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The neopentylindium(III) derivatives, $In(CH_2CMe_3)_3$, $In(CH_2CMe_3)_2Cl$, $In(CH_2CMe_3)Cl_2$ and $In(CH_2CMe_3)_2Me$, have been prepared and characterized by elemental analyses, cryoscopic molecular weight studies in benzene, IR and ^1H NMR spectroscopic data and Lewis acidity studies. Molecular weight studies suggest that $In(CH_2CMe_3)_3$ and $In(CH_2CMe_3)_2Me$ are monomeric molecules whereas $In(CH_2CMe_3)_2Cl$ is dimeric in benzene solution. The dichloro derivative $In(CH_2CMe_3)Cl_2$, which has insufficient solubility in benzene for molecular weight studies, crystallizes in the acentric space group $P2_12_12_1$ with $a = 6.717(4)$ Å,

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$b = 12.217(4)\,\text{Å}$, $c = 22.658(7)\,\text{Å}$, $V = 1859\,\text{Å}^3$, and $Z = 8$ (formula units). Diffraction data (MoKα, $2\theta = 2$-$50°$) were collected with a Enraf-Nonius CAD-4/θ-2θ diffractometer. Full matrix least-squares refinement led to a final R value of 0.062 for 1584 observed $[F_o \geq 5\sigma(F_o)]$ reflections. Dichloroneopentylindium(III) is a one-dimensional polymer with no short contacts between strands. Each indium has distorted trigonal bipyramidal geometry.

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by

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Abstract

The neopentylindium(III) derivatives, $In(CH_2CMe_3)_3$, $In(CH_2CMe_3)_2Cl$, $In(CH_2CMe_3)Cl_2$ and $In(CH_2CMe_3)_2Me$, have been prepared and characterized by elemental analyses, cryoscopic molecular weight studies in benzene, IR and ^1H NMR spectroscopic data and Lewis acidity studies. Molecular weight studies suggest that $In(CH_2CMe_3)_3$ and $In(CH_2CMe_3)_2Me$ are monomeric molecules whereas $In(CH_2CMe_3)_2Cl$ is dimeric in benzene solution. The dichloro derivative $In(CH_2CMe_3)Cl_2$, which has insufficient solubility in benzene for molecular weight studies, crystallizes in the acentric space group $P2_12_12_1$ with $a = 6.717(4)$Å, $b = 12.217(4)$Å, $c = 22.658(7)$Å, $V = 1859$Å^3, and $Z = 8$ (formula units). Diffraction data (MoKα, $2\theta = 2$-$50°$) were collected with a Enraf-Nonius CAD-4/θ-2θ diffractometer. Full matrix least-squares refinement led to a final R value of 0.062 for 1584 observed $[F_o \geq 5\sigma(F_o)]$

reflections. Dichloroneopentylindium(III) is a one-dimensional polymer with no short contacts between strands. Each indium has distorted trigonal bipyramidal geometry.

Introduction

Organometallic chemical vapor deposition (OMCVD) is one of the most useful techniques for making compound semiconductors[8] such as InP. The most desireable organometallic sources for OMCVD should be easily prepared, readily purified volatile liquids with excellent stability at room temperature. A number of homoleptic organoindium(III) compounds (InR_3 R=Me,[3] Et,[4,5] n-Pr,[5] i-Pr,[5] n-Bu,[5] i-Bu,[5] s-Bu,[5] t-Bu[6] and CH_2SiMe_3[7]) are known but only $InMe_3$ and $InEt_3$ are readily available for use in electronic applications. However, neither $InMe_3$ nor $InEt_3$ has all of the desireable physical properties. Trimethylindium[3] has the disadvantage of being a solid with a relatively high melting point of 89.5°C. In contrast, triethylindium[4,5] is a liquid at room temperature (mp -32°C) but the presence of $\overset{\text{beta}}{\beta}$-hydrogen atoms on the ligands reduces its thermal stability. Both compounds have the disadvantage of being prepared by relatively involved time-consuming procedures. In an attempt to provide alternative indium sources which can be prepared and purified easily, the chemistry of indium compounds with neopentyl ligands was investigated. The neopentyl ligand might have the inherent disorder necessary to provide a homoleptic compound which would be a liquid at room temperature. Furthermore, this organic substituent should have sufficient steric bulk to destabilize a diethylether adduct so that the homoleptic compound could be easily synthesized by a simple Grignard reaction. Lastly, the lack of β-hydrogen atoms on the organic substituent should serve to enhance the thermal stability of the compound so that it could be readily purified by distillation. Thus, in this paper we describe the synthesis and characterization of $InNp_3$ (Np = CH_2CMe_3), $InNp_2Cl$ $InNpCl_2$ and $InNp_2Me$. The characterization data include ^1H NMR, IR and mass spectroscopic data,

