Indium Complexes of 1,3-Diphenyltriazene†

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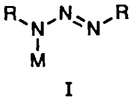
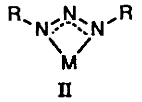
The reaction of $InCl_3$ with 1,3-diphenyltriazene (Hdpt) in the presence of NEt_3 gives the six-co-ordinate indium complex $[NHEt_3][InCl_2(dpt)_2]$ **1a**. The interaction of **1a** with $[NEt_4]Cl$ and $[N(PPh_3)_2]Cl$ allows for the isolation of the appropriate salts, $[NEt_4][InCl_2(dpt)_2]$ **1b** and $[N(PPh_3)_2][InCl_2(dpt)_2]$ **1c**. Reaction of Lewis bases, L, with **1a** yields $[InCl_2(dpt)L_2]$, L = pyridine **2**, 3,5-dimethylpyridine **3**, PEt_3 **4**, L_2 = 2,2′-bipyridine **5**, 1,10-phenanthroline **6**, $Me_2PCH_2CH_2PMe_2$ **7** or $Et_2PCH_2CH_2PEt_2$ **8**. The mechanism for these reactions is discussed. No reaction is observed between **1b** and 3,5-dimethylpyridine. The X-ray structures of **1a**, **3**, **4** and **5** have been determined. Compounds **2**–**4** are readily soluble in aromatic hydrocarbon solvents, while **5**–**8** are insoluble as a consequence of the presence of a supramolecular architecture involving dipolar In–Cl ··· N interactions in the solid state. All new compounds have been characterised by ^1H, $^{13}C-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR and IR spectroscopy.

The triazenide anion, $RN{=}N{-}NR^-$, has been reported to act as a monodentate (**I**), chelate (**II**) or bridging (**III**) ligand towards transition metals,[1] suggesting a formal analogy to the carboxylate anion, $O{=}C(R){-}O^-$.


I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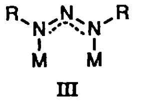
III

Despite this analogy and the wide range of Group 13 carboxylates reported in the literature,[2] the only examples of Group 13 triazenides were until recently those of thallium, *i.e.*, $[Tl(dpt)_3]$, Hdpt = 1,3-diphenyltriazene and $[Tl(ppt)_3]$, Hppt = 1-phenyl-3-(2′-pyridyl)triazene, which were characterised as tris-chelate complexes by IR spectroscopy,[3] and the dimeric $[Tl(dpt)]_2$ whose structure was determined by X-ray crystallography.[4] We have reported that the reaction of $AlMe_3$ with Hdpt leads to a single product, $[Al(dpt)_3]$ [equation (1)],

$$AlMe_3 + 3Hdpt \longrightarrow [Al(dpt)_3] + 3MeH \qquad (1)$$

$$AlMe_3 + 2Hdpt \xrightarrow[\text{1 equivalent}]{\text{3,5Me}_2\text{-py}} [AlMe(dpt)_2(3,5Me_2\text{-py})] + 2MeH \qquad (2)$$

even when a large excess of $AlMe_3$ is employed.[5] If, however, the reaction is carried out in the presence of a strong Lewis base, such as 3,5-dimethylpyridine (3,5Me_2-py) a less highly substituted compound *cis*-$[AlMe(dpt)_2(3,5Me_2\text{-py})]$ can be isolated, equation (2).[6]

X-Ray crystallographic characterisation of $[AlMe(dpt)_2(3,5\text{-}Me_2\text{-py})]$ revealed it to be the first example of a monomeric six-co-ordinate aluminium alkyl. In addition, a large *trans* influence was observed for the Al–N distance *trans* to the methyl ligand, the first observation of such an effect for an aluminium complex.

The possibility that the reactivity of six-co-ordinate Group 13 alkyls would be different from the more usual four-co-ordinate tetrahedral geometry[7] prompted further study, however this was hindered by the fact that $[AlMe(dpt)_2(3,5Me_2\text{-py})]$ could only be isolated in low yield, *ca.* 30%.[6] We, therefore, investigated alternative syntheses of mono- and di-triazenido complexes from $AlCl_3$. However, the reaction of $AlCl_3$ with Hdpt in the presence of NEt_3 yielded the tris-chelate complex, $[Al(dpt)_3]$, as the only isolable product. Since the presence of facile ligand-exchange reactions accounts for the isolation of a number of highly substituted aluminium complexes,[8] and similar reactions are known to be less accessible for the heavier Group 13 elements, we have investigated the synthesis of 1,3-diphenyltriazenide complexes of indium(III). The results of this study are reported herein.

Results and Discussion

Interaction of $InCl_3$ with either 1 or 2 equivalents of Hdpt in the presence of NEt_3 does not yield either of the expected substitution products, *i.e.*, $[InCl_2(dpt)]$ and $[InCl(dpt)_2]$, nor their amine complexes. Instead the ionic complex $[NHEt_3][InCl_2(dpt)_2]$ **1a** is formed in near quantitative yield as the only isolated indium–triazenide complex, equation (3). Compound

$$InCl_3 + 2Hdpt \xrightarrow[\text{toluene}]{2NEt_3} [NHEt_3][InCl_2(dpt)_2] + [NHEt_3]Cl \qquad (3)$$

1a is soluble in MeCN, tetrahydrofuran (thf), CH_2Cl_2 and $CHCl_3$, and has been fully characterised by elemental analysis, IR and NMR spectroscopy (see Experimental section) and X-ray crystallography.

The tetraethylammonium and $[N(PPh_3)_2]^+$ salts of $[InCl_2(dpt)_2]^-$ may readily be prepared by cation exchange [see Experimental section and equation (4)]. All the salts

$$[NHEt_3][InCl_2(dpt)_2] + MCl \longrightarrow [M][InCl_2(dpt)_2] + [NHEt_3]Cl \qquad (4)$$

$$M = NEt_4\ \mathbf{1b} \text{ or } N(PPh_3)_2\ \mathbf{1c}$$

show conductivities in MeCN consistent with 1:1 electrolytes (see Experimental section).[9]

The structure of compound **1a** is shown in Fig. 1; selected bond lengths and angles are given in Table 1. Compound **1a** consists of a $[InCl_2(dpt)_2]^-$ anion hydrogen-bonded *via* one of the chlorides to a triethylammonium cation [Cl(2) ··· H(10a) 1.94(2) Å, Cl(2) ··· N(7) 3.142(9) Å]. The co-ordination geometry around indium is a highly trigonally distorted octahedron [Cl(1)–In–N(1) 154.8(2), Cl(2)–In–N(3) 151.6(2),

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

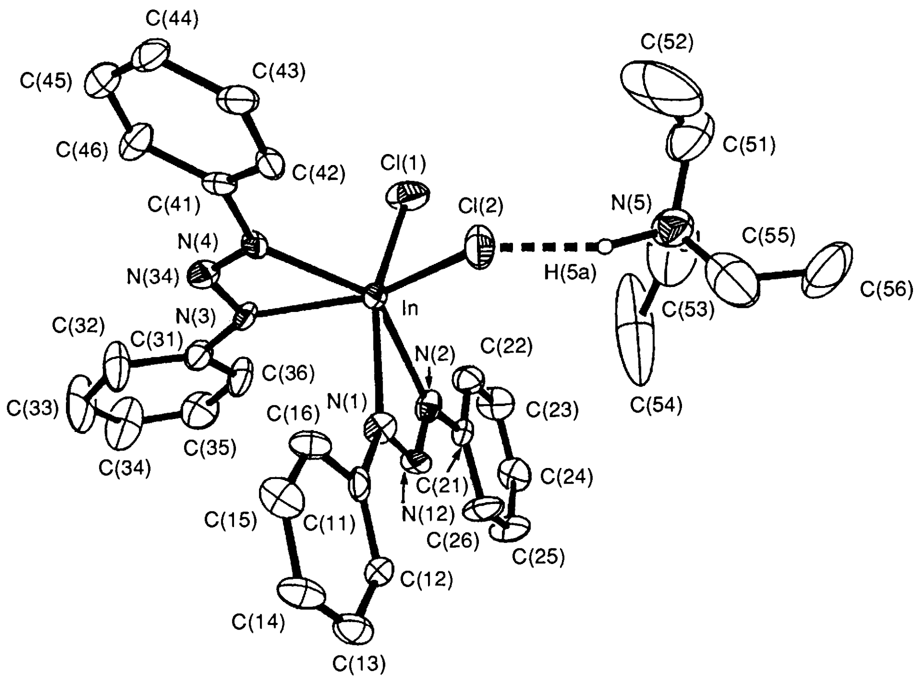


Fig. 1 The structure of $[NHEt_3][InCl_2(dpt)_2]$ **1a**. Thermal ellipsoids are drawn at the 40% level, and all carbon-bound hydrogens are omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°) for $[NHEt_3][InCl_2(dpt)_2]$ **1a**

