Synthesis and Thermal Properties of Adducts of Trimethylindium with Nitrogen-containing Lewis Bases†

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Adducts of trimethylindium with a range of nitrogen-containing Lewis bases have been prepared, and their thermal properties investigated. No adduct formation is observed with triphenylamine or *N,N,N′,N′*-tetramethyl-1,8-naphthalenediamine. From Lewis-base solvents such as diethyl ether, volatile 1 : 1 adducts can be isolated with 3,3′-bipyridyl (3,3′-bipy), 4,4′-bipy, 4-dimethylamino-pyridine, and *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (tmpd), as well as a volatile 2 : 1 ($InMe_3$: Lewis base) adduct formed with *N,N,N′,N′*-tetramethylethylenediamine. In order to prepare 2 : 1 ($InMe_3$: Lewis base) adducts of 3,3′-, 4,4′-bipy, and tmpd it is necessary to use non-co-ordinating hydrocarbon solvents. Of these, the 3,3′-bipy and tmpd adducts dissociate on heating *in vacuo* to afford the corresponding 1 : 1 adducts and trimethylindium, whereas the 4,4′-bipy adduct sublimes intact. In both co-ordinating and non-co-ordinating solvents, 2,2′-bipy forms non-stoicheiometric adducts whose properties have not been investigated further. Factors influencing adduct stoicheiometry are discussed.

The growth of epitaxial layers of semiconductors comprising compounds of Groups 3 and 5 or 2 and 6 by metal–organic chemical vapour deposition (m.o.c.v.d.) has become of major importance to the electronics industry. Extensive studies have shown that the electrical properties of these layers depend critically upon the purity of the metal alkyl sources employed in their growth, and this has provided an exciting challenge to the organometallic chemist in the development of purification techniques for the removal of metal-containing impurities in these alkyls to levels below 1 p.p.m.

One method that has been successfully employed by ourselves,[1–3] and others,[4,5] involves the formation of involatile adducts with Lewis bases containing Group 5 or 6 elements, which dissociate on heating at atmospheric pressure or *in vacuo* to liberate the metal alkyl. Volatile impurities can be removed by evacuation at temperatures below the dissociation temperature of the adduct, whilst involatile impurities remain when the adduct is dissociated. Using this approach, trimethylgallium[1] and trimethylindium[2] have been purified by the use of adducts with high-boiling ether solvents, whilst dimethylzinc and dimethylcadmium have been purified from adducts formed with nitrogen-donor Lewis bases.[3,4]

The purification of trimethylindium from high-boiling ethers suffers from two major drawbacks. First, trimethylindium cannot be prepared directly in these solvents and the purification procedure is therefore complicated,[2] and secondly ethers contain oxygen which even when incorporated at very low levels may have detrimental effects upon the electrical or optoelectronic properties of layers of Group 3–Group 5 semiconductors. In view of these problems we have surveyed a range of reactions between trimethylindium and Group 5 donor ligands, with a view to finding adducts which may be more suitable for the purification of trimethylindium than those with high-boiling ethers.

During the course of these studies, which led[6] to the successful discovery of a new purification method for trimethylindium from an adduct with an involatile nitrogen-donor Lewis base, we have synthesised a number of stable, volatile adducts of trimethylindium with bidentate nitrogen-donor ligands: examples of such adducts are known for monodentate nitrogen-donor ligands.[7] We now report the results of these studies.

Experimental

All solvents were carefully dried by distillation from sodium diphenylketyl and were degassed prior to use. The Lewis bases (Aldrich) were reagent grade and were purified by crystallisation from an ether solution or, by sublimation *in vacuo*. Reactions were carried out in an atmosphere of argon purified by passing through a column consisting of Cr^{2+} on silica. Greaseless joints and taps were employed and manipulations were carried out using standard Schlenk-line and catheter-tubing techniques.

Microanalyses (C, H, and N) were performed on a Carlo-Erba 1106 carbon, hydrogen, and nitrogen analyser. Proton n.m.r. spectra were recorded on a Bruker Associates WP-80 spectrometer and mass spectra on an Associated Electrical Industries MS 902 double-focusing spectrometer using a solid probe. Molecular-weight determinations were conducted cryoscopically using benzene as solvent.

