Square Pyramidal, Organo-indium Complexes. Preparation and *X*-Ray Crystal Structure of $\mathrm{MeIn\{[MeN(CH_2)_2NMe]Me_2In[MeN(CH_2)_2NMe]Me_2In\}}$ and $\mathrm{MeIn[MeNC(CH)_4N]_2}$

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The *X*-ray structure of $\mathrm{MeIn\{[MeN(CH_2)_2NMe]Me_2In[MeN(CH_2)_2NMe]Me_2In\}}$ (**1**) reveals a central, 5-co-ordinate, square pyramidal indium atom (with an apical methyl group) and two peripheral, tetrahedral indium atoms; the *X*-ray structure of $\mathrm{MeIn[MeNC(CH)_4N]_2}$ (**2**) also contains square pyramidal indium.

Almost all polynuclear indium organometallic compounds previously reported have been oligomers, frequently of the form $(\mathrm{R_2InX})_n$, *e.g.* $(\mathrm{Me_2InNMe_2})_2$,[1] $(\mathrm{Me_2InPEt_2})_3$,[2] $(\mathrm{Me_2InCN})_4$,[3] in which *n* ligands bridge the metal atoms, thus completing the octet and giving a co-ordination number of four. Examples of 5-co-ordinated indium which persist in solution are known[4] but they are distorted trigonal bipyramids except when constrained by the configuration of the ligand as in alkylindium porphyrins.[5] That indium would adopt a square pyramidal co-ordination if packing effects in the crystal were favourable, was shown by the $\mathrm{InCl_5}^{2-}$ ion.[6]

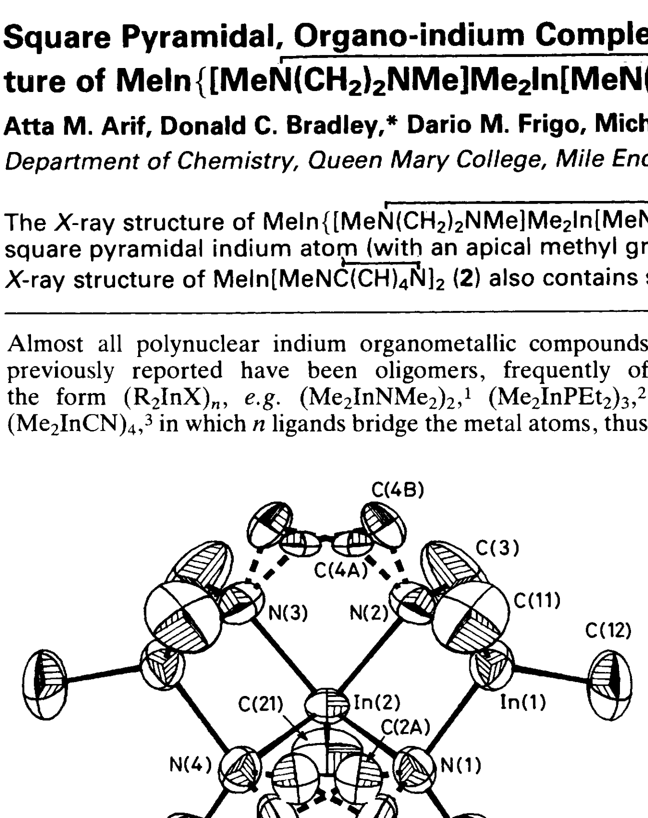

Figure 1. The structure of compound (**1**). (Note that the $\mathrm{CH_2–CH_2}$ bridges are disordered at both sites and this feature has introduced large apparent thermal parameters in some attached atoms.) Selected bond lengths (Å) and angles (°) are as follows: In(1)–C(11) 2.202(15), In(1)–C(12) 2.177(15), In(1)–N(1) 2.218(11), In(1)–N(2) 2.197(12), In(2)–C(21) 2.210(17), In(2)–N(1) 2.282(10), In(2)–N(2) 2.271(10); N(1)–In(1)–N(2) 85.1(4), C(11)–In(1)–C(12) 125.6(8), N(1)–In(2)–N(2) 82.0(4), N(1)–In(2)–N(3) 78.5(5), N(2)–In(2)–N(4) 79.1(4), C(21)–In(2)–N(1) 114.4(5), C(21)–In(2)–N(2) 113.9(5).

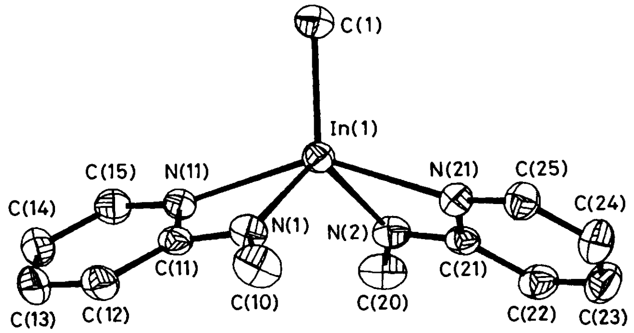

Figure 2. The structure of compound (**2**). Selected bond lengths (Å) and angles (°) are as follows: In(1)–C(1) 2.138(7), In(1)–N(1) 2.145(6), In(1)–N(2) 2.144(6), In(1)–N(11) 2.354(6), In(1)–N(21) 2.333(6); N(1)–In(1)–N(11) 59.6(2), N(2)–In(1)–N(21) 59.5(3), N(1)–In(1)–N(21) 99.3(3), N(2)–In(1)–N(11) 100.5(2), C(1)–In(1)–N(1) 123.5(3), C(1)–In(1)–N(2) 123.8(3), C(1)–In(1)–N(11) 106.5(3), C(1)–In(1)–N(21) 108.7(3).