In–Cl(1)	2.428(3)	In–Cl(2)	2.474(3)
In–N(1)	2.272(8)	In–N(2)	2.272(7)
In–N(3)	2.283(7)	In–N(4)	2.250(7)
N(1)–N(12)	1.294(10)	N(1)–C(11)	1.431(13)
N(2)–N(12)	1.284(10)	N(2)–C(21)	1.452(11)
N(3)–N(34)	1.289(10)	N(3)–C(31)	1.436(12)
N(4)–N(34)	1.276(10)	N(4)–C(41)	1.427(11)
Cl(1)–In–Cl(2)	96.3(1)	Cl(1)–In–N(1)	154.8(2)
Cl(1)–In–N(2)	100.4(2)	Cl(1)–In–N(3)	95.4(2)
Cl(1)–In–N(4)	103.0(2)	Cl(2)–In–N(1)	89.1(2)
Cl(2)–In–N(2)	108.2(2)	Cl(2)–In–N(3)	151.6(2)
Cl(2)–In–N(4)	97.4(2)	N(1)–In–N(2)	54.8(3)
N(1)–In–N(3)	91.3(3)	N(1)–In–N(4)	100.6(3)
N(2)–In–N(3)	95.0(2)	N(2)–In–N(4)	142.9(3)
N(3)–In–N(4)	54.7(2)	In–N(1)–N(12)	98.3(5)
In–N(1)–C(11)	144.9(6)	N(12)–N(1)–C(11)	166.8(8)
In–N(2)–N(12)	98.6(5)	In–N(2)–C(21)	145.0(6)
N(12)–N(2)–C(21)	116.3(7)	In–N(3)–N(34)	97.3(5)
In–N(3)–C(31)	146.7(6)	N(31)–C(3)–C(31)	115.9(7)
In–N(4)–N(34)	99.3(5)	In–N(4)–C(41)	143.2(6)
N(34)–N(4)–C(41)	116.7(7)	N(1)–N(12)–N(2)	108.3(7)
N(3)–N(34)–N(4)	108.6(8)		

N(2)–In–N(4) 142.9(3)°], with the chloride ligands mutually *cis*, and the two triazenides acting as bidentate chelating ligands. It is unclear as to whether this conformation is retained in solution, since only a single set of resonances is observed for the triazenide ligands in the ^1H NMR spectrum. The N–In–N chelate angles [N(1)–In–N(2) 54.8(3), N(3)–In–N(4) 54.7(2)°] are larger than those observed for aluminium triazenide compounds [64.1–64.2°],[10] consistent with the increased ionic radii for In^{3+} (0.81 Å) *versus* Al^{3+} (0.51 Å).[11] The In–N distances in **1a** [2.250(7)–2.283(7) Å] are comparable to those reported for other six-co-ordinate indium complexes [2.233(6)–2.299(4) Å][12,13] as well as the axial substituents in the trigonal-bipyramidal complex $[InCl\{C_6H_4(CH_2NMe_2)\}_2]$ [2.442(3) and 2.482(2) Å],[14] and the four-co-ordinate pyrazolylborate complexes reported by Reger *et al.*[15] [2.131(2)–2.257(3) Å]. The range of values, and their relatively high estimated standard deviations, do not allow the confirmation of any significant *trans* influence (see below). The In–Cl distances in **1a** [In–Cl(1) 2.428(3), In–Cl(2) 2.474(3) Å] are significantly larger than found for the four-co-ordinate compounds $[InMeCl_2]$ [2.384(1) Å][16] and $[InMeCl_3]^-$ [2.394(3), 2.397(4) and 2.409(3) Å].[17] This difference is as would be expected from a consideration of both steric and electronic factors. The In–Cl distances in **1a** are dissimilar, with that hydrogen bonded to the triethylammonium cation being 0.046 Å longer. Since the chlorides are similarly oriented to their *trans* ligands we can assume this difference is real and possibly due to the presence of the hydrogen bonding to the triethylammonium cation. We have observed similar differences in M–Cl distances for anionic aluminium dichloride complexes in which hydrogen bonding interactions are present.[18] The In–Cl distance for the chloride not involved in hydrogen bonding [2.428(3) Å] is identical to those in the six-co-ordinate indium pyrazolylborate complex $[InCl_2(NCMe)\{(3,5Me_2\text{-}pz)_3BH\}]$ [2.428(2) and 2.429(2) Å] ($3,5Me_2$-pz = 3,5-dimethylpyrazolyl).[13]

The insolubility of **1a** in the reaction solvents toluene (the medium of choice, see Experimental section), pentane and diethyl ether cannot be responsible for the isolation of **1a**, in the absence of $[In(dpt)_3]$ or any other intermediate products, irrespective of the $InCl_3$/Hdpt ratio, since if the reaction is carried out in CH_2Cl_2, MeCN or thf a homogeneous solution is obtained in which **1a** is the only isolated indium–triazenide complex. Therefore the stability of **1a** towards further reaction is in contrast to the analogous reaction between $AlCl_3$, Hdpt and NEt_3 where $[Al(dpt)_3]$ is the only product observed.

Although we have no direct evidence for the mechanism of the reaction leading to **1a**, we propose the following based on analogy with other Group 13 systems. We have observed that NEt_3 does not deprotonate Hdpt, in fact $[NHEt_3]^+$ is sufficiently acidic to react with Na(dpt) to yield Hdpt, *i.e.*, equation (5). We must therefore assume that Hdpt reacts

$$Na(dpt) + [NHEt_3]^+ \longrightarrow Hdpt + Na^+ + NEt_3 \quad (5)$$

directly with $InCl_3$ to yield the four-co-ordinate complex

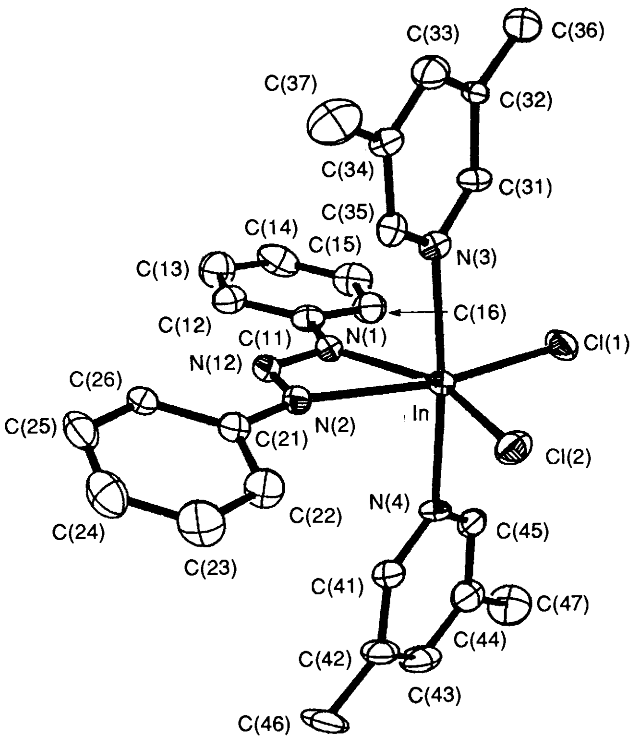


Fig. 2 The molecular structure of [$InCl_2(dpt)(3,5Me_2\text{-}py)_2$] **3**. Thermal ellipsoids are drawn at the 50% level, and all hydrogens are omitted for clarity

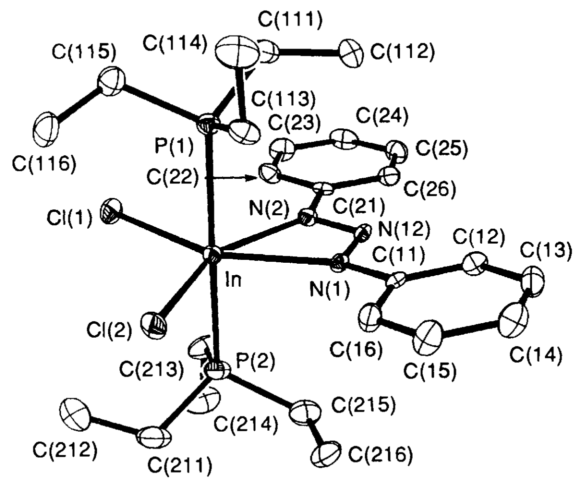


Fig. 3 The molecular structure of [$InCl_2(dpt)(PEt_3)_2$] **4**. Thermal ellipsoids are drawn at the 40% level, and all hydrogen atoms are omitted for clarity