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molecular weight studies and Lewis acidity studies. In addition, an X-ray structural study of $InNpCl_2$ is described.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or in a purified argon atmosphere. All solvents were purified before use. Indium(III) chloride was purchased from Johnson Matthey, Inc. and was used as received. The neopentyl Grignard reagent was prepared as previously described.[8] The compound InI_3 was prepared from indium metal and iodine in diethylether[9]. Neopentyl chloride was purchased from Fairfield Chemical Co. and was distilled prior to use. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with the abbreviations vs (very strong), s (strong), m (medium), w (weak) and sh (shoulder). The ^1H NMR spectra were recorded at 90MHz by using a Varian Model EM-390 spectrometer. All samples for NMR spectra were contained in sealed NMR tubes. Chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ as δ 0.00 and benzene as δ 7.13. Melting points were observed in sealed capillaries. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver and Drezdzon.[10]

Synthesis of $InNp_3$. A flask charged with 29.1 g (58.3 mmol) of InI_3 dissolved in 100mL of dry diethyl ether (from Na/benzophenone) was fitted with a condenser, magnetic stir bar and a pressure equalizing addition funnel. Under a cover of argon, approximately 80 mL of a solution containing 0.232 mol of neopentyl magnesium chloride in diethyl ether was transferred to the addition funnel. The Grignard reagent was then added to the InI_3 solution over a period of 20 minutes. After the addition was complete, the reaction mixture was stirred at room temperature for 18 hours. The condenser and addition funnel were then replaced by a stopper and a Teflon valve adapter, and the diethyl ether was removed by vacuum distillation at room temperature. The crude product, a $InNp_3$ - Et_2O mixture, was isolated by vacuum distillation at 110°C. The distillation was continued for approximately 8 hours. The diethyl ether was then removed from the $InNp_3$ - Et_2O mixture by simple vacuum distillation at room temperature for 8 hours. The product, a crystalline solid, was finally purified by vacuum sublimation at 30°C with the receiving flask at -10°C. The yield of purified $InNp_3$ was 17.7g (54.0 mmol, 92.6% based on InI_3). $InNp_3$:[11] Colorless crystalline solid. mp 54-55°C. Sublimes at 27°C, 0.01 mm. Anal. Calcd. C, 54.89; H,10.13. Found C, 54.66; H, 10.12. Hydrolysis: 3.02mol CMe_4/mol $In(CH_2CMe_3)_3$. Cryoscopic molecular weight, benzene solution, formula weight 328 (obsd molality, obsd mol wt, association): 0.0940, 312, 0.951; 0.0628, 332, 1.01; 0.0472, 338, 1.03. ^1H NMR (benzene) δ 1.11 (s, 9H, CMe_3); 1.07 (s, 2H, $InCH_2$). IR (Nujol mull, cm^{-1}) 1379 (s), 1371 (s), 1228 (vs), 1212 (s), 1091 (m,sh), 1007 (s), 990 (m), 922 (w), 800 (w), 734 (m), 685 (s), 570 (s), 446 (m), 372 (m), 275 (w), 260 (m), 250 (m), 245 (m), 240 (m). $In(CH_2CMe_3)_3$ is not pyrophoric but the compound is extremely sensitive to oxygen and water.

Synthesis of $InNp_2Cl$. The compound $InNp_2Cl$ was prepared by a ligand redistribution reaction. Stoichiometric quantities of $InCl_3$ (2.21g, 10.0mmol) and $InNp_3$ (6.56g, 20.0mmol) were placed in a reaction tube equipped with a stir bar. Approximately 50mL of dry diethyl ether was distilled into the reaction tube. The reaction tube was placed in an oil bath (40°C) and stirred for 48h. The reaction tube was removed from the bath and fitted with a sintered glass frit which was attached to a 100mL Schlenk flask (equipped with a stir bar). The solution was filtered to remove any insoluble impurities and then the diethyl ether was removed by vacuum distillation. The product was finally dried in vacuo to leave 8.067g (27.59 mmol, 91.9%) of $InNp_2Cl$. **$InNp_2Cl$**: Colorless, crystalline solid. mp 162-165°C; sublimes at 110°C, 0.01mm. ^1H NMR (benzene) δ 1.09 (s,9H,CMe_3); 1.56 (s,2H,$InCH_2$). IR (Nujol mull, cm^{-1}) 3180 (w), 1360 (s), 1259 (w), 1233 (s), 1120 (s), 1111 (s), 1088 (s), 1000 (s), 594 (m), 574 (m), 448 (m), 377 (m). IR (Kel F mull, cm^{-1}) 2950 (m), 2924 (m), 2860 (s), 1460 (s), 1376 (m), 1360 (s), 1354 (s). Cryoscopic molecular weight, benzene solution, formula weight 292 (obsd molality, obsd mol wt, association): 0.0374, 643, 2.19; 0.0297, 611, 2.09; 0.0209, 566, 1.93. Solubility: soluble in benzene, pentane, Et_2O and THF. Anal. Calcd: C, 41.06; H, 7.58. Found: C, 41.34; H, 7.57.