Preparations.—Trimethylindium(III). A modified version of the procedure outlined by Runge *et al.*[8] was employed. A Grignard solution, prepared by reaction of MeI (220 cm^3, 3.51 mol) with magnesium turnings (88.5 g, 3.64 mol) in diethyl ether (2 000 cm^3), was added to a stirred suspension of anhydrous $InCl_3$ (221 g, 1.00 mol) in diethyl ether (100 cm^3) so as to maintain a steady reflux (*ca.* 3 h). The resulting dirty grey solution was externally refluxed for a further 3 h. The product and diethyl ether were collected into a −196 °C cold-trap as a clear colourless solution by vacuum distillation at temperatures up to 200 °C for 7 h. Distillation of excess of diethyl ether at atmospheric pressure through an 18-in column packed with Fenske helices afforded the ether adduct $Me_3In{\cdot}OEt_2$. Repeated distillation of the etherate at room temperature *in vacuo* afforded $InMe_3$ (147 g, 92%) as a white microcrystalline solid, identified by comparison of its proton n.m.r. spectrum with an authentic sample. The product was stored under vacuum and transferred *via* condensation at −196 °C to an evacuated Schlenk tube.

(*3,3′-Bipyridyl*)*trimethylindium*(III). 3,3′-Bipyridyl (2.77 g,

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† *Non-S.I. units employed:* in = 2.54×10^{-2} m, Torr ≃ 133 Pa.

17.7 mmol) was added to InMe$_3$ (2.83 g, 17.7 mmol) in diethyl ether (25 cm^3). The resulting pale yellow solution was allowed to stand at room temperature overnight, and the air-stable, white, needle-shaped crystals which formed were collected, washed with light petroleum (b.p. 40—60 °C) and dried *in vacuo*. Addition of light petroleum (25 cm^3) to the mother-liquor followed by cooling to -30 °C afforded a second batch of crystals which were similarly treated (5.32 g, 95%).

Reaction in diethyl ether of 3,3′-bipy with a 2:1 excess of InMe$_3$ afforded only [InMe$_3$(3,3′-bipy)], no 2:1 adduct [(InMe$_3$)$_2$(3,3′-bipy)] could be isolated when using diethyl ether as the solvent.

(4,4′-Bipyridyl)trimethylindium(III). Following the above procedure, [InMe$_3$(4,4′-bipy)] was isolated as air-stable, white, needle-shaped crystals (5.64 g, 93%) from 4,4′-bipy (3.00 g, 19.2 mmol) and InMe$_3$ (3.07 g, 19.2 mmol) in diethyl ether (40 cm^3) [Found: *M* (cryoscopic) 319. C$_{13}$H$_{17}$InN$_2$ requires *M* 316]. No 2:1 adduct, [(InMe$_3$)$_2$(4,4′-bipy)], could be isolated when using a 2:1 excess of InMe$_3$ and diethyl ether as the solvent.

Trimethyl(N,N,N′,N′-*tetramethyl*-1,4-*phenylenediamine*)-*indium*(III). Following the above procedure, [InMe$_3$(tmpd)] was isolated as white needle-shaped crystals (4.19 g, 88%) on cooling to -30 °C of a diethyl ether (40 cm^3) solution of *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (tmpd) (2.42 g, 14.7 mmol) and InMe$_3$ (2.37 g, 14.8 mmol). These crystals turned pale yellow on standing in air for several hours. No 2:1 adduct, [(InMe$_3$)$_2$(tmpd)], could be isolated when using a 2:1 excess of InMe$_3$ and diethyl ether as the solvent.

Heating [InMe$_3$(tmpd)] (10.0 g) at 100 °C *in vacuo* led to the slow release of InMe$_3$ (0.47 g, 9.5% after 6 h), which was collected at -196 °C. Raising the temperature above 100 °C caused the intact adduct to sublime in addition to release of InMe$_3$.

