42, $M - 3Me$) 161[40, $HN(SiMe_3)_2$] 146[100, $HN(SiMe_3)(SiMe_2)$] 143(12, unassigned) 130 [100, $N(SiMe_3)SiMe$] 115(63, In).

Bis(μ-di-t-butylphosphido)-tetramethyldi-indium(III)

Methyllithium (75 cm^3 of 1.81 *M* solution, 136 mmol) was added dropwise to a stirred suspension of $InCl_3$ (10.0 g, 45 mmol) in diethyl ether (50 cm^3). The precipitate (LiCl) was filtered off and to the filtrate was added $PHBu_2^t$ (6.6 g, 45 mmol) in benzene (50 cm^3). The ether was fractionated off through a 20 cm glass helices column and finally the benzene was removed in vacuo to leave a white solid, which was shown by ^1H NMR spectroscopy to be $Me_3In \cdot PHBu_2^t$. This was kept at 170 °C under one atmosphere of nitrogen for 6 h until the molten adduct had been entirely converted (via loss of methane) into the required product, which is a solid at this temperature. The solid was sublimed at 160 °C/10^{-2} mmHg to give large colourless crystals of $(Me_2InPBu_2{}^t)_2$; 10.7 g, 82% yield based upon $InCl_3$. IR (below 1500 cm^{-1}): 1387m, 1367s, 1362m sh, 1344w sh, 1310 w br, 1262m, 1204w, 1173s, 1147s, 1130w, 1021s, 1011m, 975vw br, 953w, 936m, 933m sh, 910–930m vbr, 862w br, 819 m, 802m, 717s, 690s, 657m br, 602w, 578w sh, 534w, 503w, 478vs, 444m, 371w cm^{-1}; m/z (98 °C, 41 eV) 733 (13%, unassigned) 581(6, $M_2 + H$) 580(3, M_2) 565(94, $M_2 - Me$) 535(10, $M_2 - PCH_2$) 493(10, $M_2 + H - PBu^t$) 436(12, $M + PHBu_2{}^t$ or $M + Me_2In + H$) 435(76, $M + PBu_2{}^t$ or $M + Me_2In$) 405(19, $M +$ In) 275(227, $M -$ Me) 260(10, $M -$ 2Me) 146(9, $PHBu_2{}^t$) 145(18, Me_2In or $PBu_2{}^t$) 115(65, In).

Bis(μ-diphenylphoshido)-tetramethyldi-indium(III)

Methyllithium (38.7 cm^3 of 2.0 *M* solution, 77.4 mmol) was added dropwise to a stirred suspension of $InCl_3$ (57.0 g, 25.7 mmol) in diethyl ether (50 cm^3). The $Me_3In \cdot OEt_2$ and excess of ether were distilled off in vacuo, the distillate was cooled to −80 °C, and a solution of diphenylphosphine (4.8 g, 26 mmol) in ether (25 cm^3) was added. The mixture was stirred and allowed to warm to room temperature. At ca. 0 °C gas evolution occurred, followed by the deposition of a white solid. The mixture was stirred at room temperature overnight to allow the

Table 4

Crystal data, and details of intensity measurements and structure refinement for $[Me_2InL]_2$