Synthesis of $InNpCl_2$. In a ligand redistribution reaction, $InCl_3$ (0.844g, 3.99 mmol) and $InNp_3$ (0.658g, 2.00 mmol) were weighed and quantitatively transferred to a reaction tube equipped with a stir bar. Approximately 25 mL of dry diethyl ether was distilled into the reaction tube. The reaction tube was placed in an oil bath (40°C) and stirred for five days. The reaction tube was then removed from the bath and attached to a 100mL round bottom flask. The reaction mixture was transferred to the evacuated flask and the solvent was removed by vacuum distillation. The product was finally purified by vacuum sublimation to produce a total of 1.20g (4.56 mmol, 77.6%). The product $InNpCl_2$ sublimes in two fractions, one at 110°C, 0.01 mm and the other at 140°C, 0.01 mm. **$InNpCl_2$ (110°**

Fraction): Colorless, crystalline solid. mp 122-125°C (partial melting), 208-210°C (phase change with complete melting). ^{1}H NMR (solvent d^8-THF; ref benzene): δ 1.00 (s,9H,CMe_3), 1.17 (s,2H, $InCH_2$). IR (Nujol mull, cm^{-1}) 3178 (w), 2715 (m), 1302 (m), 1238 (s), 1168 (m), 1155 (m), 1120 (m), 1093 (m), 1015 (m), 1000 (m), 915 (w), 890 (w), 842 (w), 767 (w), 733 (s), 590 (w), 450 (w), 385 (w), 306 (m), 278 (m), IR (Kel F mull, cm^{-1}) 2960 (s), 2939 (s), 2865 (m), 2310 (w), 1733 (w), 1464 (m), 1384 (m), 1368 (m), 1360 (s), 308 (m), 280 (m), 278 (m). Solubility: soluble in Et_2O, THF, and slightly soluble in benzene. Anal calcd: C, 23,38; H, 4.28. Found: C, 23.51; H, 4.22. This fraction was 12% of the overall yield. **$InNpCl_2$ (140°C fraction):** Colorless, crystalline solid. mp 208-210°C. ^{1}H NMR (solvent, d^8-THF; ref benzene) δ 1.03 (s,9H, CMe_3), 1.13 (s,2H, $InCH_2$). IR (Nujol mull, cm^{-1}) 3180 (w), 2730 (m), 1305 (m), 1169 (m), 1155 (m), 1125 (m), 1118 (m), 1095 (m), 1017 (m), 1003 (m), 970 (m), 932 (m), 920 (w), 890 (w), 848 (w), 800 (w), 770 (w), 735 (s), 599 (w), 450 (w), 380 (w), 310 (m), 271 (m). IR (Kel F mull, cm^{-1}) 2952 (vs), 2930 (s), 2880 (s), 2860 (s), 2320 (m), 1468 (s), 1457 (s), 1383 (s), 1370 (vs), 1360 (vs), 300 (s), 280 (s), 270 (vs). Solubility: soluble in Et_2O, THF, and slightly soluble in benzene. Anal. Calcd: C, 23.38; H, 4.28. Found: C, 23.52; H, 4.49. This fraction was 88% of the overall yield.

X-ray Data Collection, Structure Determination, and Refinement for $InNpCl_2$. A transparent single crystal of $InNpCl_2$ was mounted in a glass capillary under argon and transferred to the goniometer. The space group was determined to be the acentric space group $P2_12_12_1$ from the systematic absences. A summary of data collection parameters is given in Table I.

Least-squares refinement with isotropic thermal parameters led to R = 0.139. The methylene hydrogen atoms were placed in calculated positions 0.95Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 $Å^2$. The methyl hydrogen atoms were not located. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of R = 0.062 and R_w = 0.063. The final values of the positional parameters are given in Table II.

