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ADDUCTS OF TRIMETHYLINDIUM WITH AMINE AND PHOSPHINE LIGANDS; X-RAY CRYSTAL STRUCTURE OF $Me_3InNHCMe_2(CH_2)_3CMe_2$, $Me_3InN(CH_2CH_2)_3N$ AND $Me_3InNHMe(CH_2)_2NHMeInMe_3$ *

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Summary

Treatment of trimethylindium diethyletherate separately with a number of amines and a phosphine has given the products Me_3InL where $L = NH(C_6H_{11})_2$ (**1**), $NHCHMe(CH_2)_3CHMe$ (**2**), $NHCMe_2(CH_2)_3CMe_2$ (**3**), $N(CH_2CH_2)_3CH$ (**4**), $N(CH_2CH_2)_3N$ (**5**), $(CH_2NEt)_3$ (**6**) and $P(NMe_2)_3$ (**7**). The complexes $Me_3InNHMe(CH_2)_2NHMeInMe_3$ (**8**) and $Me_2InCl[MeNHC(CH)_4N]$ (**9**) have also been made by direct reaction of Lewis acid etherate and Lewis base. The X-ray crystal structure of **3** shows a longer In–N bond (2.50 Å) than that found in the crystal structure of **8** (2.38 Å); both possess distorted tetrahedral metal environments. The X-ray crystal structure of **5** shows a linear polymer of alternating Me_3In and $N(CH_2CH_2)_3N$ units; the Me_3In unit is planar and the indium is almost perfectly trigonal bipyramidal and the In–N bonds are very long (2.62 Å) compared with **3** and **8**. Variable temperature ^1H NMR studies of **6** show the adduct bond is very labile: rapid exchange between adduct components is occurring even at $-70\,°C$.

Introduction

The use of trimethylindium (TMI) and more recently its adducts with amines and phosphines, for the Metal-Organic Chemical Vapour Deposition (MOCVD) [1] of indium pnictides, has led to renewed interest in organo-indium chemistry in general. The desire to produce volatile MOCVD precursors which do not present the fire and toxicity hazards of TMI has prompted the present work.

Initial work by Coates et al. produced 1/1 adducts of TMI with $L = NH_3$, $NHMe_2$, NMe_3, PMe_3, $AsMe_3$, OEt_2 and SMe_2 [2] and subsequently $PHMe_2$,

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$PHEt_2$ and $AsHMe_2$ [3]. Other workers have prepared a varied host of 1/1 adducts e.g. with $L = SbEt_3$ [4], piperidine [5], $Me_3P{=}CH_2$ [6], as well as 2/1 adducts $L = Me_2N(CH_2)_xNMe_2$ ($x = 2, 3$) [7], urotropin [8], the last also giving a 1/1 and 3/1 adduct. In these compounds the metal environment is thought to be 4-coordinate and distorted tetrahedral; similar adducts have been obtained from the organometallic halides e.g. Me_2InX(pyridine) (X = Cl, I) [9]. Complexes with bidentate ligands are known in which the metal is believed to be 5-coordinate and probably trigonal bipyramidal e.g. $Me_3In(Me_2NCH_2NMe_2)$ [7], $Me_2InCl \cdot L$ where L = 1,10-phenanthroline, 2,2′-bipyridyl [10].

We have prepared some complexes of TMI with some amines and one phosphine, plus a complex between Me_2InCl and a diamine. The X-ray crystal structures (which are relatively scarce for compounds of this type) show examples of the metal in both tetrahedral and trigonal bipyramidal environments.

Results and discussion

A series of compounds Me_3InL where $L = NH(C_6H_{11})_2$ (**1**), $\overline{NHCHMe(CH_2)_3CHMe}$ (**2**), $\overline{NHCMe_2(CH_2)_3CMe_2}$ (**3**), $N(CH_2CH_2)_3CH$ (**4**), $N(CH_2CH_2)_3N$ (**5**), $(CH_2NEt)_3$ (**6**) and $P(NMe_2)_3$ (**7**), have been prepared by reaction of L with Me_3InOEt_2 in 1/1 molar ratio. Also $Me_3InNHMe(CH_2)_2NHMeInMe_3$ (**8**) was prepared by treating Me_3InOEt_2 with L in either 2/1 or 1/1 molar ratio. Finally, $Me_2InCl[MeNHC\overline{(CH)_4N}]$ (**9**) was prepared by a similar route. Selected analytical data are presented in Table 1.

The adducts have properties broadly similar to those first described by Coates et al. [2], being volatile, white, crystalline solids at room temperature; the only exception is **6** which melts at 0.5–3.0 °C (vide infra). Almost all are very soluble in organic solvents and are very air- and moisture-sensitive; only **5** is neither appreciably soluble nor air-sensitive.