L	NEt_2	NPr^i_2	$N(SiMe_3)_2$	PBu^t_2
Formula	$[C_6H_{16}InN]_2$	$[C_8H_{20}InN]_2$	$[C_8H_{24}InSi_2]_2$	$[C_5H_{12}InP]_2$
M	434.04	490.15	526.32	465.90
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$C2/c$
a (Å)	7.543(2)	7.639(2)	15.525(4)	13.847(4)
b (Å)	8.349(1)	10.587(2)	11.538(3)	12.860(4)
c (Å)	8.462(2)	13.814(2)	16.939(8)	15.408(1)
α (°)	76.51(1)	85.06(1)	90.0	90.0
β (°)	118.37(2)	81.41(2)	111.97(3)	103.59(1)
γ (°)	104.02(2)	76.37(2)	90.0	90.0
U ($Å^3$)	450.5	1071.97	2810.96	2666.92
Z	1	2	4	4
D_c (g cm^{-3})	1.60	1.52	1.24	1.16
$F(000)$	216	496	1248	920
μ (cm^{-1})	23.50	19.80	16.72	16.96
hkl range	$0 \rightarrow 8$	$0 \rightarrow 9$	$-18 \rightarrow 18$	$-21 \rightarrow 21$
	$-9 \rightarrow 9$	$-12 \rightarrow 12$	$0 \rightarrow 13$	$0 \rightarrow 18$
	$-10 \rightarrow 10$	$-16 \rightarrow 16$	$0 \rightarrow 20$	$0 \rightarrow 19$
Total No. of reflections	1598	3850	2932	4174
No. of unique reflections	1574	3776	2388	3881
Significance test.	$F_0 > 3\sigma(F_0)$	$F_0 > 3\sigma(F_0)$	$F_0 > 3\sigma(F_0)$	$F_0 > 6\sigma(F_0)$
No. of observed reflections	1524	3417	2180	2512
No. of refined parameters	137	118	112	141
Weighting scheme parameter g in $w = 1/[\sigma^2(F_0) + gF_0{}^2]$	0.00006	0.002	0.00003	0.0004
Final R	0.0256	0.0310	0.0273	0.0263
Final R_w	0.0267	0.0327	0.0277	0.0282

reaction to reach completion, and the solvent and any excess of phosphine were then removed in vacuo at just above room temperature; 8.2 g, 81% yield based upon $InCl_3$. IR (below 2000 cm^{-1}): 1578m, 1562m, 1472s, 1429s, 1325m, 1305m, 1265w, 1188m, 1160w, 1090w br, 1069w, 1025m, 1000m, 970w, 916w br, 845w, 752s, 745s, 695vs, 508s, 496m, 472m, 470m sh, 435w br, 380w, 250vw cm^{-1}; δ(H) (80 MHz, C_6D_6): 0.18(12H, s, Me) 6.8–7.7(20H, two overlapping complex multiplets, Ph); δ(C) (100.6 MHz, C_6D_6): −1.1 (Me) multiplet around solvent 125–128 plus multiplets at 133.2 and 133.4 (Ph); δ(P) (162 MHz, C_6D_6, relative to phosphoric acid): −53.1 ppm; m/z (165 °C, 70 eV): 661(0.2%, M_2 + H) 491(2, M_2 − Me − 2Ph) 370(100, Ph_2PPPh_2) 262(7,Ph_3P) 185(100, Ph_2P) 145(52, Me_2In) 139(9, PhP_2) 130(6, MeIn) 115(30, In) 109(11, PhPH) 108(92, PhP) 107(50, C_6H_4P).

Table 5

Atomic coordinates ($\times 10^4$) for $[Me_2In(NEt_2)]_2$

Atom	x	y	z
In(1)	1872(1)	947(1)	1651(1)
N(1)	283(4)	8338(3)	1242(3)
C(1)	1648(6)	7220(4)	1433(5)
C(2)	3278(7)	6824(6)	3361(6)
C(3)	−787(7)	7654(5)	2406(5)
C(4)	−2070(9)	5935(5)	2059(8)
C(5)	1047(7)	1851(5)	3352(5)
C(6)	4933(6)	1206(6)	1918(7)