Synthesis of $InNp_2Me$. In a typical synthetic reaction freshly sublimed $InNp_2Cl$ (5.847g, 19.99 mmol) was reacted at 0°C in Et_2O with LiMe (11.78 mL, 20.0 mmol, 1.7 M solution in Et_2O) in a round bottom flask equipped with a magnetic stir bar. The LiMe solution was slowly added with stirring over a 10 minute period. After the reaction mixture had stirred for 2h, the Et_2O was removed by vacuum distillation. The flask was then fitted with a sintered glass frit which was attached to a 100 mL Schlenk flask equipped with a magnetic stir bar. The product $InNp_2Me$ was immediately separated from LiCl by extraction and filtration by using 30 mL of pentane. In order to insure that the last traces of solvent (Et_2O or pentane) had been removed, the sample was continuously evacuated for 3h at room temperature. Further purification was achieved by a vacuum distillation by using a short path still with a bath temperature of 80°C and a head temperature of 55°C. The final product $InNp_2Me$ (3.35g,12.3 mmol) was isolated in 61.6% yield based on $InNp_2Cl$. **$InNp_2Me$:**[14] Colorless liquid. bp 55°C, 0.01 mm. ^1H NMR (benzene) δ -0.07 (s,3H, In-Me), 0.89 (s,4H, $InCH_2$), 1.06 (s,18H, CMe_3). IR (Neat liquid, cm^{-1}): 2958 (vs), 2905 (s), 2880 (s), 2860 (s), 1465 (m), 1457 (s), 1382 (w), 1360 (m), 1260 (w), 1234 (m), 1109 (m), 1090 (m), 1055 (w), 1012 (m), 995 (w), 797 (w), 737 (w), 688 (m), 575 (w), 482 (m), 450 (w), 372 (w). Cryoscopic molecular weight, formula weight $In(CH_2CMe_3)_2Me$ 272 (obsd molality, obsd mol wt, association): 0.0875, 318, 1.16; 0.0598, 314, 1.15; 0.0167, 324, 1.19. Solubility: soluble in benzene, pentane, Et_2O and THF. Anal. Calcd: C, 48.72; H, 9.19. Found: C, 48.58; H, 9.19.

Attempted Synthesis of $InNpMe_2$. In a typical synthetic reaction, freshly sublimed $InNpCl_2$ (2.569g, 10.00 mmol) was reacted at -78°C in Et_2O with LiMe (12.05 mL, 20.5 mmol, 1.7M solution in Et_2O). The LiMe solution was slowly added while stirring over a 10 minute period. The reaction mixture was stirred at low temperature for 15 h. The reaction mixture was then warmed to -10°C (ice/isopropanol) and the Et_2O was removed by vacuum distillation. The apparatus was then fitted with a sintered glass frit which was attached to a 100 mL Schlenk flask. Separation of the product $InNpMe_2$ from LiCl was attempted by extraction and filtration by using 50 mL of pentane. The product was a clear liquid. The ^1H NMR spectrum of a benzene solution of this liquid revealed a 1:1 ratio of indium methyl groups to Et_2O. ^1H NMR (benzene) δ -0.30 (s,3H, InMe), 0.79 (t,3H,Me of Et_2O), 0.94 (s,2H,$InCH_2$), 1.31 (s,9H,CMe_3), 3.03 (q,2H,CH_2 of Et_2O). After 20 h, a solid precipitated from the liquid product. This liquid-solid mixture was transferred to a round bottom flask and was extracted with filtration a second time with pentane. The pentane soluble liquid was again collected and the ^1H NMR spectrum revealed the same results as previously noted. After 24 h a solid had again precipitated from the liquid and another extraction/filtration was repeated. Each time, the solid which had precipitated out of the liquid, was collected and tests (flame test and halogen test) suggested this solid was LiCl. When the liquid was left for 48 h after the last extraction, no solid appeared. The liquid was then transferred to a Schlenk flask, which in turn was attached to a second Schlenk flask by using a glass V-neck. The receiving flask was cooled to -196°C and the liquid was pumped on dynamically for 2 h. After this time a clear liquid was collected at -196°C and a solid remained behind. A ^{1}H NMR spectrum was observed for each fraction. Solid fraction ^{1}H NMR (solvent d^8-THF, ref benzene): -0.77 (s,3H,InMe), 0.38 (s,2H,$InCH_2$), 0.99 (t,3H,Me of Et_2O), 1.09 (s,9H,CMe_3), 3.24 (q,2H,CH_2 of Et_2O). Liquid fraction ^{1}H NMR (benzene): 0.03 (s), 1.13 (s). The two prominent lines of the liquid portion (1.06 and 1.13) correspond to the ^{1}H NMR spectrum recorded for $InNp_3$. The ^{1}H NMR spectrum indicated that disproportionation occurred. Diethyl ether could not be completely removed from the product.