(4-Dimethylaminopyridine)trimethylindium(III). Following the above procedure, [InMe$_3$(dmapy)] was isolated as air-stable, white, needle-shaped crystals (4.29 g, 91%) on cooling to -30 °C of a diethyl ether (30 cm^3)–light petroleum (60 cm^3) solution of 4-dimethylaminopyridine (dmapy) (2.06 g, 16.8 mmol) and InMe$_3$ (2.67 g, 16.7 mmol) [Found: *M* (cryoscopic) 284. C$_{10}$H$_{19}$InN$_2$ requires *M* 282]. No 2:1 adduct, [(InMe$_3$)$_2$(dmapy)], could be isolated when using a 2:1 excess of InMe$_3$ and either diethyl ether or light petroleum as the solvent.

Hexamethyl-μ-(N,N,N′,N′-*tetramethylethylenediamine*)-*di-indium*(III).[9] Following the above procedure, [(InMe$_3$)$_2$(tmen)] was isolated as white needle-shaped crystals (4.81 g, 83%) on cooling to -30 °C of a diethyl ether (40 cm^3) solution of *N,N,N′,N′*-tetramethylethylenediamine (tmen) (1.54 g, 13.3 mmol) and InMe$_3$ (4.40 g, 27.5 mmol). These crystals turned pale yellow on standing in air for several hours. No 1:1 adduct, [InMe$_3$(tmen)], could be isolated when using a stoicheiometric equivalent of InMe$_3$ and tmen and either diethyl ether or light petroleum as the solvent.

Hexamethyl-μ-(N,N,N′,N′-*tetramethyl*-1,4-*phenylene-diamine*)-*di-indium*(III). The diamine (2.50 g, 15.2 mmol) was added in several fractions over 30 min to a stirred suspension of InMe$_3$ (4.92 g, 30.8 mmol) in light petroleum (200 cm^3). In order to obtain complete dissolution of the InMe$_3$, some warming of the reactants was required. The cloudy solution was filtered before cooling to -30 °C, and the white needle-shaped crystals so formed were collected, washed with ice-cold light petroleum, and dried *in vacuo*. The mother-liquor was reduced to *ca.* 100 cm^3 and cooled to -30 °C to afford a second batch of product which was treated in a similar manner (6.84 g, 93%). These crystals turn yellow on exposure to air for only a few minutes.

Trimethylindium (2.54 g, 48%) was released from these crystals (8.0 g) on heating at 100 °C *in vacuo* for 4 h, and collected at -196 °C. Heating at 100 °C for longer periods yielded no further InMe$_3$ and raising the temperature led only to sublimation of the residual 1:1 adduct. Contamination of the

Table 1. Adducts of trimethylindium with nitrogen-donor Lewis bases

Lewis base (L)	Solvent(s)[a]	L:In ratio in adduct	Yield (%)	Class of adduct	Thermal behaviour/°C		
					Melting point[b]	Sublimation point[c]	Dissociation point
NPh$_3$	(a)			*d*			
	(b)			*d*			
tmnd	(a)			*d*			
	(b)			*d*			
2,2′-bipy	(a)	*e*					
	(b)	*e*					
3,3′-bipy	(a)	1:1[f]	95	*g*	101—103	100	
	(b)/(c)	1:2	81	*h*	86—90		150[i]
4,4′-bipy	(a)	1:1[f]	93	*g*	153—155	70	
	(b)/(c)	1:2	75	*g*	142—144	80	
tmpd	(a)	1:1[f]	88	*j*	68—70	70	100[k]
	(b)	1:2	93	*h*	88—92		100[i]
tmen	(a)	1:2[f]	83	*g*	88—91[l]	60[m]	
	(b)	1:2[f]					
dmapy	(a)	1:1[f]	91	*g*	77—81	80	
	(b)	1:1[f]					