The compounds **1**, **2**, **3** and **8**, are all capable of eliminating methane with the formation of metal-amido compounds; a reaction first noted by Coates et al. None of these compounds readily performed this reaction and could be sublimed repeatedly without visible decomposition; in fact the synthesis of **3** involved prolonged heating in boiling toluene, but still gave no decomposition product. In contrast, the adduct formed between TMI and *N*-methylpiperazine was not recovered as after 2 h in diethyl ether at room temperature the elimination to $[Me_2In\overline{N(CH_2)_2NMeCH_2CH_2}]_2$ was complete [11]. Alkane elimination between TMI and 2-methylaminopyridine to form $MeIn[MeN\overline{C(CH)_4N}]_2$ was even more facile, occurring rapidly at ca. 0 °C. [11,12]. On the other hand, elimination between TMI and $NHMe_2$ required heating to 140–160 °C for 30 min [2]. Why there should be this remarkable difference in reactivity is not clear, but the ease of reaction with *N*-methylpiperazine and 2-methylamidopyridine may be due to these being diamines: upon ligation 5-coordinate indium may be formed which, because of steric crowding and/or bonding changes caused by the different geometry, facilitates elimination. This does not explain however, why 1/1 treatment of TMI with *N*,*N*′-dimethylethylenediamine gave rise to what appeared from ^1H NMR data to be a 1/1 adduct (probably 5-coordinate also), but upon sublimation at 90 °C/10^{-1} mmHg, only **8** was obtained, with no evidence of alkane elimination products.

The facile formation of $MeIn[MeN\overline{C(CH)_4N}]_2$ can be contrasted with that of **9**:

TABLE 1

SELECTED ANALYTICAL DATA FOR THE COMPOUNDS

Compound	M.p. (°C)	^{1}H NMR (C_6D_6) δ(Me-In)	Analysis (%) [a]		
			C	H	N
Me_3In	88.4 [b]	−0.18	–	–	–
$Me_3InNH(C_6H_{11})_2$ (1)	43–45	0.13	52.5	9.3	4.0
			(52.8)	(9.4)	(4.1)
$Me_3In\overline{NHCHMe(CH_2)_3CHMe}$ (2)	37.5–38.5	0.03	40.2	7.9	4.9
			(44.0)	(8.9)	(5.1)
$Me_3In\overline{NHCMe_2(CH_2)_3CMe_2}$ (3)	60.5–62.5	0.12	44.1	8.5	4.3
			(46.3)	(8.5)	(4.3)
$Me_3InN(CH_2CH_2)_3CH$ (4)	85.5–91	−0.07	42.3	7.7	5.1
			(44.3)	(8.2)	(5.2)
$Me_3InN(CH_2CH_2)_3N$ (5)	160–164 [c]	−0.15 [d]	39.1	7.8	10.0
			(39.7)	(7.8)	(10.3)
$Me_3In(CH_2NEt)_3$ (6)	0.5–3.0	−0.02	43.1	8.9	12.7
			(43.5)	(9.1)	(12.7)
$Me_3InP(NMe_2)_3$ (7)	139–142	0.09	32.9	8.2	12.7
			(33.5) [e]	(8.4)	(13.0)
$(Me_3In)_2$dmed [f] (8)	64.5–69.5	−0.08	28.7	7.4	6.6
			(29.4)	(7.4)	(6.9)
$Me_2InCl[MeNH\overline{C(CH)_4N}]$ (9)	83–86	0.21	33.4	4.9	9.4
			(33.3) [g]	(4.9)	(9.7)

[a] Required values in parentheses. [b] Reference 13. [c] Crystal shrinkage followed by sublimation at ca. 180 °C. [d] Nature of solution species is unknown. [e] Also P: 9.8 (9.6)%. [f] dmed = $NHMe(CH_2)_2NHMe$. [g] Also Cl: 12.5 (12.3)%.

another compound believed to be 5-coordinated (vide infra) and which can be sublimed at 90 °C/10^{-2} mmHg without loss of CH_4 or HCl.

The X-ray crystal structures of **3** and **8** are shown in Figs. 1 and 2 with parameters in Tables 2 and 3 respectively. The metal exhibits the expected distorted tetrahedral geometry. The amine lone pair in **8** is relatively unhindered sterically and possesses an In–N distance of 2.37 Å; in **3** this parameter is 2.50 Å, longer by 5%. In the amine adducts generally the structures appear to be arranged to minimize Van der Waals repulsion between substituents on the indium and on the nitrogen by staggering these as much as possible. Therefore, the longer In–N bond in **3** is probably due to repulsion between the indium methyl groups and the 4 methyls on the amine. This contrasts with the structure of Me_3InPMe_3 in which the substituents are eclipsed, believed to be due to Van der Waals attraction because the In–P bond is much longer than the In–N [14].

The X-ray crystal structure of **5** (see Figs. 3 and 4 and Table 4) shows infinite linear chains of planar TMI unit (the plane exactly normal to the chain axis) bridged by the two amine functions of the $N(CH_2CH_2)_3N$ ligand (dabco). The methyl groups of all the TMI units are eclipsed but each is perfectly staggered with respect to the ethylene bridges of the dabco. The indium is thus in a trigonal bipyramidal configuration and the chain axis constitutes a pseudo-3-fold rotation axis (one of the In–C distances is very slightly shorter than the other two). The In–N length is very long: at 2.62 Å it is 11% longer than in **8**. This is probably due to the metal being 5-coordinate: using a valence-bond approach, the metal is