Lewis Acidity Studies of $InNp_3$ and $InNp_{3-n}X_n$ (X = Cl, n = 1,2 ; Me, n = 1). The Lewis acidity of the neopentyl indium compounds was determined by reacting a stoichiometric quantity of the desired acid with excess base. The bases used in this study were Et_2O, THF, NMe_3 and TMEDA. A reaction tube (equipped with a Teflon valve) was tarred and a weighed amount of the desired acid was transferred to the tube in the dry box. The valve was closed and the reaction tube was brought out of the dry box, evacuated, and then weighed. Excess base was then distilled into the reaction tube. After the reaction mixture had warmed to room temperature, it was left for 12h. The volatile components were removed by pumping on the sample dynamically for typically 2 h. Due to the volatility of the $In(CH_2CMe_3)_2Me$, dynamic pumping was only carried out for 20 minutes. After this amount of time, the reaction tube was reweighed. If a stoichiometric quantity of the base was retained by the acid, then the adduct was removed from the reaction tube and characterized. Stable adducts were characterized by mass measurements, mp and ^{1}H NMR and/or IR spectra. No stable room temperature adducts were formed for InNp$_2$Cl with Et$_2$O, THF, NMe$_3$ or TMEDA. The possibility of forming two to one (2:1) adducts of InNp$_3$ and InNpCl$_2$ with TMEDA were not investigated.

InNp$_3$•NMe$_3$: Forms a stable 1:1 adduct. Colorless solid. mp 120-122°C. ^{1}H NMR (benzene) 0.86 (s,2H,InCH$_2$), 1.26 (s,9H,CMe$_3$), 1.73 (s,9H,NMe$_3$). **InNp$_3$•TMEDA:** Forms a stable 1:1 adduct. Colorless solid. mp 100-107°C. ^{1}H NMR (benzene) 0.95 (s,2H,InCH$_2$), 1.21 (s,9H,CMe$_3$), 1.88 (s,3H,CH$_3$ of TMEDA), 2.33 (s,2H,CH$_2$ of TMEDA). **InNpCl$_2$•NMe$_3$:** Forms a stable 1:1 adduct. Tan solid. mp 70-73°C. ^{1}H NMR (benzene) 1.06 (s,9H,CMe$_3$), 1.16 (s,2H,InCH$_2$), 1.83 (s,9H,NMe$_3$). **InNpCl$_2$•TMEDA:** Forms a stable 1:1 adduct. Colorless solid. mp 113-117°C. ^{1}H NMR (benzene) 1.23 (s,2H,InCH$_2$), 1.28 (s,9H,CMe$_3$), 1.85 (s,4H,CH$_2$ of TMEDA), 2.08 (s,12H,CH$_3$ of TMEDA). **InNp$_2$Me•THF:** Forms a stable 1:1 adduct. Colorless liquid. ^{1}H NMR (benzene) 0.01 (s,3H,In-Me), 0.89 (s,4H,InCH$_2$), 0.99 (m,2H,THF), 1.21 (s,9H,CMe$_3$), 3.29 (m,2H,THF). IR (Neat, cm^{-1}) 2920 (vs), 2818 (s), 1461 (vs), 1440 (s), 1410 (m), 1380 (s), 1358 (vs), 1344 (s), 1293 (m), 1234 (vs), 1215 (s), 1150 (m), 1110 (s), 1096 (m), 1070 (m), 1010 (vs), 996 (s), 914 (m), 880 (vs), 800 (vs), 740 (m), 680 (vs), 573 (s), 510 (m), 480 (s), 450 (s), 380 (m). **InNp$_2$Me•NMe$_3$:** Forms a stable 1:1 adduct. Colorless liquid. ^{1}H NMR (benzene) -0.12 (s,3H,InMe), 0.79 (s,2H,InCH$_2$), 1.13 (s,9H,CMe$_3$), 1.66 (s,9H,NMe$_3$). IR (Neat, cm^{-1}) 2950 (vs), 2892 (vs), 2860 (vs), 2800 (s), 1466 (vs), 1458 (m), 1383 (m), 1359 (m), 1252 (vs), 1232 (m), 1212 (vs), 1155 (m), 1110 (w), 1100 (m), 1010 (m), 998 (s), 925 (m), 910 (w), 813 (w), 739 (s), 680 (m), 568 (s), 510 (m), 471 (m), 460 (s), 447 (s), 410 (m), 380 (m). **InNp$_2$Me•TMEDA:** Forms a stable 1:1 adduct.