The present report concerns the preparation and the *X*-ray crystal structures† of (**1**) and (**2**) (Figures 1 and 2) which are, to our knowledge, the first examples of square pyramidal indium organometallics besides the alkylindium porphyrin systems. Also (**1**) is the first tri-indium compound which is not a trimer, there being a central, square pyramidal indium, the base formed by two chelating diamine ligands each of which also bridges two distorted tetrahedral Me_2In units. All the metal atoms are in their usual +3 oxidation state and the central metal in (**1**) is 0.93 Å above the square plane formed by the nitrogen atoms, a similar distance to that in (**2**), although in (**2**) the nitrogens are not perfectly planar.

$$3MeNH(CH_2)_2NMeLi + 3Me_2InCl \rightarrow CH_4 + 3LiCl + MeNH(CH_2)_2NHMe$$

$$+ MeIn\{[Me\overline{N(CH_2)_2NMe]Me_2In[MeN(CH_2)_2NMe]Me_2In}\}$$

(**1**)

$$Me_3In + 2MeNH\overline{C(CH)_4N} \rightarrow MeIn[MeN\overline{C(CH)_4N}]_2 + 2CH_4$$

(**2**)

N,N'-Dimethylethylenediamine (dmed) was mono-*N*-lithiated by reaction with one equivalent of n-butyl-lithium in diethyl ether and to this was added one equivalent of Me_2InCl^7 suspended in diethyl ether. The contents were heated under reflux for one hour, the LiCl filtered off and concentration *in vacuo* gave white crystals. Sublimation at 90 °C/0.01 mm Hg gave large, colourless crystals (*ca.* 65% yield) which were characterized as (**1**) by spectroscopic and *X*-ray analyses. Satisfactory elemental analyses (C, H, N) were obtained; m.p. 195—200 °C (melts as orange liquid); ^1H n.m.r. (C_6D_6, 80 MHz) δ −0.10 (3H, s, apical Me–In), −0.03 and −0.01 (12H, 2 singlets due to Me–In proximal and distal to apical Me–In), 2.50 (12H, s, N–Me), and 2.75 (8H, AA'BB', CH_2); ^{13}C n.m.r. (C_6D_6, 63 MHz) δ −10.7, −10.5, −10.3 (Me–In), 43.0 (N–Me), and 54.9 (CH_2). Presumably, the initial product is $MeNH(CH_2)_2NMeInMe_2$ which perhaps trimerizes. Subsequent loss of methane and metathesis between a peripheral N–H and central In–N bonds would give (**1**). Dimethylindium amides can also be formed by methane elimination from trimethylindium and a secondary amine.[1] Interestingly, we have found that treatment of trimethylindium with dmed in 1:1 molar ratio gave not (**1**) but $[(Me_3In)_2(dmed)]$ which is stable to methane elimination up to 90 °C.

A two-fold excess of 2-methylaminopyridine was condensed *in vacuo*, onto trimethylindium held at −196 °C. Upon warming to 0 °C rapid evolution of methane occurred and continued until the contents had been heated to 50 °C for one hour. The resulting yellow oil was dissolved in pentane and cooling to −25 °C gave off-white crystals (*ca.* 70% yield) which were characterized as (**2**) by spectroscopic and *X*-ray analyses. Satisfactory elemental analyses were obtained; m.p. decomp. 140 °C; ^1H n.m.r. (C_6D_6, 80 MHz) δ 0.28 (3H, s, Me–In), 2.71 (6H, s, N–Me), and 6.00—7.68 (8H, 3 distinct multiplets, aromatics).

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† *Crystal data* for (**1**). $C_{13}H_{35}N_4In_3$, $M = 591.91$, orthorhombic, space group *Pnam* (alt. setting *Pnma*, No. 62), $a = 15.039(2)$, $b = 8.497(1)$, $c = 17.006(2)$ Å, $U = 2173.2$ Å^3, $D_c = 1.81$ g cm^{-3}, $Z = 4$, $\mu(Mo\text{-}K_\alpha) = 29.2$ cm^{-1}, $R = 0.041$ (unit weight) for 1411/1972 observed reflections $[I > 1.5\sigma(I)]$ measured on a diffractometer (Nonius CAD4). *Crystal data* for (**2**). $C_{13}H_{17}N_4In$, $M = 344.13$, monoclinic, space group $P2_1/a$, $a = 8.094(2)$, $b = 20.592(4)$, $c = 8.808(1)$ Å, $\beta = 94.76(2)°$, $U = 1463.0$ Å^3, $D_c = 1.56$ g cm^{-3}, $Z = 4$, $\mu(Mo\text{-}K_\alpha) = 14.7$ cm^{-1}, $R = 0.029$ (unit weight) for 2007/2580 observed reflections $[I > 1.5\sigma(I)]$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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