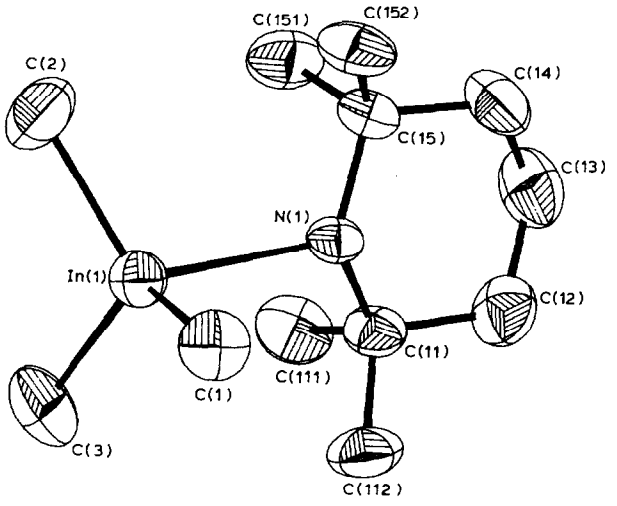

Fig. 1. Molecular structure of $Me_3InNHCMe_2(CH_2)_3CMe_2$ (**3**) showing the numbering scheme.

probably sp^3d hybridized i.e. donation from the nitrogen lone pairs is into a combination of $5p_z$ and $5d_{z^2}$ orbitals on the metal; these would be weaker interactions than donations into a single vacant hybrid (as is probably the case in normal 1/1 adducts). It is for this reason that 5-coordinate indium which persists in solution, normally only occurs with chelating ligands [7,10]. That the In–N interaction in **5** is weak is shown by the fact that it can be sublimed repeatedly. It is not known whether discrete 1/1 adduct molecules, small oligomers or even uncomplexed TMI and dabco, are present in the gas phase. Volatility data on **5** suggest that complete dissociation is unlikely [15].

Compound **5** is unique in being the only adduct of TMI which is completely air-stable in the solid state. Presumably the metal centre is so effectively shielded by its own 3 methyl groups, 2 nitrogens and 2 sets of 3 methylene groups, that atmospheric oxygen and water cannot penetrate. This may also explain its slow and sparing solubility in organic solvents; even tetrahydrofuran, acetonitrile or pyridine: the polymer would tend to be broken down by a strong donor solvent, but this is

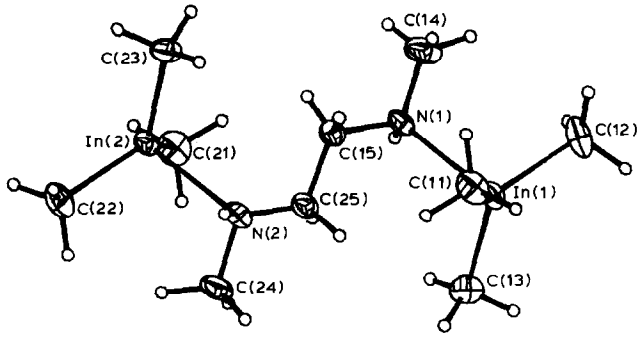

Fig. 2. Molecular structure of $Me_3InNHMe(CH_2)_2NHMeInMe_3$ (**8**) showing the numbering scheme.

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR COMPOUND **3**

C(1)–In(1)	2.170(5)	C(2)–In(1)	2.186(6)
C(3)–In(1)	2.174(6)	N(1)–In(1)	2.502(5)
C(11)–N(1)	1.515(5)	C(15)–N(1)	1.503(6)
C(12)–C(11)	1.535(7)	C(111)–C(11)	1.537(6)
C(112)–C(11)	1.530(6)	C(13)–C(12)	1.490(7)
C(14)–C(13)	1.520(8)	C(15)–C(14)	1.533(7)
C(151)–C(15)	1.526(6)	C(152)–C(15)	1.534(7)
C(2)–In(1)–C(1)	118.9(3)	C(3)–In(1)–C(1)	116.5(3)
C(3)–In(1)–C(2)	109.3(3)	N(1)–In(1)–C(1)	92.8(2)
N(1)–In(1)–C(2)	108.2(2)	N(1)–In(1)–C(3)	109.3(2)
C(11)–N(1)–In(1)	114.6(3)	C(15)–N(1)–In(1)	117.7(3)
C(15)–N(1)–C(11)	117.3(3)	C(12)–C(11)–N(1)	110.7(4)
C(111)–C(11)–N(1)	110.5(3)	C(111)–C(11)–C(12)	111.0(4)
C(112)–C(11)–N(1)	106.7(3)	C(112)–C(11)–C(12)	108.5(4)
C(112)–C(11)–C(111)	109.3(4)	C(13)–C(12)–C(11)	114.1(4)
C(14)–C(13)–C(12)	109.8(4)	C(15)–C(14)–C(13)	113,6(4)
C(14)–C(15)–N(1)	111.6(4)	C(151)–C(15)–N(1)	110.3(4)
C(151)–C(15)–C(14)	111.3(4)	C(152)–C(15)–N(1)	106.3(3)
C(152)–C(15)–C(14)	107.6(4)	C(152)–C(15)–C(151)	109.5(4)

hindered in the same way that oxygen is. Enough **5** was dissolved in C_6D_6, C_5D_5N, or CD_3CN to obtain ^1H NMR spectra: two singlets due to the dabco (a) and the TMI (b); the ratios of the integrations of a/b however, ranged from 0.83–1.8/1 depending on the solvent used (theoretical 1.33/1), showing that simple, complete dissolution of the compound does not occur. The species in solution (and presumably in the gas phase also) is very air/moisture sensitive, consistent with a dissolved species containing indium with a lower coordination number.