Table 6

Atomic coordinates ($\times 10^4$) for $[Me_2In(NPr_2)]_2$

Atom	x	y	z
In(1)	−6337(0)	7977(0)	1369(0)
In(2)	−6635(0)	7470(0)	3717(0)
N(1)	−7129(4)	9241(3)	2656(2)
N(2)	−6512(4)	6232(3)	2444(2)
C(1)	−9032(5)	10053(4)	2843(3)
C(2)	−5710(5)	9966(3)	2746(3)
C(3)	−4716(5)	5285(4)	2335(3)
C(4)	−8237(6)	5779(5)	2442(4)
C(5)	−3447(5)	7850(4)	889(3)
C(6)	−8221(6)	8354(4)	302(3)
C(7)	−3853(5)	7166(4)	4069(3)
C(8)	−8834(7)	7579(6)	4923(3)
C(11)	−10409(5)	9242(5)	2800(3)
C(12)	−9474(7)	11256(4)	2141(4)
C(21)	−5301(6)	10916(4)	1878(3)
C(22)	−6010(6)	10649(4)	3701(3)
C(31)	−4148(7)	4640(5)	1357(4)
C(32)	−4398(8)	4219(5)	3154(4)
C(41)	−8754(8)	4959(6)	3343(4)
C(42)	−8428(8)	5198(6)	1503(4)

Table 7

Atomic coordinates ($\times 10^4$) for $[Me_2In\{N(SiMe_3)_2\}]_2$

Atom	x	y	z
In(1)	957	2301	2310
C(1)	2345(3)	2437(3)	3266(3)
C(2)	1049(3)	2172(4)	1071(3)
N(1)	0	885(3)	2500
Si(1)	−652(1)	18(1)	1611(1)
C(11)	−1091(3)	773(4)	560(2)
C(12)	−1724(3)	−554(4)	1737(3)
C(13)	26(3)	−1228(3)	1443(3)
N(2)	0	3702(3)	2500
Si(2)	450(1)	4571(1)	3433(1)
C(21)	1197(3)	3778(3)	4411(2)
C(22)	1206(3)	5767(4)	3347(3)
C(23)	−516(3)	5216(4)	3702(3)

X-ray crystallography

Crystals of the four compounds examined were sealed under argon in thin-walled glass capillaries. All X-ray measurements were made using a CAD4 diffractometer operating in the $\omega/2\theta$ scan mode and graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å), following procedures previously described in detail [18]. In each case, one asymmetric unit of data were recorded in the range $1.5 < \theta < 25°$ and corrected for absorption empirically [19]. The structures were solved via routine heavy atom methods and refined via full matrix least squares with the non-hydrogen atoms assigned anisotropic temperature factors. For the ethyl- and isopropyl-amides and the di-t-butylphosphide, most hydrogen atoms were located experimentally, but it proved to be more convenient to refine those of the methylene and methyl groups as components of rigid bodies with a common overall U_{iso} value.

The idealised positions generated were all consistent with the experimental positions. For the silylamide all hydrogens were located and refined isotropically. In the final stages of refinement the weighting scheme $w = [\sigma^2(F_0) + g(F_0)^2]^{-1}$ was

Table 8

Atomic coordinates ($\times 10^4$) for $[Me_2In(PBu^t_2)]_2$

Atom	x	y	z
In(1)	3096.5(2)	6140.2(2)	324.6(2)
P(1)	1946.1(6)	7466.8(7)	939.4(5)
C(1)	2427(4)	4641(3)	−154(3)
C(2)	4562(4)	5860(4)	1185(3)
C(11)	2528(3)	7989(3)	2096(2)
C(21)	666(3)	6914(3)	865(3)
C(111)	3560(3)	8380(4)	2054(3)
C(112)	1952(4)	8909(5)	2347(4)
C(113)	2659(5)	7156(5)	2806(3)
C(211)	294(3)	6541(4)	−99(3)
C(212)	693(4)	5975(4)	1479(4)
C(213)	−64(4)	7719(5)	1051(4)

used with values of *g* selected to give flat agreement analyses. Details of the data collection and refinement are given in Table 4. Computer programs were used and sources of scattering factor data were as given in Ref. 18. Final atomic positional parameters are given in Tables 5–8. Lists of thermal parameters and observed and calculated structure factors are available from the authors.

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