[$InCl_2(dpt)$] and HCl [equation (6)], the latter being trapped by the triethylamine.

$$\text{Hdpt} + InCl_3 \xrightarrow{-HCl} [InCl_2(dpt)] \qquad (6)$$

The mono-dpt complex may be converted to the five-co-ordinate bis-dpt complex [$InCl(dpt)_2$], the obvious precursor to **1**, by two possible routes. First, [$InCl_2(dpt)$] reacts with a second equivalent of Hdpt, *i.e.*, equation (7). Secondly, a ligand disproportionation may occur as per equation (8).

$$[InCl_2(dpt)] \xrightarrow[-HCl]{+Hdpt} [InCl(dpt)_2] \qquad (7)$$

$$2[InCl_2(dpt)] \longrightarrow [InCl(dpt)_2] + InCl_3 \qquad (8)$$

Given that the isolation of **1a** is independent of the order of reactant addition during the reaction, and the observation of similar exchange reactions for other Group 13 complexes, we believe the latter option to be the more likely. The subsequent reassociation of chloride to the co-ordinatively unsaturated monochloride [$InCl(dpt)_2$] leads to **1a**, equation (9).

$$[InCl(dpt)_2] + Cl^- \longrightarrow [InCl_2(dpt)_2]^- \qquad (9)$$

We presume therefore that in the case of the reaction of $AlCl_3$ with Hdpt and NEt_3 the five-co-ordinate monochloride complex [$AlCl(dpt)_2$] undergoes further ligand exchange to give the tris-triazenide complex, equation (10). Similar reactivity is also

$$2[AlCl(dpt)_2] \longrightarrow [Al(dpt)_3] + [AlCl_2(dpt)] \qquad (10)$$

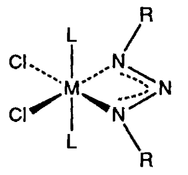
observed for aryloxide and acetylacetonate complexes of aluminium.[8,19]

Reaction of [$NHEt_3$][$InCl_2(dpt)_2$] *with Lewis Bases.*—Treatment of compound **1a** with monodentate Lewis base, L, results in a nearly quantitative yield of [$InCl_2(dpt)L_2$] [L = pyridine (py) **2**, 3,5Me_2-py **3** or PEt_3 **4**)] [equation (11)]. No

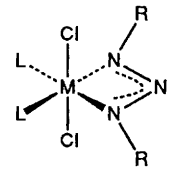
$$[NHEt_3][InCl_2(dpt)] \xrightarrow[-Hdpt]{+L\ (excess)} [InCl_2(dpt)L_2] \qquad (11)$$

reaction is observed between **1a** and MeCN, NEt_3, $P(OMe)_3$, PPh_3, PPh_2Me, $PPhMe_2$, PBu^t_3 or thf.

Compounds **2**–**4** are all soluble in thf, CH_2Cl_2, $CHCl_3$ and MeCN (**3** only sparingly), and in the latter show conductivities consistent with molecular species. In addition, **2** and **4** are sufficiently soluble in benzene to obtain NMR spectra. Each compound has been characterised by IR and NMR spectroscopy (see Experimental section). The presence of a single set of resonances for the Lewis base ligand L, in ^1H, $^{13}C\text{-}\{^1H\}$, and for **4** $^{31}P\text{-}\{^1H\}$, NMR spectra suggests that they are either mutually *trans*, with the chloride ligands *cis* (**IV**) or *trans* (**V**). The problem of assessing the relative stabilities of InX_2L_4 species has been discussed by Carty and Tuck[20] using the model of ligand steric angles developed by Zahrobsky,[21] the conclusion being that the *cis* dichloro isomer **IV** is more stable than the *trans* dichloro isomer **V**. In addition, structure **IV** should be favoured over **V** due to a co-operativity between the highly basic triazenide ligand and the electronegative chlorides. Such effects are often found in the structural Lewis acid–base chemistry of the heavier main-group elements as a result of the nature of the acceptor orbitals at the metal centre. The structures of **3** and **4** have been determined by X-ray crystallography, and have shown structure **IV** to be correct.



IV



V

The molecular structures of **3** and **4** are shown in Figs. 2 and 3 respectively; selected bond lengths and angles are given in Tables 2 and 3. Both compounds are monomeric with no unusual intermolecular contacts. The indium atoms are six-co-ordinate equatorially distorted octahedral with the chlorides *cis*, and the 3,5Me-py (**3**) and PEt_3 (**4**) ligands mutually *trans*-axial. In each case the triazenide ligand is bidentate and chelating. The In–Cl and In–N distances in both compounds are comparable to those in **1a**. The In–P distances in **4** [In–P(1) 2.647(8), In–P(1) 2.650(8) Å] are as expected slightly larger than those found for four-co-ordinate indium complexes

Table 2 Selected bond lengths (Å) and angles (°) for $[\mathrm{InCl_2(dpt)}$-$(3,5\mathrm{Me_2}\text{-py})_2]$ **3**

In–Cl(1)	2.426(4)	In–Cl(2)	2.414(4)
In–N(1)	2.276(6)	In–N(2)	2.304(6)
In–N(3)	2.312(6)	In–N(4)	2.301(6)
N(1)–N(12)	1.300(7)	N(1)–C(11)	1.404(7)
N(2)–N(12)	1.296(7)	N(2)–C(21)	1.403(7)
Cl(1)–In–Cl(2)	102.4(1)	Cl(1)–In–N(1)	104.2(2)
Cl(1)–In–N(2)	159.2(2)	Cl(1)–In–N(3)	92.0(2)
Cl(1)–In–N(4)	90.6(2)	Cl(2)–In–N(1)	153.4(1)
Cl(2)–In–N(2)	98.5(2)	Cl(2)–In–N(3)	92.7(2)
Cl(2)–In–N(4)	91.7(2)	N(1)–In–N(2)	55.0(2)
N(1)–In–N(3)	88.4(2)	N(1)–In–N(4)	86.1(2)
N(2)–In–N(3)	87.1(2)	N(2)–In–N(4)	88.6(2)
N(3)–In–N(4)	174.3(2)	In–N(1)–N(12)	98.5(3)
In–N(1)–C(11)	114.4(4)	N(12)–N(1)–C(11)	117.1(5)
In–N(2)–N(12)	97.2(3)	In–N(2)–C(21)	145.8(4)
N(12)–N(2)–C(21)	116.9(4)	N(1)–N(12)–N(2)	109.2(4)

Table 3 Selected bond lengths (Å) and angles (°) for $[\mathrm{InCl_2(dpt)}$-$(\mathrm{PEt_3})_2]$ **4**

In–Cl(1)	2.467(7)	In–Cl(2)	2.467(7)
In–P(1)	2.647(8)	In–P(2)	2.650(8)
In–N(1)	2.317(8)	In–N(2)	2.338(8)
P(1)–C(111)	1.822(9)	P(1)–C(113)	1.832(8)
P(1)–C(115)	1.804(8)	P(2)–C(211)	1.774(9)
P(2)–C(213)	1.804(8)	P(2)–C(215)	1.847(9)
N(1)–N(12)	1.309(8)	N(1)–C(11)	1.400(9)
N(2)–N(12)	1.304(8)	N(2)–C(21)	1.406(9)
Cl(1)–In–Cl(2)	106.4(2)	Cl(1)–In–P(1)	88.9(2)
Cl(1)–In–P(2)	90.0(2)	Cl(1)–In–N(1)	153.7(2)
Cl(1)–In–N(2)	99.8(2)	Cl(2)–In–P(1)	90.6(2)
Cl(2)–In–P(2)	91.7(2)	Cl(2)–In–N(1)	99.6(2)
Cl(2)–In–N(2)	153.6(2)	P(1)–In–P(2)	177.6(2)
P(1)–In–N(1)	87.1(2)	P(1)–In–N(2)	92.6(2)
P(2)–In–N(1)	92.9(2)	P(2)–In–N(2)	85.5(2)
N(1)–In–N(2)	54.5(2)	In–P(1)–C(111)	115.2(3)
In–P(1)–C(113)	110.9(3)	In–P(1)–C(115)	113.8(3)
C(111)–P(1)–C(113)	107.3(3)	C(111)–P(1)–C(115)	103.5(3)
C(113)–P(1)–C(115)	105.4(4)	In–P(2)–C(211)	115.4(3)
In–P(2)–C(213)	111.9(3)	In–P(2)–C(215)	112.7(3)
C(211)–P(2)–C(213)	106.5(4)	C(211)–P(2)–C(215)	105.7(4)
C(213)–P(2)–C(215)	103.7(4)	In–N(1)–N(12)	98.6(4)
In–N(1)–C(11)	144.0(4)	N(12)–N(1)–C(11)	116.9(5)
In–N(2)–N(12)	97.7(4)	In–N(2)–C(21)	145.5(4)
N(12)–N(2)–C(21)	116.7(5)	N(1)–N(12)–N(2)	109.2(5)

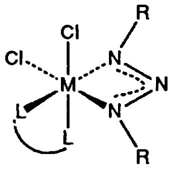
[2.481(3)–2.58(1) Å].[22] A comparison of the bond distances and angles around the indium centre for **3** and **4** indicates that while the triazenide ligation is essentially identical, the In–Cl and In–N (triazenide) distances, and the Cl(1)–In–Cl(2) angle, are larger in **4** than in **3** (see Tables 2 and 3). These differences are all consistent with greater steric congestion around the indium atom in **4**, due to $\mathrm{PEt_3}$ being sterically larger than $3,5\mathrm{Me_2}$-py.