TABLE 3

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR COMPOUND **8**

N(1)–In(1)	2.369(7)	C(11)–In(1)	2.170(9)
C(12)–In(1)	2.176(10)	C(13)–In(1)	2.183(9)
N(2)–In(2)	2.393(7)	C(21)–In(2)	2.174(9)
C(22)–In(2)	2.147(10)	C(23)–In(2)	2.178(8)
C(14)–N(1)	1.470(10)	C(15)–N(1)	1.479(9)
C(24)–N(2)	1.482(10)	C(25)–N(2)	1.432(9)
C(25)–C(15)	1.517(12)		
C(11)–In(1)–N(1)	96.3(3)	C(12)–In(1)–N(1)	98.8(4)
C(12)–In(1)–C(11)	117.6(4)	C(13)–In(1)–N(1)	101.4(3)
C(13)–In(1)–C(11)	119.6(4)	C(13)–In(1)–C(12)	115.9(4)
C(21)–In(2)–N(2)	96.6(3)	C(22)–In(2)–N(2)	99.5(4)
C(22)–In(2)–C(21)	119.8(4)	C(23)–In(2)–N(2)	100.9(3)
C(23)–In(2)–C(21)	120.2(4)	C(23)–In(2)–C(22)	113.0(4)
C(14)–N(1)–In(1)	109.2(5)	C(15)–N(1)–In(1)	117.4(5)
C(15)–N(1)–C(14)	110.9(7)	C(24)–N(2)–In(2)	107.9(5)
C(25)–N(2)–In(2)	116.8(5)	C(25)–N(2)–C(24)	109.0(6)
C(25)–C(15)–N(1)	112.9(6)	C(15)–C(25)–N(2)	112.3(6)

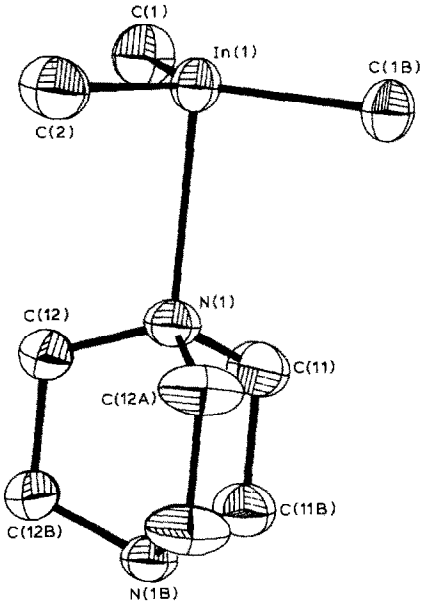

Fig. 3. Molecular structure of $Me_3InN(CH_2CH_2)_3N$ (**5**) showing the numbering scheme.

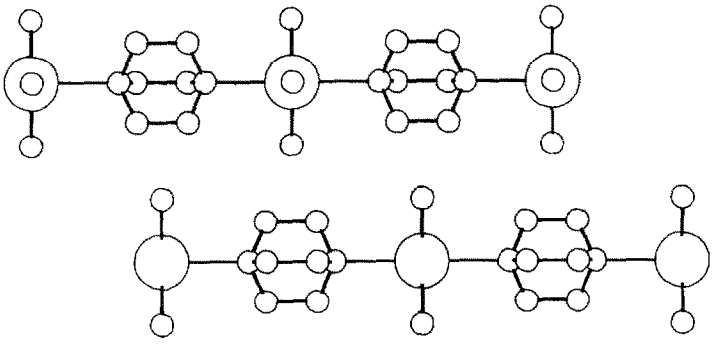

Fig. 4. Crystal packing of $Me_3InN(CH_2CH_2)_3N$ (**5**).

TABLE 4

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR COMPOUND **5**

C(1)–In(1)	2.176(5)	C(2)–In(1)	2.172(7)
C(11)–N(1)	1.475(6)	C(12)–N(1)	1.472(4)
C(11)–C(11a)	1.545(8)	C(12)–C(12a)	1.536(7)

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z):
(a) x, $0.5-y$, z

C(2)–In(1)–C(1)	119.4(2)	C(12)–N(1)–C(11)	107.8(3)
C(12)–N(1)–C(12)	108.7(4)		

It appears to be a general rule that in the ^1H NMR, the chemical shifts of the Lewis base are moved upfield upon ligation to indium. This has been observed previously [16] and is here illustrated with respect to the shift of the protons on the carbon α to the coordinating nitrogen where the effect is most marked (80 MHz, C_6D_6, δ(ppm)): **4** δ 2.48 compared to free quinuclidine δ 2.78; **5** δ 2.03 compared to free dabco δ 2.47. Furthermore, the chemical shift of the proton in the 2-position of the pyridine ring in **9** is 7.34 ppm, as compared with 8.22 ppm in the free amine; that of the N-Me protons in **9** is at δ 2.15 ppm, as compared with 2.56 ppm in the free amine. We regard this as strong evidence that both nitrogens in **9** are coordinated to the metal which would consequently be 5-coordinate.