[a] (a) Diethyl ether, (b) light petroleum (b.p. 40—60 °C), and (c) toluene (required in order to dissolve base). [b] Determined on an electrothermal melting-point apparatus in closed capillaries under argon (760 Torr), and uncorrected. [c] At $\approx 10^{-2}$ Torr; the figures given represent the approximate temperatures at which sublimation, although very slow, was first observed around the insides of a heated flask. Much higher temperatures were required in order to sublime (or distil) the adducts into a -196 °C cold-trap. [d] No adduct formation. [e] No fixed stoicheiometry; varied with L:In ratio used in the adduct preparation and solution concentration, *etc.* [f] Independent of whether a L:In ratio of 1:1 or 1:2 was used in the adduct preparation. [g] Adduct which sublimes/distils without dissociation. [h] Adduct dissociates on heating *in vacuo* to give InMe$_3$ and the corresponding 1 : 1 adduct. [i] Heating the adducts at the temperatures given ($\approx 10^{-2}$ Torr) allowed trimethylindium to be readily collected in a -196 °C cold-trap together with trace amounts of the corresponding 1:1 adducts so formed. These impurities were then readily removed by subsequent sublimation of the trimethylindium at much lower temperatures (*ca.* 40 °C). [j] Adduct sublimes with a minor amount of dissociation. [k] Very slow rate of trimethylindium collection; higher temperatures led to concomitant sublimation of large amounts of the intact adduct. [l] Lit.,[9] 90—93 °C. [m] Crystals of this adduct were grown by slow sublimation *in vacuo* at room temperature.

Table 2. Proton n.m.r. data for amine adducts of trimethylindium

Adduct	δ*/p.p.m.
[$InMe_3$(3,3′-bipy)]	0.14 (9 H, s, $InMe_3$), 6.61, 7.04, 8.31, and 8.52 (8 H, m, aryl H)
[$(InMe_3)_2$(3,3′-bipy)]	0.08 (18 H, s, 2 $InMe_3$), 6.52, 6.90, 8.12, and 8.29 (8 H, m, aryl H)
[$InMe_3$(4,4′-bipy)]	0.16 (9 H, s, $InMe_3$), 6.67 and 8.37 (8 H, m, aryl H)
[$(InMe_3)_2$(4,4′-bipy)]	0.13 (18 H, s, 2 $InMe_3$), 6.59 and 8.26 (8 H, m, aryl H)
[$InMe_3$(tmpd)]	−0.20 (9 H, s, $InMe_3$), 2.45 (12 H, s, 2 NMe_2), 6.68 (4 H, s, aryl H)
[$(InMe_3)_2$(tmpd)]	−0.21 (18 H, s, 2 $InMe_3$), 2.32 (12 H, s, 2 NMe_2), 6.69 (4 H, s, aryl H)
[$(InMe_3)_2$(tmen)]	−0.24 (18 H, s, 2 $InMe_3$), 1.81 (12 H, s, 2 NMe_2), 2.32 (4 H, s, CH_2CH_2)
[$InMe_3$(dmapy)]	0.06 (9 H, s, $InMe_3$), 2.19 (6 H, s, NMe_2), 5.78 and 7.85 (4 H, m, aryl H)

* In C_6D_6; relative to $SiMe_4$; s = singlet and m = multiplet.

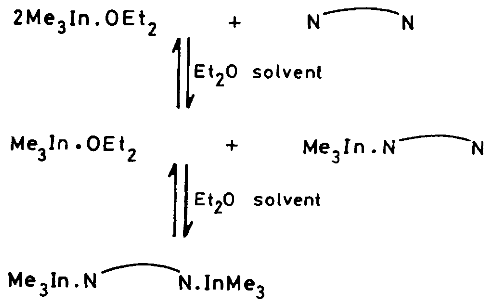
Table 3. Mass spectral and analytical data for amine adducts of trimethylindium