Given that the reaction of **1a** with monodentate Lewis-base ligands yields complexes with two mutually *trans* Lewis bases per indium then the reaction with bidentate Lewis bases, L–L would be expected to yield the corresponding complexes $[\mathrm{InCl_2(dpt)(L{-}L)}]$. This is indeed observed for L–L = 2,2′-bipyridine (bipy) **5**, 1,10-phenanthroline (phen) **6**, 1,2-bis(dimethylphosphino)ethane (dmpe) **7** and 1,2-bis(diethylphosphino)ethane (depe) **8** [equation (12)]. No reaction is observed

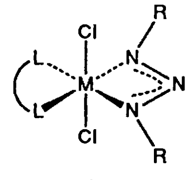
$$[\mathrm{InCl_2(dpt)}]^- \xrightarrow[-[\mathrm{dpt}]^-]{+\mathrm{L{-}L}\ (\mathrm{excess})} [\mathrm{InCl_2(dpt)(L{-}L)}] \qquad (12)$$

between **1a** and 1,2-dimethoxyethane (dme), 1,2-bis(diphenylphosphino)ethane (dppe), PhN=NPh or $\mathrm{Me_2NN{=}NNMe_2}$.

Despite their low solubility in all common solvents (see below), compounds **5**–**8** were characterised by IR and NMR spectroscopy. The solid-state $^{31}\mathrm{P}$ CP MAS NMR spectra of **7** and **8** (see Experimental section) show the presence of a single very broad resonance. Thus the existence of either a *cis*-dichloro (**VI**) or *trans*-dichloro (**VII**) configuration for **5**–**8** cannot be differentiated. However, from comparison with $[\mathrm{InCl_2(acac)}$-$(\mathrm{bipy})]$ (acac = acetylacetonate) and from a consideration of ligand sterics the former would be expected to be the more stable.[20,21] This is confirmed for compound **5** by X-ray crystallography.



VI

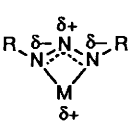


VII

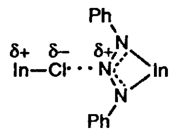
The molecular structure of $[\mathrm{InCl_2(dpt)(bipy)}]$ **5** is shown in Fig. 4; selected bond lengths and angles are given in Table 4. Compound **5** is monomeric with a six-co-ordinate indium centre. The geometry around indium in **5** is less distorted from a regular octahedron than in **1a** as a consequence of the larger bite angle of bipy [71.7(2)°] compared to dpt [54.7(2)–55.6(1)°]. The In–N distance associated with the triazenide ligand nitrogen *trans* to chloride [In–N(2) 2.301(4) Å] is significantly longer than that *trans* to the bipy nitrogen [In–N(1) 2.253(4) Å]. This lengthening is undoubtedly due to the *trans* influence of the chloride. Although the In–N distances associated with the bipy ligand are within the 3σ condition we note that the distance *trans* to chloride [N(4)] is the larger, consistent with a slightly larger *trans* influence for chloride *versus* the triazenide nitrogen. From a comparison of the indium–ligand distances in **5** and $[\mathrm{InCl_2(acac)(bipy)}]$[12] the relative ordering of *trans* influences may be determined as acac > Cl > bipy > dpt. It is perhaps surprising that bipy shows a greater *trans* influence than the triazenido ligand, however the difference may be explained in terms of a 'nearly *trans*' influence,[23] *i.e.*, Cl(2) is more nearly *trans* to N(4) than Cl(1) is to N(2) [164.3(1) *versus* 157.5(1)°].

Whereas compounds **2**–**4** show significant solubilities in non-co-ordinating solvents, compounds **5**–**8** are essentially insoluble in all solvents. It is not apparent, however, from a consideration of the *trans* (**IV**) *versus cis* (**VI**) Lewis-base structures why this difference is observed. A study of the crystal packing diagram of compound **5** (Fig. 5) reveals the presence of small intermolecular distances between Cl(1) and N(12) of the adjoining molecule [Cl(1)$\cdots$N(12′) 3.280(9) Å] resulting in the formation of a supramolecular architecture consisting of two parallel chains within the unit cell running along the *y* axis. Since the Cl$\cdots$N distances are outside any expected covalent interaction, and there is no possibility of hydrogen bonding, an interesting question arises. If there is a bonding interaction between the chloride and triazenide ligand, what is the nature of the interaction? Although at present we cannot confirm the presence and/or extent of any Cl$\cdots$N interaction we propose the following models.

(*i*) The In–Cl bond is most certainly polarised towards the chloride resulting in the presence of a signficant dipole, *viz.* $\mathrm{In^{\delta+}{-}Cl^{\delta-}}$. In contrast, the polarisation of the $\mathrm{N_3}$ unit of the co-ordinated triazenido ligand (**VIII**) is such as to place the



VIII



IX

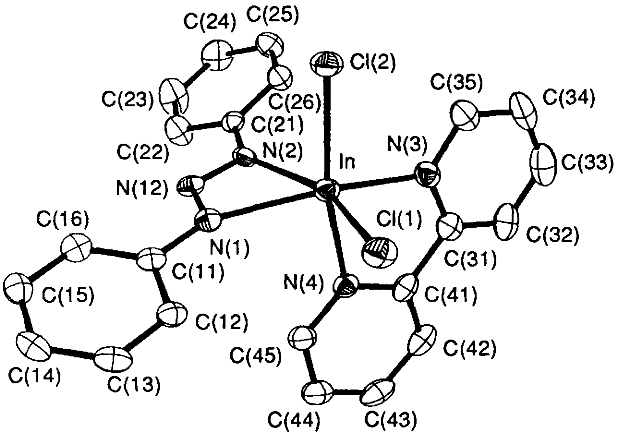


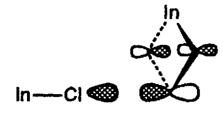
Fig. 4 The molecular structure of $[InCl_2(dpt)(bipy)]$ **5**. Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms are omitted for clarity

Table 4 Selected bond lengths (Å) and angles (°) for $[InCl_2(dpt)(bipy)]$ **5**

In–Cl(1)	2.403(2)	In–Cl(2)	2.456(2)
In–N(1)	2.253(4)	In–N(2)	2.301(4)
In–N(3)	2.274(5)	In–N(4)	2.295(4)
N(1)–N(12)	1.300(5)	N(1)–C(11)	1.415(7)
N(2)–N(12)	1.294(6)	N(2)–C(21)	1.416(6)
N(3)–C(31)	1.331(6)	N(4)–C(41)	1.345(7)
C(31)–C(41)	1.497(8)		
Cl(1)–In–Cl(2)	97.9(1)	Cl(1)–In–N(1)	102.0(1)
Cl(1)–In–N(2)	157.5(1)	Cl(1)–In–N(3)	99.3(1)
Cl(1)–In–N(4)	90.5(1)	Cl(2)–In–N(1)	102.8(1)
Cl(2)–In–N(2)	88.6(1)	Cl(2)–In–N(3)	93.6(1)
Cl(2)–In–N(4)	164.3(1)	N(1)–In–N(2)	55.6(1)
N(1)–In–N(3)	150.9(1)	N(1)–In–N(4)	88.4(1)
N(2)–In–N(3)	101.7(1)	N(2)–In–N(4)	88.8(1)
N(3)–In–N(4)	71.7(2)	In–N(1)–N(12)	98.3(3)
In–N(1)–C(11)	144.1(3)	N(12)–N(1)–C(11)	117.5(4)
In–N(2)–N(12)	96.2(3)	In–N(2)–C(21)	147.1(3)
N(12)–C(2)–C(21)	116.6(4)	In–N((3)–C(31)	118.3(4)
In–N(4)–C(41)	116.9(3)	N(3)–C(31)–C(41)	116.1(5)
N(4)–C(41)–C(31)	116.2(4)		

greatest negative charge on the terminal nitrogens, and therefore the central nitrogen, in the present case N(12), may be considered to be relatively electronic deficient. Thus, the interaction may be considered to be dipole–dipole (**IX**).