Colorless semi-solid. ^{1}H NMR (benzene) -0.04 (s,3H,InMe), 0.78 (s,2H,$InCH_2$), 1.17 (s,2H,$InCH_2$), 1.21 (s,9H,CMe_3), 1.87 (s,12H,Me of TMEDA), 2.22 (s,8H,CH_2 of TMEDA). IR (Neat, cm^{-1}) 2950 (vs), 2892 (vs), 2860 (vs), 2812 (vs), 2677 (vs), 1460 (vs), 1409 (m), 1380 (m), 1358 (vs), 1290 (m), 1260 (m), 1237 (s), 1216 (s), 1180 (m), 1155 (m), 1135 (m), 1095 (s), 1040 (m), 1030 (s), 1010 (s), 998 (m), 935 (m), 925 (m), 904 (w), 870 (m), 832 (m), 800 (m), 790 (m), 766 (m), 752 (w), 740 (m), 680 (m), 565 (m), 550 (m), 510 (m), 470 (w), 450 (m), 378 (m). **$[InNp_2Me]_2 \cdot$TMEDA:** Forms a stable 2:1 adduct. Colorless solid. ^{1}H NMR (benzene) -0.04 (s,3H,InMe), 0.78 (s,2H,$InCH_2$), 1.15 (s,2H,$InCH_2$), 1.22 (s,9H,CMe_3), 1.82 (s,12H,Me of TMEDA), 2.25 (s,8H,CH_2 of TMEDA). IR (Nujol mull, cm^{-1}) 1358 (vs), 1347 (s), 1285 (m), 1232 (vs), 1212 (s), 1163 (s), 1153 (s), 1132 (s), 1104 (sh), 1095 (s), 1020 (s), 1010 (s), 1000 (s), 970 (m), 928 (m), 896 (m), 839 (s), 789 (m), 740 (m), 720 (m), 693 (vs), 680 (vs), 658 (s), 565 (s), 512 (m), 475 (s), 448 (m), 380 (m). IR (Kel F mull, cm^{-1}) 3010 (w), 2960 (vs), 2939 (sh), 2883 (s), 2860 (vs), 1469 (s), 1455 (sh), 1410 (m), 1382 (m), 1359 (s).

^{1}H NMR Study of Various Mixtures of $InNp_3$, $InNp_2Cl$ and $(InNpCl_2)_x$. A ^{1}H NMR study of different mol ratios of neopentyl indium compounds was investigated in order to determine if ligand redistribution reactions occur on the NMR time scale. Stoichiometric quantities of the desired compounds were weighed and transferred to vials. A measured amount of benzene was placed in each vial with a magnetic stir bar. All reaction mixtures were stirred for equal amounts of time. Then, a ^{1}H NMR spectrum of each solution was recorded. The results of this study are listed in Table IV. The solvent and reference for each ^{1}H NMR spectrum was benzene.

RESULTS AND DISCUSSION

A series of neutral organoindium(III) compounds which incorporate the neopentyl ligand $InNp_nX_{3-n}$ (where X = Cl; n = 1,2 and X = Me; n = 2) have been prepared and fully characterized. These new organoindium(III) compounds exhibit high thermal stability, a property which is characteristic of compounds[7,8,15] with bulky organic ligands without β-hydrogen atoms. The elemental analyses, ^1H NMR and IR spectroscopic data, molecular weight data, Lewis acidity and solubility properties suggest the molecular formulas $InNp_3$, $(InNp_2Cl)_2$ and $InNp_2Me$. In contrast, the X-ray structural study of $(InNpCl_2)_x$ demonstrates that the bulky neopentyl ligand introduces an apparently novel polymeric structure with five coordinate indium.

The simplest compound of the series $InNp_3$[11] was readily prepared in greater than 90% yield from InI_3, an easily prepared starting material,[9] by a standard Grignard reaction in diethyl ether solution. After the ether had been removed by vacuum distillation, the resulting crystalline product was readily purified by sublimation. The observation that $InNp_3$ was a crystalline solid was unexpected because $In(CH_2SiMe_3)_3$ had been previously observed to be a liquid.[7] These observations suggest that either London dispersion forces or intermolecular interactions with bridge bonding[16] as in $InMe_3$ are sufficiently strong to induce the necessary order for $InNp_3$ to be a solid at room temperature. It is regrettable but crystals of $InNp_3$ were unsuitable for X-ray structural studies. Thus, it is not possible to definitively answer the question. The properties of hydrocarbon solutions of $InNp_3$ are indicative of a simple three coordinate indium compound. The cryoscopic molecular weight data showed the presence of monomeric species in benzene solution. The ^1H NMR and IR spectroscopic data are also consistent with this formulation. It is of interest that even though the neopentyl group is a bulky ligand, it is of insufficient size to prevent the formation of simple adducts. Even though diethyl ether and THF do not form adducts, the strong Lewis bases NMe_3 and TMEDA form adducts which are stable at room temperature.

The chloro substituted derivative $InNp_2Cl$ was readily prepared by reacting stoichiometric quantities of $InNp_3$ and $InCl_3$ in a ligand redistribution reaction (Equation 1). This preparation was initially attempted by using benzene as the solvent but the yields were low. Further

$$2\ InNp_3 + InCl_3 \xrightarrow[40°C,\ 48h]{Et_2O} 3InNp_2Cl \qquad (1)$$

studies revealed that the best solvent for this reaction was diethyl ether. The highest yield (92%) was obtained when the reaction mixture was refluxed for 48h. The product from the preparative reaction mixture was readily purified by filtration or sublimation at 110°C.