		Analysis (%)*		
Adduct	*m*/*z*	C	H	N
[$InMe_3$(3,3′-bipy)]	156[bipy]$^+$, 145[$InMe_2$]$^+$, 130[InMe]$^+$, 115[In]$^+$	49.5 (49.4)	5.4 (5.4)	8.8 (8.9)
[$(InMe_3)_2$(3,3′-bipy)]	156[bipy]$^+$, 145[$InMe_2$]$^+$, 130[InMe]$^+$, 115[In]$^+$	40.3 (40.4)	5.4 (5.5)	5.9 (5.9)
[$InMe_3$(4,4′-bipy)]	156[bipy]$^+$, 145[$InMe_2$]$^+$, 130[InMe]$^+$, 115[In]$^+$	49.4 (49.4)	5.4 (5.4)	8.7 (8.9)
[$(InMe_3)_2$(4,4′-bipy)]	156[bipy]$^+$, 145[$InMe_2$]$^+$, 130[InMe]$^+$, 115[In]$^+$	40.7 (40.4)	5.5 (5.5)	5.9 (5.9)
[$InMe_3$(tmpd)]	164[tmpd]$^+$, 149[tmpd − Me]$^+$, 145[$InMe_2$]$^+$, 134[tmpd − 2Me]$^+$, 130[InMe]$^+$, 115[In]$^+$	48.0 (48.2)	7.8 (7.8)	8.7 (8.6)
[$(InMe_3)_2$(tmpd)]	164[tmpd]$^+$, 149[tmpd − Me]$^+$, 145[$InMe_2$]$^+$, 134[tmpd − 2Me]$^+$, 130[InMe]$^+$, 115[In]$^+$	39.1 (39.7)	6.9 (7.1)	5.8 (5.8)
[$(InMe_3)_2$(tmen)]	261[$InMe_2$(tmen)]$^+$, 231[In(tmen)]$^+$, 145[$InMe_2$]$^+$, 130[InMe]$^+$, 116[tmen]$^+$, 115[In]$^+$	33.1 (33.1)	8.0 (7.9)	6.4 (6.4)
[$InMe_3$(dmapy)]	267[$InMe_2$(dmapy)]$^+$, 237[In(dmapy)]$^+$, 145[$InMe_2$]$^+$, 130[InMe]$^+$, 122 [dmapy]$^+$, 115[In]$^+$, 107[dmapy − Me]$^+$, 92[dmapy − 2Me]$^+$	42.4 (42.6)	6.8 (6.8)	9.8 (9.9)

* Required values are given in parentheses.

$InMe_3$ with minor amounts of base was detected by proton n.m.r. spectroscopy, but this impurity could readily be removed by a second vacuum sublimation of the $InMe_3$ at *ca.* 40 °C.

μ-(3,3′-*Bipyridyl*)-*hexamethyldi-indium*(III). 3,3′-Bipyridyl (2.50 g, 16.0 mmol) in toluene (20 cm^3) was added to a stirred suspension of $InMe_3$ (5.63 g, 35.2 mmol) in light petroleum (100 cm^3). Warming was required in order completely to dissolve all the $InMe_3$. The colourless solution was allowed to stand at room temperature overnight, and the air-stable, white, needle-shaped crystals which formed were collected, washed with light petroleum, and dried *in vacuo*. Cooling of the mother-liquor at 5 and −30 °C afforded two further crops of crystals which were similarly treated (6.17 g, 81%).



Scheme.

Trimethylindium (2.94 g, 46%) was released from these crystals (9.5 g) on heating at 150 °C *in vacuo* for 5 h, and collected at −196 °C. Heating for longer periods of time at this temperature did not increase the yield of liberated $InMe_3$ and increasing the temperature led only to sublimation of residual 1:1 adduct. Traces of base in the liberated $InMe_3$ were readily removed by a second sublimation at *ca.* 40 °C.

μ-(4,4′-*Bipyridyl*)-*hexamethyldi-indium*(III). Following the above procedure [$(InMe_3)_2$(4,4′-bipy)] was isolated as air-stable, yellow, diamond-shaped crystals (2.98 g, 75%) from 4,4′-bipy (1.30 g, 8.32 mmol) and $InMe_3$ (4.03 g, 25.2 mmol), *i.e.* a three-fold excess of $InMe_3$.

Similar preparations with 2,2′-bipy, in diethyl ether or light petroleum, afforded adducts whose non-integral stoicheiometry varied from one reaction to another. The thermal properties of these adducts were not investigated. Attempts to prepare adducts of trimethylindium using similar methods with triphenylamine and *N*,*N*,*N*′,*N*′-tetramethyl-1,8-naphthalenediamine (tmnd) were also unsuccessful. No evidence for the formation of crystalline adducts was obtained, and the chemical shifts of the proton signals in the ^1H n.m.r. spectra of mixtures of the Lewis base and $InMe_3$ were identical to those of the free Lewis base and free $InMe_3$.