The ^1H NMR chemical shifts of the Me-In signals for the compounds are shown in Table 1. It is significant that all shifts of the adducts are downfield of those for free TMI, from which it might be thought that, ceteris paribus, the more downfield the chemical shift, the stronger the complex. The chemical shift in C_6D_6 for Me_3InNMe_3, Me_3InPMe_3 and **3** are δ -0.09, 0.06 and 0.12 ppm, respectively, whereas the adduct bond energies are 83 ± 2 [2], 71.5 ± 3 [2] and 48 ± 5 kJ mol^{-1} [15], respectively. This trend is the reverse of that predicted above, so this simplistic approach is not very useful; also the scarcity of data hampers development of a better theory.

The adduct with 1,3,5-triethylhexahydro-1,3,5-triazine viz. **6**, is rather low melting, being a colourless liquid at room temperature. This is believed to be due in part to inherent disorder in the adduct making crystallization more difficult: flipping of the cyclohexane-type amine.

Variable temperature ^1H NMR data of **6** are presented in Table 5, together with that of the free amine and of a mixture in which the TMI/amine ratio is 1/2.5. In

TABLE 5

VARIABLE TEMPERATURE ^1H NMR DATA ON $(CH_2NEt)_3$ AND ITS ADDUCT WITH Me_3In

Compound	Temperature (K)	Chemical shifts δ(ppm) (solvent $C_6D_5CD_3$)			
		CH_2 (ring)	NCH_2CH_3 [a]	NCH_2CH_3 [b]	Me–In [c]
Pure $(CH_2NEt)_3$	303	3.27 [c]	2.40	0.98	–
(Measured at	283	3.26 [c,d]	2.38	0.98	–
80 MHz)	263	Coalesced	2.38	0.99	–
	243	3.77, 2.76 (mean 3.27) [d,e]	2.38	1.01	–
	223	3.81, 2.73 (mean 3.27) [e]	2.39	1.02	–
	203	3.82, 2.74 (mean 3.28) [d,e]	2.39 [d]	1.04 [d]	–
Me_3In and	303	3.16 [c]	2.33	0.89	−0.13
$(CH_2NEt)_3$ in 1/1	283	3.15 [c,d]	2.30	0.89	−0.09
molar ratio	263	Coalesced	2.28	0.88	−0.07
(Measured at	243	3.56, 2.66 (mean 3.11) [d,e]	2.24	0.88	−0.01
80 MHz)	223	3.58, 2.63 (mean 3.10) [e]	2.22	0.88	+0.06
	203	3.56, 2.58 (mean 3.07) [d,e]	2.17 [d]	0.86 [d]	+0.09 [d]
$(CH_2NEt)_3$ and	297	3.19 [c]	2.34	0.94	−0.15
Me_3In in 2.5/1	277	Coalesced	2.33	0.94	−0.10
molar ratio	257	3.65, 2.71 (mean 3.18) [d,e]	2.32	0.95	−0.06
(Measured at	237	3.66, 2.68 (mean 3.17) [e]	2.31	0.95	−0.01
400 MHz)	217	3.67, 2.66 (mean 3.17) [d,e]	2.29 [d]	0.96 [d]	+0.05 [d]

[a] Quartet: J 7 Hz. [b] Triplet: J 7 Hz. [c] Singlet. [d] Broad. [e] AB spectrum: J 10 Hz.

all cases the cyclohexane-type ring of the amine is rapidly flipping at room temperature: axial and equatorial protons interchanging (presumably by the chair $\rightleftharpoons$ boat process) fast enough to give a single resonance in the spectrum. As the temperature is lowered the signal collapses and subsequently separates into an AB system; J_{gem} 10 Hz.

A complete flip would also cause the ethyl groups on the nitrogens to go from tri-equatorial to tri-axial, so the nitrogens must invert as part of the fluxional process; the result is that a TMI unit initially coordinated would then be on the wrong side of the ring to coordinate. This implies that the amine is very labile. From the table the following observations are noted:

(a) The mean chemical shifts of the methylene protons both on the ring and on the ethyl groups in the free amine does not alter significantly as the temperature is lowered; those of the adduct are upfield of these values at room temperature and move further upfield as the temperature is lowered. This is consistent with the equilibrium shifting towards more associated adduct (vide supra).

(b) The coalescence temperature of the ring methylene protons is in the same range in the presence or absence of TMI viz. 243–263 K at 80 MHz, implying that the metal has little effect on the "freezing out" of the ligand fluxionality; consistent with a very labile equilibrium between associated and unassociated adduct, and/or rapid exchange of adduct components.

(c) With a 2.5/1 ratio of amine to TMI the ring methylene protons show one singlet at room temperature separating into one AB pattern at lower temperature. Therefore, there is exchange between adduct components which is so facile that it is rapid compared with the NMR timescale even at 217 K, using a 400 MHz instrument.

Insufficient information is available to obtain equilibrium constants (and hence the enthalpy of adduct formation): no values are known for the chemical shifts of the true 1/1 adduct as the values in Table 5 are the weight averaged values of free and complexed components. The low temperature values are probably quite close to the true values for the adduct, but an even better approximation would be a low temperature spectrum containing adduct with a large excess of TMI present such that nearly all amine was present as the adduct. Unfortunately the Me-In signal cannot be used since the change in chemical shift due to degree of association cannot easily be distinguished from that due to solvent anisotropy. This effect can be seen in the spectrum of the pure amine: although the methylene protons are essentially temperature independent, the methyl groups which are more peripheral in the molecule, are not.