(*ii*) The In(1)–Cl(1) vector is close to perpendicular to the InN_3 plane of the adjacent molecule (119.6°). Such an orientation would be consistent with donation of electron density from a lone-pair chlorine in the N(12) centred π^* orbital of the triazenido ligand (**X**).[24]



X

We are at present further investigating this interesting effect, however we note that we have observed a related solid-state interaction between an aromatic C–H bond of the $N(PPh_3)_2$ cation and the semi-filled π^* orbital of the ligand-centred radical anion $[Al(dpt)_3]^-$.[9]

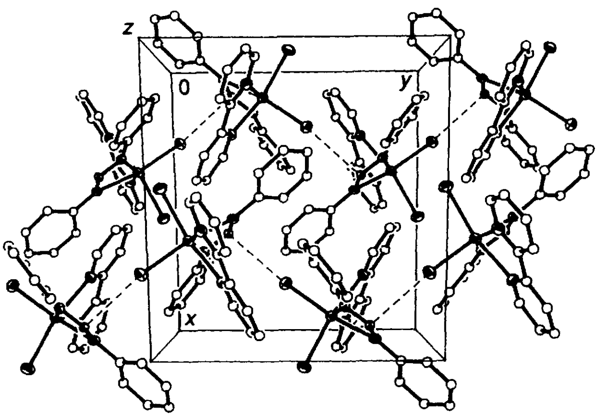


Fig. 5 Unit-cell packing diagram for $[InCl_2(dpt)(bipy)]$ **5**, viewed down the *z* axis. The In–Cl ··· N dipolar interactions are indicated by broken lines

Unfortunately we have been unable to obtain X-ray quality crystals of compounds **6**–**8**, to confirm the presence of analogous intermolecular architecture, however based solely on their insolubility it appears as though such structure may be a common motif for the *cis,cis,cis* configuration of $[InCl_2(dpt)(L\text{–}L)]$.

The formation of compounds **2**–**8** from **1a** is intriguing. Since the anion $[InCl_2(dpt)_2]^-$ may be considered as the complex of the Lewis acid $[InCl(dpt)_2]$ and a chloride ion, the reaction with Lewis bases, L, may be expected to yield the neutral complexes $[InCl(dpt)_2L]$. However, the observed reactivity involves loss of a triazenide ligand.

Although we have little direct evidence for the reaction mechanism of this unusual transformation we propose the following: while the uncomplexed triazenide anion is clearly a stronger base than NEt_3, and thus equation (13) lies sufficiently

$$Hdpt + NEt_3 \rightleftharpoons [NHEt_3][dpt] \qquad (13)$$

far to the left that $[NHEt_3][dpt]$ cannot be isolated, it is obvious that the co-ordinated triazenide anion is a considerably weaker base, *viz.* the isolation of compound **1a**. The inertness of **1b** towards reactions with 3,5Me_2-py (see above) indicates, however, that the reaction of **1a** with Lewis bases cannot follow either a simple associative or dissociative mechanism, but must involve the triethylammonium protons. Thus, while in the solid state the proton is clearly associated with the triethylamine, as confirmed by IR spectroscopy and X-ray crystallography, in solution, we propose it to be in rapid equilibrium, *i.e.*, equation (14).

$$[NHEt_3][InCl_2(dpt)_2] \rightleftharpoons NEt_3 + [InCl_2(dpt)(Hdpt)] \qquad (14)$$

An obvious consequence of the formation of a protonated dpt would be its conversion into a monodentate ligand. The resulting five-co-ordinate indium complex reacts with the Lewis base leading to the eventual substitution of the Hdpt ligand for two equivalents of L. Supporting evidence for such a protonation–substitution reaction is obtained from the following:

(*i*) While compound **1b** does not react with 3,5Me_2-py even under forcing conditions (12 h, *ca.* 83 °C), the addition of either $[NHEt_3]Cl$ or 2,6-dimethylpyridinium chloride results in the slow formation of **3**, albeit in low yield, *ca.* 25%, after a 24 h reaction time (25 °C).

(*ii*) The reaction of **1b** with 3,5Me_2-py in the presence of trifluoroacetic acid results in the formation of **3** in *ca.* 90% yield [equation (15)].

$$[NEt_4][InCl_2(dpt)_2] + CF_3CO_2H \xrightarrow[-[NEt_4][O_2CCF_3]]{+2\ 3,5Me_2\text{-py}} [InCl_2(dpt)(3,5Me_2\text{-py})_2] + Hdpt \qquad (15)$$

(*iii*) While the reaction of **1a** with the Lewis bases may conceivably proceed *via* the protonated base, such a reaction is highly unlikely in light of their relative proton basicities as compared to NEt_3; pK_B NEt_3 (3.36) *versus* 3,5Me_2-py (7.85), PEt_3 (8.69), py (8.75), phen (9.16) and bipy (9.56).[25]

Experimental

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, New York. Melting points were determined in sealed capillaries and are uncorrected. Infrared spectra (4000–400 cm^{-1}) were recorded on a Nicolet 205 FT-IR spectrometer in KBr pellets, NMR spectra on Bruker AM-250 (^1H) and AM-500 ($^{13}C-\{^1H\}$ and $^{31}P-\{^1H\}$) spectrometers [δ relative to external $SiMe_4$ (^1H and ^{13}C) and 95% H_3PO_4 (^{31}P)]. Solid-state ^{31}P cross-polarisation magic angle spinning (CP MAS) NMR spectra were obtained on a Chemagnetics CMC-200A spectrometer. Conductivities were determined on approximately 1×10^{-3} mol dm^{-3} solutions with an A. H. Thomas Co. Serfas AC conductivity bridge RCM 15B1 using a cathode-ray oscillograph as a null detector. All manipulations were carried out under nitrogen. Solvents were dried, distilled and degassed before use. Acetonitrile for conductivity measurements was specially purified by successive distillation from CaH_2, P_2O_5 and CaH_2. 1,3-Diphenyltriazene was prepared following the literature method.[26] All remaining Lewis bases were used as received from commercial sources.

Triethylammonium cis-*Dichlorobis*(1,3-*diphenyltriazenido*)-*indate*(III) **1a**.—A solution of 1,3-diphenyltriazene (2.83 g, 14.3 mmol) and NEt_3 (1.45 g, 2.00 cm^3, 14.5 mmol) in toluene (20 cm^3) was added dropwise *via* cannula over a period of 30 min to a suspension of $InCl_3$ (1.59 g, 7.19 mmol) in toluene (30 cm^3). The resulting bright orange slurry was heated at 80 °C for 30 min following the addition. After standing overnight at −24 °C in a freezer, the reaction mixture was filtered, washed with pentane (2 × 50 cm^3) and vacuum dried. Yield: 5.38 g of an approximately equimolar mixture of **1a** and $[NHEt_3]Cl$ (92% of theoretical). Crystallisation of this crude precipitate from a saturated solution of MeCN gave large, bright-orange, X-ray quality crystals of **1**. An analytically pure sample was obtained by briefly washing with cold methanol (20 cm^3) to remove a small quantity of $[NHEt_3]Cl$ that had co-crystallised with the product: yield 2.79 g, 57%; m.p. 170 °C (Found: C, 52.90; H, 5.35; N, 14.50. Calc. for $C_{30}H_{36}Cl_2InN_7$: C, 52.95; H, 5.35; N, 14.40%). IR (cm^{-1}): 3450(br) m, ν(N–H), 3026m, 2818w, 2736w, 2546(br) w, 1948w, 1875w, 1801w, 1738w, 1592s, 1498m, 1483s, 1459m, 1416w, 1392w, 1363s, 1334s, 1310s, 1280s, 1237s, 1218s, 1168m, 1156m, 1074m, 1010m, 905m, 833w, 763s, 693s, 661s, 613w, 517m, 487m and 412w. NMR (CD_3CN): ^1H, δ 7.54 [8 H, d, *J*(H–H) 6.8, *o*-C_6H_5], 7.25 [4 H, apparent t, *J*(H–H) 6.2, *m*-C_6H_5], 7.04 [2 H, apparent t, *J*(H–H) 5.8, *p*-C_6H_5], 3.11 [6 H, q, *J*(H–H) 6.1 Hz, NCH_2] and 1.22 [9 H, t, *J*(H–H) 6.1 Hz, NCH_2CH_3]; ^{13}C, δ 148.2 (N–C), 130.1 (*m*-C_6H_5), 124.8 (*p*-C_6H_5), 119.7 (*o*-C_6H_5), 48.1 (NCH_2CH_3) and 9.3 (NCH_2CH_3). Conductivity: Λ_M 120 Ω^{-1} cm^2 mol^{-1}.