Results and Discussion

Adduct Preparations.—The results of these studies are summarised in Table 1. Details of the ^1H n.m.r. spectroscopic data of the adducts are given in Table 2, mass spectral and microanalytical data in Table 3.

The observation that in diethyl ether the Lewis bases 3,3′-bipy, 4,4′-bipy, tmpd, and dmapy afford 1:1 adducts with trimethylindium, independent of whether a [$InMe_3$]:[Lewis base] ratio of 1 : 1 or 2:1 is used, whereas tmen affords a 2:1 ($InMe_3$:Lewis base) adduct, even when using an equimolar ratio of reactants, can be rationalised by looking at both the nature of the carbon backbone of the donor ligands and the nature of the solvent in which the preparations were carried out. For bidentate amines with aromatic carbon backbones, *i.e.* 3,3′-bipy, 4,4′-bipy, tmpd, and dmapy, co-ordination by one trimethylindium unit has the effect of withdrawing electron density from the second nitrogen-donor atom by both the purely 'inductive effect' of the co-ordinated Lewis-acid group and by a more powerful 'resonance effect' through the aromatic rings. In a Lewis-base solvent such as diethyl ether, which competes with the diamines for donation to trimethylindium *via* a series of equilibria such as those outlined in the Scheme, the dramatically reduced basicity of the second nitrogen-donor atom has the effect of making the second equilibrium unfavourable towards the formation of 2:1 ($InMe_3$:Lewis base) adducts, thus manifesting itself in the observed isolation of 1:1 adducts.

The ^{1}H n.m.r. spectra of [InMe$_3$(3,3′-bipy)], [InMe$_3$(4,4′-bipy)], and [InMe$_3$(tmpd)], all of which show the presence of only one resonance for protons that are equivalent in the free Lewis bases {*e.g.* a single resonance for the NMe groups of [InMe$_3$(tmpd)]}, support the suggestion of intermolecular exchange *via* a rapid dissociative mechanism since intramolecular exchange *via* a five-co-ordinate transition state for indium is ruled out for these aromatic diamines on geometrical grounds. Attempts to resolve the proton resonances of the free and bound nitrogen-donor groups by obtaining spectra at low temperature, where fast intermolecular exchange should be slowed down, have been frustrated by adduct crystallisation. However, molecular-weight determinations carried out on two of the adducts, giving good agreement between calculated (316 and 282) and found (319 and 284) values for [InMe$_3$(4,4′-bipy)] and [InMe$_3$(dmapy)] respectively, confirm the presence of monomeric species in solution. The ^{1}H n.m.r. data for [InMe$_3$(dmapy)], showing a single resonance for the InMe$_3$ protons at δ 0.06, closer to those observed for the bipyridyl adducts (δ 0.08—0.16) as opposed to those with NMe$_2$ donor groups (δ -0.20 to -0.24), suggest that in this adduct donation occurs through the aromatic nitrogen atom rather than the NMe$_2$ donor group.

With tmen, which has the nitrogen-donor atoms linked by an aliphatic carbon backbone, the reduced basicity of the second nitrogen-donor atom will be much less pronounced, occurring as it does *via* a purely inductive effect, so that the second equilibrium in the Scheme is now much more favourable, leading to the isolation of the 2:1 (InMe$_3$:Lewis base) adduct from diethyl ether.

By extending this hypothesis one step further, we argued that adduct preparations in hydrocarbon solvents, which have no Lewis-base activity, would be more likely to lead to the formation of 2:1 adducts for the 'aromatically linked' diamines. This has indeed been found to be the case for 3,3′-bipy, 4,4′-bipy, and tmpd, but not with dmapy. The smaller, more compact, nature of the dmapy ligand presumably causes a higher degree of electron withdrawal from and consequent lowering of basicity of the second nitrogen atom, on co-ordination of the first trimethylindium group.