The mass spectra of all of the adducts were dominated by peaks due to Me_2In^+, $MeIn^+$, In^+, the Lewis bases and products of fragmentation from the base. The parent molecular ion (M) is rarely observed, even at low electron energy (ca. 20 eV) however, there are frequently peaks present in low abundance with $m/z > M$.

Experimental

All operations were performed under an atmosphere of purified nitrogen using Schlenk-style apparatus and a glove box. Solvents were distilled from sodium benzophenone under nitrogen. Anhydrous $InCl_3$, all amines and solutions of MeLi (in Et_2O), were obtained from commercial sources. ^1H NMR spectra were obtained using a Bruker WP80 FT and WH400 FT spectrometer; mass spectra using an AEI

MS902 spectrometer (only principal peaks are reported; in assignments, In refers to ^{115}In); and micro-analyses were by the Microanalytical Laboratory of University College, London. The presence of indium was detected qualitatively by the performance of a simple flame test (purple).

Me_2InCl was prepared as in the literature: $InCl_3$ was treated with MeLi in a 1/2 molar ratio [9]. Melting points and elemental analyses are presented in Table 1.

Trimethyl(dicyclohexylamine)indium(III) (1)

MeLi (33.5 cm^3 of 1.67 *M* solution, 56 mmol) was added dropwise to a stirred suspension of $InCl_3$ (4.1 g, 18 mmol) in diethyl ether (35 cm^3) at 0 °C. The contents were allowed to warm to room temperature and the white precipitate filtered off, leaving a clear, colourless filtrate, to which was added $NH(C_6H_{11})_2$ (3.85 cm^3, 19 mmol). After stirring at room temperature for 20 min, the ether was removed in vacuo to leave a sticky, pale green liquid. This was dissolved in pentane (10 cm^3) and cooled to give white crystals which sublimed at 55 °C/10^{-2} mmHg; 4.7 g, 77% yield. δ(H) (80 MHz, C_6D_6) 0.13 (9H, s, Me-In) 0.90–1.85 (21H, br, m, CH_2 and NH) 2.55 ppm (2H, br m, CH); *m/z* 181 (17%, amine) 145 (46, Me_2In) 138 (100, amine − C_3H_6) 130 (6, MeIn) 115 (24, In).

Trimethyl(2,6-dimethylpiperidine)indium(III) (2)

This was prepared in a similar manner to **1** using $InCl_3$ (1.0 g, 4.5 mmol), MeLi (11.5 cm^3 of 1.20 *M* solution) and 2,6-dimethylpiperidine (0.85 cm^3, 6 mmol). Solvent was removed from the reaction mixture at −20 °C, in vacuo to leave a white solid; this was recrystallized from pentane and sublimed at 30 °C/10^{-1} mmHg 0.97 g, 79% yield. δ(H) (80 MHz, C_6D_6) 0.03 (9H, s, Me-In) 0.5–1.5 (7H, br m, CH_2 and NH) 0.90 (6H, d, *J* 6Hz, -CH*Me*-) 2.27 ppm (2H, br m, -C*H*Me-); *m/z* 160 (0.5%, Me_3In) 145 (100, Me_2In) 130 (12, MeIn) 115 (45, In) 113 (21, amine) 112 (11, amine − H).

Trimethyl(2,2,6,6-tetramethylpiperidine)indium(III) (3)

MeLi (13.5 cm^3 of 1.67 *M* solution, 22.5 mmol) was added to a suspension of $InCl_3$ (1.7 g, 7.5 mmol) in diethyl ether (25 cm^3) at 0 °C. This was allowed to warm to room temperature and the white precipitate filtered off. Then 2,2,6,6-tetramethylpiperidine (1.45 cm^3, 8.6 mmol) in toluene (25 cm^3) was added to the filtrate and ether was fractionated off at atmospheric pressure using a 15 cm glass helices column. The toluene was removed in vacuo and the white solid residue was sublimed at 30 °C/10^{-1} mmHg; 1.8 g, 82% yield. δ(H) (80 MHz, C_6D_6) 0.12 (9H, s, Me-In) 0.9–1.4 (7H, br m, CH_2 and NH) 1.12 ppm (12H, s, -CMe_2-); *m/z* 301 (8%, *M*), 149 (10, unassigned) 145 (100, Me_2In) 142 (13, amine + H) 141 (8, amine) 130 (17, MeIn) 127 (10, amine − CH_2) 126 (42, amine − Me) 115 (50, In).

Trimethyl(quinuclidine)indium(III) (4)

This was prepared in a similar manner to **1** using $InCl_3$ (2.5 g, 11 mmol), MeLi (18.5 cm^3 of 1.83 *M* solution, 34 mmol) and quinuclidine (1.3 g, 12 mmol). The product sublimed at 75 °C/10^{-1} mmHg; 2.5 g, 81% yield. δ(H) (80 MHz, C_6D_6) −0.07 (9H, s, Me-In) 1.03 (6H, m, CH-CH_2) 1.26 (1H, sept. *J* 3 Hz, CH) 2.48 ppm (6H, m, N-CH_2); *m/z* 347 (17%, unassigned) 345 (28, unassigned) 256 (5, *M* − Me) 145 (100, Me_2In) 130 (9, MeIn) 115 (28, In) 110 (55, amine − H).