The new compound $InNp_2Cl$ is a colorless, crystalline solid at room temperature. Molecular weight studies indicate that this chloroindium compound exists as a dimer in benzene solution. The most likely structure of the dimer would involve chlorine bridges as observed for other organogroup 3 halogen compounds. The gallium and indium monochloride derivatives $GaNp_2Cl$[8], $In(CH_2SiMe_3)_2Cl$[7] and $Ga(C_5Me_5)_2Cl$[17] also exist as dimers in solution. The ^1H NMR spectrum of $InNp_2Cl$ in benzene solution shows two singlets with the resonances of the CH_2 protons being downfield of the CH_3 protons. The presence of the methylene proton resonance being downfield of the methyl resonance has been observed for all bis(neopentyl) and bis(trimethylsilylmethyl) gallium[8] and indium monochloride[7] derivatives. No stable adducts with Et_2O, THF, NMe_3, or TMEDA were formed for $InNp_2Cl$.

These observations suggest that the dimer molecules remain intact in the presence of the various bases.

The dichloro derivative $InNpCl_2$ was prepared by reacting stoichiometric quantities of $InNp_3$ and $InCl_3$ in a ligand redistribution reaction. The solvent of choice for this reaction is diethyl ether. Poor yields of an impure product were obtained when benzene was used. Due to the limited solubility of $InCl_3$ in diethyl ether, the reaction mixture was refluxed for a period of 5 days for the reaction to go to completion. Careful sublimation of the product led to the separation of two fractions. One fraction sublimed at 110°C (12% of the overall yield) and the other at 140°C (88% of the overall yield). Each fraction was characterized by IR and ^1H NMR spectroscopic data, elemental analyses (C,H) and melting point data. Each fraction was soluble in diethyl ether, dibutyl ether and tetrahydrofuran but was not sufficiently soluble in benzene to enable molecular weight measurements to be completed. The fraction which sublimed at 110°C showed partial melting with a phase change at 122-125°C and complete melting at 208-210°C. The fraction which sublimed at 140°C exhibited no phase change, but melted at 208-210°C. The elemental analyses of each fraction were consistent with the empirical formula $In(CH_2CMe_3)Cl_2$.

The crystal of $InNpCl_2$ (fraction subliming at 140°C) consists of (theoretically infinite) strands of the one-dimensional polymer $[InNp(\mu\text{-}Cl)_2]_\infty$. There are no short contacts between strands. A section of one such strand with atomic labelling is shown in Figure 1. Interatomic distances and angles are collected in Table V. Each indium atom has distorted trigonal bipyramidal coordination geometry which is achieved by four chlorine atoms and one (terminal-neopentyl) carbon atom. The axial groups are bridging chlorine atoms, whereas the equatorial positions are occupied by two chlorine atoms bridging two different metal centers and one neopentyl group. Alternatively, the polymer can be considered to be constructed from $InNpCl_2$ dimers which are linked by chlorine bridges. Thus, the chlorine atoms which would have been terminal atoms in a trans arrangement of a dimer are bridging chlorine atoms in the polymer. This trans arrangement of groups leads in turn to a stair-step polymer.

The four chlorine atoms form bridges between indium atoms. The chlorine atoms which are in axial positions have significantly longer distances (In(1)-Cl(3) = 2.700(6) and In(1)-Cl(4a) = 2.821(6)Å; In(2)-Cl(1) = 2.701(6) and In(2)-Cl(2b) = 2.752(5)Å) than those in equatorial positions (In(1)-Cl(1) = 2.436(5), and In(1)-Cl(2) = 2.410(5)Å; In(2)-Cl(3) = 2.452(5) and In(2)-Cl(4) = 2.393(6)Å). The In-C distances are In(1)-C(1) = 2.12(2)Å and In(2)-C(6) = 2.17(2)Å. Both the In-Cl and In-C distances are comparable to those determined for other compounds such as $InMe_3$[16], $InMe_2Cl$[18], $InMeCl_2$[19], $(Me_2InNMe_2)_2$[20], $[Me_2InN(Me)(Ph)]_2$[21] and $[(Me_3SiCH_2)_2InPPh_2]_2$[22].

Each indium atom has a rather distorted trigonal bipyramidal coordination environment. The two axial chlorine and indium atoms form angles (Cl(4a)-In(1)-Cl(3) and Cl(1)-In(2)-Cl(2b)) of 161.5(2)° and 163.0(2)°, respectively. The atoms in the equatorial positions form angles (Cl(1)-In(1)-Cl(2), C(1)-In(1)-Cl(1), C(1)-In(1)-Cl(2)) of 102.2(2), 128.8(6)° and 128.5(6)°, respectively, and (Cl(3)-In(2)-Cl(4), Cl(3)-In(2)-C(6) and C(6)-In(2)-Cl(4)) of 104.5(2)°, 121.7(6)° and 133.8(6)°, respectively.