Tetraethylammonium cis-*Dichlorobis*(1,3-*diphenyltriazenido*)-*indate*(III) **1b**.—Compound **1a** (5.103 g, 7.54 mmol) was dissolved in MeCN (90 cm^3) and $[NEt_4]Cl$ (1.243 g, 7.50 mmol) added in one portion. After stirring for 10 min a voluminous precipitate appeared. The reaction was heated to effect dissolution and the volume of the solvent reduced to 50 cm^3 under vacuum. Slow cooling to −24 °C, followed by washing with Et_2O (2 × 20 cm^3) and vacuum drying gave orange crystals, yield 3.20 g, 60%; m.p. 213–214 °C (Found: C, 54.25; H, 5.60; N, 13.90. Calc. for $C_{32}H_{40}Cl_2InN_7$: C, 54.25; H, 5.70; N, 13.85%). IR (cm^{-1}): 3071w, 2989w, 1590s, 1497m, 1482s, 1458m, 1438w, 1392m, 1365m, 1331s, 1307s, 1280s, 1233s, 1217m, 1187w, 1172m, 1152w, 1072w, 996m, 900m, 766s, 751s, 694s, 663s, 613w, 518m, 486m and 415w. NMR (CD_3CN): ^1H, δ 7.54 [8 H, d, *J*(H–H) 6.6, *o*-C_6H_5], 7.26 [8 H, apparent, *J*(H–H) 6.5, *m*-C_6H_5], 7.06 [4 H, apparent t, *J*(H–H) 6.2, *p*-C_6H_5], 3.12 [8 H, q, *J*(H–H) 6.1, NCH_2], 1.18 [12 H, t of t, *J*(H–H) 7.3, *J*(N–H) 1.8 Hz, NCH_2CH_3]; ^{13}C, δ 148.4 (N–C), 130.1 (*m*-C_6H_5), 124.8 (*p*-C_6H_5), 119.8 (*o*-C_6H_5), 53.4 (NCH_2CH_3) and 7.8 (NCH_2CH_3). Conductivity: Λ_M 124 Ω^{-1} cm^2 mol^{-1}.

Bis(*triphenylphosphoranylidene*)*ammonium* cis-*Dichlorobis*-(1,3-*diphenyltriazenido*)*indate*(III) **1c**.—Prepared as for **1b** using **1a** (0.50 g, 0.73 mmol) and $[N(PPh_3)_2]Cl$ (0.422 g, 0.73 mmol) in MeCN (20 cm^3). No precipitate formed, so the solvent was reduced to half its initial volume and cooled. Yield: 0.728 g, 89%, m.p. 148 °C. IR (cm^{-1}): 3061w, 1592m, 1483s, 1438m, 1364m, 1330s, 1308s, 1280s, 1235m, 1185w, 1167w, 1114m, 1072w, 1027w, 997w, 762m, 724m, 692s, 662m, 546m, 533m, 499m. NMR (CD_3CN): ^1H, δ 7.52 (38 H, br m, C_6H_5), 7.23 [8 H, apparent t, *J*(H–H) 7.9, *m*-C_6H_5] and 7.01 [4 H, apparent t, *J*(H–H) 6.5 Hz, *p*-C_6H_5]; ^{13}C, δ 148.3 (NC), 134.6, 133.3, 130.4, 127.9 [C_6H_5, $N(PPh_3)_2$], 130.0 (*m*-C_6H_5), 124.8 (*p*-C_6H_5) and 119.7 (*o*-C_6H_5). Conductivity: Λ_M 90 Ω^{-1} cm^2 mol^{-1}.

cis-*Dichloro*-trans-(1,3-*diphenyltriazenido*)*di*(*pyridine*)-*indium*(III) **2**.—Compound **1a** (2.00 g, 2.94 mmol) was dissolved in MeCN (30 cm^3) and an excess of pyridine (2 cm^3) added *via* syringe. The reaction solution was refluxed for 2 h. Removal of the solvent and excess pyridine, under vacuum, gave a fine granular orange-yellow solid which was washed with pentane (2 × 20 cm^3) and vacuum dried. Yield: 0.83 g, 52%; m.p. 193–194 °C. IR (cm^{-1}): 3080w, 1603m, 1484s, 1446s, 1332s, 1314s, 1283s, 1244w, 1216m, 1155w, 1067m, 1040m, 1012m, 901w, 758s, 692s, 657m, 634m, 513w and 488w. NMR (CD_3CN): ^1H, δ 8.79 [4 H, d, *J*(H–H) 4.8, *o*-C_5H_5N], 7.99 [2 H, apparent t, *J*(H–H) 7.7 Hz, *p*-C_5H_5N], 7.76 [4 H, d, *J*(H–H) 7.6, *o*-C_6H_5], 7.54 [4 H, apparent t, *J*(H–H) 7.0, *m*-C_5H_5N], 7.36 [4 H, apparent t, *J*(H–H) 7.9, *m*-C_5H_5] and 7.12 [2 H, apparent t, *J*(H–H) 7.3 Hz, *p*-C_6H_5]; ^{13}C, δ 148.7 (*o*-C_5H_5N), 148.2 (NC_6H_5), 141.4 (*p*-C_5H_5N), 130.4 (*m*-C_6H_5), 126.6 (*m*-C_5H_5N), 125.7 (*p*-C_6H_5) and 120.0 (*o*-C_6H_5). Conductivity: Λ_M 10 Ω^{-1} cm^2 mol^{-1}.

cis-*Dichloro*-trans-*bis*(3,5-*dimethylpyridine*)(1,3-*diphenyltriazenido*)*indium*(III) **3**.—Compound **1a** (1.22 g, 1.79 mmol) was dissolved in MeCN (30 cm^3) and 3,5-dimethylpyridine (0.45 cm^3, 0.42 g, 3.9 mmol) added *via* syringe. A yellow precipitate was instantly formed and the resulting suspension was stirred for 1 h. Removal of the solvent and excess 3,5-dimethylpyridine under vacuum gave a fine granular, orange-yellow solid which was washed with pentane (2 × 20 cm^3) and vacuum dried. Crystals suitable for study by X-ray diffraction were grown at −24 °C from a saturated solution of CH_2Cl_2 (30 cm^3) layered with pentane (15 cm^3). Yield: 1.05 g, 98%; m.p. 252 °C (Found: C, 51.20; H, 4.65; N, 11.55. Calc. for $C_{26}H_{28}Cl_2InN_5$: C, 52.35; H, 4.75; N, 11.75%). IR (cm^{-1}): 3047(br) w, 2963w, 2921w, 1603m, 1592s, 1484s, 1459m, 1441w, 1384m, 1354w, 1334s, 1307s, 1281s, 1215w, 1171m, 1147m, 1076m, 1038m, 910m, 865m, 761s, 696s, 662m, 537w, 522w, 485m, and 404m. NMR ($CDCl_3$): ^1H, δ 8.43 (4 H, s, *o*-CH, 3,5Me_2-py), 7.76 [4 H, d, *J*(H–H) 8.1, *o*-C_6H_5], 7.38 (2 H, s, *p*-CH, 3,5Me_2-py), 7.30[4, H, apparent t, *J*(H–H) 8.2, *m*-C_6H_5], 7.05 [2 H, apparent t, *J*(H–H) 7.3 Hz, *p*-C_6H_5]; ^{13}C, δ 147.4 (NC_6H_5), 145.4 (*o*-CH, 3,5Me_2-py), 140.6 (*p*-CH, 3,5Me_2-py), 134.5 (*m*-CH, 3,5Me_2-py), 129.2 (*m*-C_6H_5), 124.2 (*p*-C_6H_5), 119.2 (*o*-C_6H_5) and 18.4 (*m*-CH_3, 3,5Me_2-py). Conductivity: Λ_M 35 Ω^{-1} cm^2 mol^{-1}.

cis-*Dichloro*-trans-(1,3-*diphenyltriazenido*)*bis*(*triethylphosphine*)*indium*(III) **4**.—Compound **1a** (2.06 g, 3.03 mmol) was dissolved in MeCN (20 cm^3) and PEt_3 (0.50 cm^3, 0.40 g, 3.4 mmol) added *via* syringe. No precipitate formed in the reaction, so after 1 h at room temperature the solvent was gradually removed under vacuum to promote precipitation. After gently warming to redissolve the solid, the solution was cooled slowly

Table 5 Summary of X-ray diffraction data[a]