Catena-trimethyl-μ-1,4-diazabicyclo[2.2.2]octane-N,N'-indium(III) (5)

This was prepared in a similar manner to **1** using $InCl_3$ (1.3 g, 6 mmol), MeLi (11.5 cm^3 of 1.54 *M* solution, 18 mmol) and 1,4-diazabicyclo[2.2.2]octane (0.7 g, 6 mmol). Upon removal of the reaction solvent in vacuo, the resulting white solid could not be redissolved, even in pyridine, tetrahydrofuran or acetonitrile. It was sublimed at 95 °C/10^{-2} mmHg; 1.0 g, 61% yield. δ(H) (80 MHz, C_6D_6) singlets at −0.15 and 2.03 ppm in the ratio 1.2/1, but see Results and Discussion, above; *m/z* 145 (85%, Me_2In) 143 (7, $Me_2In - 2H$) 130 (15, MeIn) 115 (64, In) 113 (9, amine + H) 112 (64, amine) 97 (7, amine − Me) 84 (19, amine − C_2H_4).

Trimethyl(1,3,5-triethylhexahydro-1,3,5-triazine)-indium(III) (6)

This was prepared in a similar manner to **1** using $InCl_3$ (2.0 g, 9 mmol), MeLi (20 cm^3 of 1.35 *M* solution, 27 mmol) and 1,3,5-triethylhexahydro-1,3,5-triazine (1.75 cm^3, 9 mmol). Removal of solvent in vacuo left a creamy, white liquid which was distilled at 50 °C/10^{-1} mmHg to give a clear colourless liquid; 2.2 g, 74% yield. δ(H) (80 MHz, C_6D_6) −0.02 (9H, s, Me-In) 0.87 (9H, t, *J* 7 Hz, N-CH_2-CH_3) 2.30 (6H, q, *J* 7 Hz, N-CH_2-CH_3) 3.16 ppm (6H, br s, ring CH_2); see also variable temperature data in Results and Discussion, above; *m/z* 317 (1.4%, *M* − CH_2) 316 (8, *M* − Me) 171 (25, amine) 170 (17, amine − H) 145 (100, Me_2In) 130 (11, MeIn) 115 (34, In) 114 (32, amine − C_2H_4 − C_2H_5) 113 (amine − $2C_2H$).

Trimethyl[tris(dimethylamido)phosphine-P]indium(III) (7)

This was prepared in a similar manner to **1** using $InCl_3$ (3.3 g, 15 mmol), MeLi (38 cm^3 of 1.17 *M* solution, 45 mmol) and hexamethylphosphorustriamide (2.8 cm^3, 16 mmol). The product was sublimed at 50 °C/10^{-1} mmHg; 3.3 g, 68% yield. δ(H) (80 MHz, C_6D_6) 0.09 (9H, s, Me-In) 2.33 (18H, d, *J*(P–H) 9.4 Hz, N-Me); *m/z* 308 (0.8%, *M* − Me) 164 (3, Phosphine + H) 163 (36, Phosphine) 145 (67, Me_2In) 130 (8, MeIn) 120 [6, $PH(NMe_2)_2$] 119 [99, $P(NMe_2)_2$] 115 (35, In) 76 (100, $PHNMe_2$).

Hexamethyl-μ-[1,2-bis(methylamino)ethane-N,N']di-indium(III) (8)

This was prepared in a similar manner to **1** using $InCl_3$ (2.35 g, 10.5 mmol), MeLi (18.5 cm^3 of 1.75 *M* solution, 32 mmol) and *N,N'*-dimethylethylenediamine (0.60 cm^3, 5.7 mmol). Removal of ether in vacuo, gave a white solid which was distilled at 90 °C/10^{-1} mmHg; 1.1 g, 52% yield. δ(H) (80 MHz, C_6D_6) −0.08 (18H, s, Me-In) 0.68 (2H, br m, NH) 1.77 (6H, d, *J* 7 Hz, N-Me) 2.08 ppm (4H, m, CH_2); δ(C) (20.1 MHz, C_6D_6) −7.2 (Me-In) 35.9 (N-Me) 49.0 (CH_2); *m/z* 233 (9%, amine + Me_2In) 203 (1, amine + In) 145 (100, Me_2in) 130 (28, MeIn) 115 (99, ^{115}In) 113(5, ^{113}In).

Chlorodimethyl(2-methylaminopyridine-N,N')indium(III) (9)

Me_2InCl (1.3 g, 7.2 mmol) was dissolved in diethyl ether (40 cm^3) and 2-methylaminopyridine (0.85 cm^3, 8 mmol) was added. The contents were heated to reflux for 2 h, and after cooling to room temperature, solvent was removed in vacuo to leave an off-white solid residue. This was recrystallized from toluene and sublimed at 90 °C/10^{-2} mmHg; 1.2 g, 59% yield based on Me_2InCl. δ(H) (80 MHz, C_6D_6) 0.21 (6H, s, Me-In) 2.15 (3H, d, *J* 5.3 Hz, N-Me) 5.7–7.4 ppm (4H, 3 distinct multiplets, aromatic protons); *m/z* 145 (1%, Me_2In) 108 (8, amine) 107 (100, amine − H) 106 (27, amine − 2H) 79 (52, amine − NMe).