The same electronic arguments have been invoked to explain the increasing stability of the 2:1 complexes formed from MMe$_3$ (M = B, Al, Ga, or In) and Me$_2$N(CH$_2$)$_n$NMe$_2$ (n = 1, 2, or 3) with increasing carbon chain length. Thus, the reduced basicity of the second nitrogen atom in these diamines after complexing of the first nitrogen atom (inductive effect) is less pronounced the longer is the connecting carbon chain, leading to the observed trend in stabilities for the 2:1 complexes.[9]

We could not isolate, under any conditions, stoicheiometric adducts of trimethylindium with 2,2′-bipy. Reaction of equimolar quantities of trimethylindium and 2,2′-bipy in hydrocarbon solvents afforded several crystalline fractions on cooling to -30 °C, which were shown by ^{1}H n.m.r. spectroscopy to vary in [InMe$_3$]:[2,2′-bipy] ratio from 0.4:1 to 1.7:1. Use of a 3:1 excess of trimethylindium, again in non-co-ordinating hydrocarbon solvents, gave very similar results. This behaviour does not appear to be due to electronic effects since 2,2′-, 3,3′-, and 4,4′-bipy have very similar pK_b values of 9.6, 9.6, and 9.2 respectively.[10] Steric effects also appear to be ruled out in light of the known stoicheiometric adduct formation of 2,2′-bipy with both tricyclopentadienylindium, [In(C$_5$H$_5$)$_3$(2,2′-bipy)],[11] and tris(pentafluorophenyl)indium, [{In(C$_6$F$_5$)$_3$}$_2$(2,2′-bipy)].[12] Steric effects clearly dominate in preventing the co-ordination of tmnd since it is the strongest of the Lewis bases used [pK_b[10]: tmnd (1.7) < dmapy (4.3) < tmen (4.9) < tmpd (7.6) < bipy (9.2—9.6) < NPh$_3$ (19)], whereas electronic effects dominate in preventing the co-ordination of the very weak base NPh$_3$.

Thermal Behaviour of the Adducts.—For the successful purification of trimethylindium employing an adduct with a Lewis base, the main requirements of that Lewis base are: (*a*) that it can form an adduct with trimethylindium which is essentially involatile; (*b*) that this adduct can then release trimethylindium on heating, preferably *in vacuo*; and (*c*) that the free Lewis base should have a very low volatility relative to trimethylindium at the adduct dissociation temperature. This last criterion is of particular importance, explaining our concentration on Lewis bases which have very low volatilities.

Clearly, those adducts which can be isolated from strongly co-ordinating solvents such as diethyl ether will have relatively higher In–N bond strengths than those which require the use of non-co-ordinating hydrocarbon solvents in their preparation. This observation is clearly reflected in the thermal behaviour of the adducts we have prepared. Thus, [InMe$_3$(3,3′-bipy)], [InMe$_3$(4,4′-bipy)], [InMe$_3$(tmpd)], [InMe$_3$(dmapy)], and [(InMe$_3$)$_2$(tmen)], all of which can be isolated from diethyl ether, sublime when heated *in vacuo* with little dissociation in the case of the tmpd adduct, and no dissociation in the other cases. These volatile adducts may prove to be convenient adduct sources[13,14] of trimethylindium for the 'metal–organic vapour phase epitaxial' growth of indium-based semiconductor materials, particularly since they are in general stable to air and moisture, and are therefore easier to handle and purify than trimethylindium itself. The adducts [(InMe$_3$)$_2$(3,3′-bipy)] and [(InMe$_3$)$_2$(tmpd)] on the other hand, which can only be isolated from hydrocarbon solvents, both dissociate upon heating *in vacuo* to afford the corresponding 1:1 adducts and trimethylindium. The adduct [(InMe$_3$)$_2$(4,4′-bipy)], which requires both the use of hydrocarbon solvents and a 3:1 excess of trimethylindium in its preparation, sublimes intact upon heating *in vacuo* and clearly behaves as an exception to the above trend.

The successful dissociation of [(InMe$_3$)$_2$(3,3′-bipy)] and [(InMe$_3$)$_2$(tmpd)] to trimethylindium suggests that these adducts may be useful for the purification of small amounts of trimethylindium, but maximum yields of 50% limit the utility of these processes.

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