Compound	**1a**	**3**	**4**	**5**
Formula	$C_{30}H_{36}Cl_2InN_7$	$C_{26}H_{28}Cl_2InN_5$	$C_{24}H_{40}Cl_2InN_3P_2$	$C_{22}H_{18}Cl_2InN_5$
M	680.4	596.3	618.3	538.1
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	*Pbca*	*Pbca*	$P2_1/n$
a/Å	9.883(3)	9.246(3)	18.80(1)	13.052(4)
b/Å	15.405(2)	15.84(3)	15.84(1)	11.653(4)
c/Å	20.926(4)	36.49(1)	19.45(6)	14.540(6)
β/°	91.69(2)			104.91(3)
U/Å^3	3183(5)	5344(4)	5801(4)	2137(1)
Z	4	8	8	4
D_c/g cm^{-3}	1.171	1.482	1.416	1.672
F(000)	11 484	2416	2544	1072
Crystal dimensions/mm	0.24 × 0.45 × 0.41	0.33 × 0.25 × 0.4	0.20 × 0.23 × 0.30	0.24 × 0.25 × 0.27
μ/cm^{-1}	0.76	0.11	0.11	0.13
2θ limits/°	4.0–40.0	4.0–55.0	4.0–40.0	4.0–45.0
No. of collected data	3761	7664	3208	2379
No. of unique data	2980	6104	2699	1999
Observed data	2752	4414	2335	1809
R[b]	0.0757	0.0559	0.0345	0.0283
R′[c]	0.0811	0.0894	0.0474	0.0363
Maximum final residual/e Å^{-3}	1.29	1.17	1.12	0.56

[a] Details in common: $T = -80$ °C; Mo-Kα radiation, $\lambda = 0.710\,73$ Å; criterion for observed data, $F > 4\sigma(F)$. [b] $R = \Sigma||F_o| - |F_c|/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = \sigma^2(|F_o|) \times x(|F_o|^2)$, x = 0.0105 **1a**, 0.008 **3**, 0.0004 **4**, 0.0003 **5**.

Table 6 Atomic coordinates (× 10^4) for $[NHEt_3][InCl_2(dpt)_2]$ **1a**

Atom	*x*	*y*	*z*
In	218(1)	8 874(1)	2 444(1)
Cl(1)	−1 872(3)	8 530(2)	2 969(1)
Cl(2)	−238(3)	7 974(2)	1 482(1)
N(1)	2 471(8)	8 759(5)	2 273(3)
N(12)	2 807(7)	8 304(5)	2 773(3)
N(2)	1 735(8)	8 159(5)	3 089(3)
C(11)	3 533(11)	8 978(5)	1 852(5)
C(12)	4 835(10)	8 721(6)	1 919(5)
C(13)	5 801(11)	8 987(6)	1 508(5)
C(14)	5 429(9)	9 540(7)	1 010(5)
C(15)	4 105(11)	9 785(7)	923(5)
C(16)	3 156(10)	9 525(7)	1 328(4)
C(21)	1 920(9)	7 677(6)	3 681(4)
C(22)	825(10)	7 582(7)	4 049(5)
C(23)	982(11)	7 147(7)	4 634(5)
C(24)	2 207(10)	6 842(6)	4 839(5)
C(25)	3 324(10)	6 939(7)	4 476(5)
C(26)	3 174(9)	7 365(7)	3 881(5)
N(3)	525(7)	10 187(4)	2 933(3)
N(34)	97(7)	10 664(6)	2 463(3)
N(4)	−228(7)	10 173(5)	1 992(3)
C(31)	1 025(10)	10 644(6)	3 489(5)
C(32)	1 331(14)	11 517(7)	3 504(6)
C(33)	1 824(17)	11 897(8)	4 050(7)
C(34)	1 913(17)	11 423(9)	4 621(5)
C(35)	1 561(12)	10 578(9)	4 613(6)
C(36)	1 114(12)	10 163(7)	4 055(5)
C(41)	−863(9)	10 579(6)	1 449(4)
C(42)	−923(9)	10 122(6)	881(5)
C(43)	−1 502(9)	10 489(7)	334(5)
C(44)	−2 073(11)	11 318(7)	354(5)
C(45)	−2 015(10)	11 773(7)	930(5)
C(46)	−1 433(11)	11 425(7)	1 462(5)
N(5)	−922(11)	5 994(6)	1 631(5)
C(51)	−2 282(20)	5 938(11)	1 322(13)
C(52)	−2 729(25)	6 364(14)	892(16)
C(53)	−953(23)	5 793(13)	2 264(9)
C(54)	349(34)	6 082(11)	2 597(9)
C(55)	92(17)	5 497(11)	1 219(9)
C(56)	−196(17)	4 553(9)	1 202(9)

Table 7 Atomic coordinates (× 10^4) for $[InCl_2(dpt)(3,5Me_2\text{-}py)_2]$ **3**

Atom	*x*	*y*	*z*
In	6 185(1)	1 234(1)	8 039(1)
Cl(1)	7 270(1)	−419(1)	8 588(1)
Cl(2)	4 484(1)	230(1)	7 470(1)
N(1)	6 624(3)	1 662(3)	6 678(3)
N(12)	6 002(3)	2 540(3)	6 421(3)
N(2)	5 488(3)	2 743(3)	7 056(3)
C(11)	7 252(4)	1 318(4)	6 065(3)
C(12)	8 086(4)	578(4)	6 423(4)
C(13)	8 726(4)	213(4)	5 852(4)
C(14)	8 538(4)	584(4)	4 919(4)
C(15)	7 696(4)	1 313(4)	4 562(4)
C(16)	7 062(4)	1 687(4)	5 128(3)
C(21)	4 764(4)	3 672(4)	6 872(3)
C(22)	4 799(4)	4 530(4)	6 224(4)
C(23)	4 057(5)	5 383(5)	6 074(4)
C(24)	3 278(4)	5 416(5)	6 560(4)
C(25)	3 248(4)	4 578(5)	7 211(4)
C(26)	3 985(4)	3 692(4)	7 367(4)
N(3)	5 839(3)	1 776(3)	9 432(3)
C(31)	6 576(4)	2 370(4)	10 052(4)
C(32)	6 450(5)	2 685(5)	10 928(4)
C(33)	5 542(5)	2 369(5)	11 188(4)
C(34)	4 786(5)	1 742(5)	10 551(4)
C(35)	4 942(4)	1 457(5)	9 675(4)
N(4)	7 525(3)	2 422(3)	8 830(3)
C(41)	7 525(4)	2 726(4)	9 722(4)
C(42)	8 341(4)	3 348(4)	10 282(4)
C(43)	9 163(4)	3 704(4)	9 907(4)
C(44)	9 156(4)	3 403(4)	8 990(4)
C(45)	8 323(4)	2 760(4)	8 472(4)

to −24 °C, from which large orange, X-ray quality crystals grew overnight. Following solvent removal *via* cannula, the crystals were washed with Et_2O (10 cm^3) and vacuum dried. Yield: 1.27 g, 68%; m.p. 165–167 °C (Found: C, 46.95; H, 6.60; N, 6.95. Calc. for $C_{24}H_{40}Cl_2InN_3P_2$: C, 46.60; H, 6.50; N, 6.80%). IR (cm^{-1}): 3036(br) w, 2967s, 2937s, 2909s, 2879s, 1961w, 1883w, 1809w, 1744w, 1592s, 1503m, 1482s, 1458s, 1414s, 1382m, 1351s, 1332s, 1308s, 1276s, 1236s, 1167m, 1155m, 1073m, 1035m, 908s, 765s, 726s, 694s 660s, 613m, 517m and 184m. NMR ($CDCl_3$): ^1H, δ 7.78 [4 H, d, *J*(H–H) 7.6, *o*-C_6H_5], 7.30 [4 H, apparent t, *J*(H–H) 7.9, *m*-C_6H_5], 7.04 [2 H, apparent t, *J*(H–H) 7.9 Hz, *p*-C_6H_5], 1.69 (12 H m, PCH_2CH_3) and 0.99 (18 H, m, PCH_2CH_3); ^{13}C, δ 147.8 (NC_6H_5), 129.9 (*m*-C_6H_5), 123.9 (*p*-C_6H_5), 119.0 (*o*-