X-ray crystallography

Crystals of all three compounds were sealed under nitrogen 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 (λ 0.71069 Å), following previously detailed procedures [17]. The structures were solved via the heavy atom method and refined via full matrix least-squares, with all non-hydrogen atoms assigned anisotropic temperature factors. For compound **3**, methyl hydrogens were inserted in idealised positions and refined as parts of rigid groups with group U_{iso} values; other hydrogens were located experimentally and freely refined isotropically. For compound **5**, all hydrogen were freely refined isotropically, except those attached to C(2) which are disordered. For compound **8**, hydrogens were treated as for compound **3**. In the final stages of refinement the

TABLE 6

CRYSTAL DATA, DETAILS OF INTENSITY MEASUREMENTS AND STRUCTURE REFINEMENT FOR COMPOUNDS **3**, **5** AND **8**

	3	**5**	**8**
Formula	$InNC_{12}H_{28}$	$InN_2C_9H_{23}$	$In_2N_2C_{10}H_{30}$
M	301.154	274.094	407.960
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/a$	$Pmmn$	$P2_1/n$
a (Å)	15.086(2)	10.831(3)	11.527(3)
b (Å)	12.714(3)	7.835(1)	13.487(4)
c (Å)	7.771(2)	6.740(2)	11.948(3)
α (°)	90	90	90
β (°)	94.15(1)	90	111.74(2)
γ (°)	90	90	90
U (Å^3)	1486.59	571.96	1725.31
Z	4	2	4
D_c (g cm^{-3})	1.345	1.591	1.570
F(000)	624	276	800
μ (cm^{-1})	24.51	14.34	18.62
θ-range (°)	2.0, 30.0	2.0, 30.0	1.5, 25.0
h, k, l range	0– > 21, 0– > 17, −10– > 10	−15– > 15, 0– > 11, 0– > 9	0– > 13, 0– > 16, −14– > 14
Total no. of reflections	4645	1895	3444
No. of unique reflections	4318	930	3028
Significance test	$F_0 > 3\sigma(F_0)$	$F_0 > 6\sigma(F_0)$	$F_0 > 3\sigma(F_0)$
No. of observed reflections	3565	841	2191
No. of refined parameters	183	46	184
Max. least-squares	−0.224	−0.406	−0.214
Min. and Max. height in final difference map, $\Delta\rho$ (ē Å^{-3})	−0.772, 0.605	−1.489, 2.237	−0.837, 0.885
Function minimized	$\Sigma w(\|F_0\| - \|F_c\|)^2$	$\Sigma w(\|F_0\| - \|F_c\|)^2$	$\Sigma w(\|F_0\| - \|F_c\|)^2$
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.00002	0.0005	0.0006
Final R	0.0354	0.0230	0.0435
Final R_w	0.0360	0.0291	0.0469

TABLE 7

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR COMPOUND **3**

Atom	*x*	*y*	*z*
In(1)	1478(0.5)	651(0.5)	941(0.5)
C(1)	1166(3)	2074(3)	−522(4)
C(2)	1917(4)	−739(3)	−418(6)
C(3)	533(3)	180(4)	2779(6)
N(1)	2807(2)	1467(2)	2530(3)
C(11)	2663(2)	1809(2)	4356(4)
C(12)	3458(3)	2452(3)	5118(5)
C(13)	4336(3)	1939(4)	4956(6)
C(14)	4457(2)	1700(3)	3071(5)
C(15)	3706(2)	1034(2)	2197(4)
C(111)	2495(3)	849(3)	5490(4)
C(112)	1839(3)	2515(3)	4246(5)
C(151)	3779(3)	−113(3)	2769(6)
C(152)	3780(3)	1102(4)	243(5)

TABLE 8

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR COMPOUND **5**

Atom	*x*	*y*	*z*
In(1)	7500	7500	7972(0.5)
C(1)	5750(3)	7500	6386(6)
C(2)	7500	7500	11195(8)
N(1)	7500	4149(3)	7949(4)
C(11)	7500	3486(4)	5901(5)
C(12)	6395(3)	3480(3)	8957(6)

TABLE 9

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR COMPOUND **8**

Atom	*x*	*y*	*z*
In(1)	2409(0.5)	1276(0.5)	2224(0.5)
In(2)	2830(0.5)	1222(0.5)	8022(0.5)
N(1)	2606(5)	2199(4)	3972(5)
N(2)	2731(5)	274(4)	6296(5)
C(11)	4214(7)	551(6)	2971(7)
C(12)	2218(8)	2504(7)	985(7)
C(13)	712(6)	427(6)	1946(7)
C(14)	3353(8)	3093(6)	4021(8)
C(15)	3069(7)	1670(6)	5139(6)
C(21)	1064(7)	1994(6)	7169(7)
C(22)	2967(8)	36(7)	9263(7)
C(23)	4587(6)	2008(5)	8412(6)
C(24)	1939(8)	−606(5)	6228(7)
C(25)	2279(7)	775(6)	5157(6)

weighting scheme $w = [\sigma^2(F) + g(F_0)^2]$ was used with g values chosen to give flat agreement analyses. Full details of experimental data are given in Table 6. Final atomic coordinates are given in Tables 7–9. Lists of thermal parameters and structure factors are available from the authors.

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