Table 8 Atomic coordinates (× 10^4) for [$InCl_2$(dpt)(PEt_3)$_2$] **4**

Atom	*x*	*y*	*z*
In	6800(1)	1147(1)	3628(1)
Cl(1)	7530(1)	2007(1)	4416(1)
Cl(2)	7625(1)	176(1)	3039(1)
N(1)	5754(3)	799(3)	3067(2)
N(12)	5316(3)	1269(3)	3423(3)
N(2)	5671(3)	1668(3)	3898(2)
C(11)	5473(3)	384(4)	2492(3)
C(12)	4780(3)	459(3)	2264(3)
C(13)	4557(4)	43(4)	1680(3)
C(14)	5017(4)	−463(5)	1309(3)
C(15)	5709(4)	−535(5)	1535(3)
C(16)	5945(3)	−124(4)	2118(3)
C(21)	5278(3)	2197(4)	4337(3)
C(22)	5640(3)	2624(4)	4851(3)
C(23)	5289(4)	3141(4)	5304(3)
C(24)	4557(4)	3251(4)	5255(3)
C(25)	4192(4)	2835(4)	4737(3)
C(26)	4544(3)	2315(4)	4276(3)
P(1)	7000(1)	2299(1)	2661(1)
C(111)	6360(3)	3163(4)	2660(3)
C(112)	5636(3)	2982(5)	2357(3)
C(113)	6980(4)	1819(4)	1804(3)
C(114)	7167(4)	2394(5)	1213(3)
C(115)	7846(3)	2829(4)	2717(3)
C(116)	8494(3)	2263(5)	2676(4)
P(2)	6571(1)	41(1)	4626(1)
C(211)	7264(4)	−699(5)	4765(4)
C(212)	7968(4)	−307(6)	4992(5)
C(213)	6414(4)	553(5)	5441(3)
C(214)	6321(5)	8(5)	6077(3)
C(215)	5758(4)	−591(5)	4488(3)
C(216)	5816(4)	−1207(4)	3919(4)

C_6H_5), 13.2 (PCH_2CH_3) and 7.30 (PCH_2CH_3); ^{31}P, δ −5.7. Conductivity: Λ_M 33 Ω^{-1} cm^2 mol^{-1}.

cis-(2,2′-*Bipyridine*)*dichloro*(1,3-*diphenyltriazenido*)*indium*(III) **5**.—Prepared in an analogous manner to **2**, with **1a** (0.50 g, 0.73 mmol), MeCN (20 cm^3) and bipy (0.114 g, 0.730 mmol). Yield: 0.25 g of orange crystals, 64%; m.p. 280 °C (decomp.) (Found: C, 49.45; H, 3.45; N, 13.20. Calc. for $C_{22}H_{18}Cl_2InN_5$: C, 49.10; H, 3.35; N, 13.00%). IR (cm^{-1}) 3062(br) w, 1593m, 1578w, 1496w, 1483m, 1443m, 1361w, 1330m, 1306s, 1283s, 1249w, 1238w, 1217w, 1177m, 1170m, 1025m, 898w , 772w, 759s, 730w, 692s, 517w, 487w and 416w. Conductivity: Λ_M 10 Ω^{-1} cm^2 mol^{-1}.

cis-*Dichloro*(1,3-*diphenyltriazenido*)(1,10-*phenanthroline*)-*indium*(III) **6**.—Prepared in an analogous manner to **2**, with **1a** (0.60 g, 0.88 mmol) and 1,10-phenanthroline hydrate (0.175 g, 0.88 mmol). Yield: 0.349 g, 70%; m.p. 281 °C (decomp.) (Found: C, 51.65; H, 3.15; N, 12.75. Calc. for $C_{24}H_{18}Cl_2InN_5$: C, 51.30; H, 3.25; N, 12.45%). IR (cm^{-1}): 3059(br) mw, 1593m, 1586m, 1523w, 1493m, 1481m, 1431m, 1360w, 1329s, 1307s, 1283s, 1239w, 1227w, 1167w, 1144w, 1106w, 853m, 761m, 722m, 692m, 661m, 515w and 486w. Conductivity: Λ_M 8.6 Ω^{-1} cm^2 mol^{-1}.

cis-[1,2-*Bis*(*dimethylphosphino*)*ethane*]*dichloro*(1,3-*diphenyltriazenido*)*indium*(III) **7**.—Prepared in an analogous manner to **2**, with **1a** (1.00 g, 1.5 mmol) and dmpe (0.27 cm^3, 0.24 g, 1.6 mmol). Yield 0.736 g, 94%; m.p. 216 °C (decomp.). IR (cm^{-1}): 3272w, 3062w, 2977w, 1601m, 1591s, 1507w, 1497w, 1481s, 1468w, 1459w, 1421m, 1352w, 1332s, 1308s, 1277s, 1167m, 1153w, 1111m, 1073w, 950m, 906s, 763s, 755s, 691s, 660s, 518w and 483w. CP MAS NMR: ^{31}P, δ −14.5. Conductivity: Λ_M 51 Ω^{-1} cm^2 mol^{-1}.

Table 9 Atomic coordinates (× 10^4) for [$InCl_2$(dpt)(bipy)] **5**

Atom	*x*	*y*	*z*
In	634(1)	5534(1)	1258(1)
Cl(1)	364(2)	4379(1)	827(1)
Cl(2)	−264(2)	4925(1)	1820(1)
N(1)	1513(5)	6615(3)	913(1)
N(12)	1644(5)	7177(3)	1170(1)
N(2)	1199(5)	6858(3)	1478(1)
C(11)	1914(6)	6859(4)	557(2)
C(12)	2611(7)	7624(4)	479(2)
C(13)	3022(9)	7809(5)	119(2)
C(14)	2728(8)	7246(5)	−159(2)
C(15)	2011(8)	6497(5)	−83(2)
C(16)	1614(7)	6300(4)	268(2)
C(21)	1278(7)	7379(3)	1788(2)
C(22)	419(8)	7148(4)	2092(2)
C(23)	418(9)	7641(5)	2403(2)
C(24)	1270(9)	8357(4)	2424(2)
C(25)	2148(8)	8577(4)	2130(2)
C(26)	2127(6)	8118(3)	1810(2)
N(3)	2994(5)	5156(3)	1389(1)
C(31)	3744(6)	4751(4)	1162(2)
C(32)	5156(7)	4283(3)	1239(2)
C(33)	5782(7)	5665(4)	1561(2)
C(34)	4998(6)	5189(4)	1799(2)
C(35)	3611(7)	5416(3)	1697(2)
C(36)	5927(8)	3799(4)	983(2)
C(37)	5649(8)	5476(5)	2156(2)
N(4)	−1625(5)	6035(3)	1108(1)
C(41)	−2265(7)	6595(4)	1334(2)
C(42)	−3623(7)	6945(4)	1272(2)
C(43)	−4321(7)	6701(5)	954(2)
C(44)	−3701(7)	6116(4)	715(2)
C(45)	−2328(7)	5811(4)	800(2)
C(46)	−4226(8)	7565(5)	1540(2)
C(47)	−4467(8)	5820(6)	377(2)

cis-[1,2-*Bis*(*diethylphosphino*)*ethane*]*dichloro*(1,3-*diphenyltriazenido*)*indium*(III) **8**.—Prepared in an analogous manner to **2**, with **1a** (2.65 g, 3.89 mmol) and depe (1.00 cm^3, 0.884g, 4.29 mmol). Yield 1.92 g, 84%; m.p. 235 °C (Found: C, 44.45; H, 6.05; N, 7.00. Calc. for $C_{22}H_{34}Cl_2InN_3P_2$: C, 44.90; H, 5.85; N, 7.15%). IR (cm^{-1}): 2967m, 2938m, 2905m, 2882m, 1592s, 1483s, 1457m, 1408m, 1388w, 1352w, 1332s, 1306s, 1281s, 1216w, 1194w, 1185w, 1165w, 1107m, 1073w, 1050w, 1027w, 905m, 763s, 694s, 659s, 614w, 517w and 481w. CP MAS NMR: ^{31}P, δ −9.5. Conductivity: Λ_M 43 Ω^{-1} cm^2 mol^{-1}.

X-Ray Crystallographic Studies.—A crystal data summary is given in Table 5; fractional actomic coordinates are listed in Tables 6–9. Crystals of compounds **1a**, **3**, **4** and **5** were mounted directly onto the goniometer with silicon grease. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[27] using a Nicolet R3m/v diffractometer operating in the θ–2θ scan mode. Data collection was controlled by using the Nicolet P3 program.[28] Empirical absorption corrections were applied to the data using the program PSICOR. Further experimental data are given in Table 5.

The structures were solved using the direct methods program XS, which revealed the position of most of the heavy atoms. Most but not all of the hydrogens were visible in the final difference map. Hydrogens were included as fixed atom contributors in the final cycles, *d*(C–H) 0.96 Å and *U*(iso) 0.08 Å^2. Details of the refinement are given in Table 5. Atomic scattering factors and anomalous scattering parameters were as given in ref. 29.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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