The structural study of a crystal from the 140°C sublimation fraction of $(InNpCl_2)_x$ permits speculation about the structure of the species comprising the 110°C fraction, even though no X-ray quality crystals were obtained. One possible structure is a polymer composed of chlorine bridged

$InNpCl_2$ dimers which have the cis orientation. The cis orientation of neopentyl groups would lead to increased interactions and the observed lower sublimation temperature. Thus, the phase change observed at 122-125°C for the 110°C fraction might be related to the isomerization of the dimeric repeating unit to form the more stable trans arrangement of neopentyl groups. The observations that the melting points of the two fractions was identical, 208-210°C, would support the hypothesis of isomerization. An alternate arrangement of groups in the 110°C fraction could involve bridging neopentyl groups but this would seem less likely. Chlorine bridge bonds should be stronger than carbon bridge bonds.

The Lewis acidity of $InNpCl_2$ (140°C fraction, but not the 110° fraction) was investigated. This study showed that $InNpCl_2$ formed stable 1:1 adducts at room temperature with NMe_3 and TMEDA, but did not form stable adducts with Et_2O or THF. Clearly, $InNpCl_2$ is a stronger Lewis acid than $InNp_2Cl$, a compound which formed no adducts with any of the bases studied (Table III).

The ligand exchange reactions between pairs of reagents selected from $InNp_3$, $InNp_2Cl$ and $InNpCl_2$ have been examined by ^1H NMR spectroscopy. When $InNp_3$ and $InNpCl_2$ were combined in benzene at room temperature, the initially benzene insoluble $InNpCl_2$ disappeared and $InNp_2Cl$ formed. Similarly, when equimolar amounts of $InNp_2Cl$ and $InNpCl_2$ were combined, a solution was observed and the ^1H NMR spectrum, 4 lines (Table IV), revealed the presence of both reactants. When $InNp_2Cl$ and $InNpCl_2$ were mixed in a 1:2 mol, only half of the $InNpCl_2$ dissolved. Thus, it appeared that the solubility of $InNpCl_2$ was limited by the amount of $InNp_2Cl$ present in the solution. These results suggest that $InNp_2Cl$ and $InNpCl_2$ react to form each other. However, after the product is formed, solvation hinders further association of $InNpCl_2$ dimers to form the insoluble polymer. No new species such as a sesquihalide dimer $In_2Np_3Cl_3$ was suggested by the ^1H NMR spectra.

The methyl substituted derivative $InNp_2Me$[14] has been readily prepared by reacting a slight excess (3%) of the stoichiometric quantity of LiMe with $InNp_2Cl$ in diethyl ether solution at 0°C. The ether was readily removed and the compound was easily purified by vacuum distillation at 55°C/0.01mm. The derivative $InNp_2Me$ is a clear, colorless liquid which is extremely air and moisture sensitive but not pyrophoric. After replacing a neopentyl group in $InNp_3$ with a methyl group, the physical and chemical properties changed. The physical state changed from solid to liquid. Related observations have been made for $InMe_2Et$,[23] also a liquid at room temperature. However, the existence of $InMe_2Et$ as a single compound has been questioned.[24] The Lewis acidity of the indium in $InNp_2Me$ (Table III) also increased as stable 1:1 room temperature adducts were formed with THF, NMe_3 and TMEDA. No adduct was formed with Et_2O. A stable 2:1 adduct $[InNp_2Me]_2 \cdot$TMEDA was also formed by reacting two moles of $InNp_2Me$ with one mol of TMEDA. It is significant that $InNp_3$ did not form a stable adduct with THF.

Since $InNp_2Me$ might be used to make semiconductor films, the thermal and photolytic stability of the compound was investigated. In an attempt to learn more about the thermal stability of $InNp_2Me$, a sample contained in a previously evacuated tube was heated at 100°C for 13 days. Neither disproportionation nor decomposition occurred. The compound was also heated in the presence of mercury and still no decomposition occurred. The photolytic properties of $InNp_2Me$ were examined in a qualitative experiment. The compound contained in sealed glass capillary tubes was exposed to sunlight for 60 days. After this time the colorless liquid phase turned yellow and a gray residue deposited on the walls. These observations suggest photolytic decomposition. This presents another interesting and useful feature of this compound for the electronics industry as $InNp_2Me$ could be used to deposit a thin indium film directly onto a substrate by a laser-assisted decomposition.

Since $InNp_2Me$ was a volatile liquid which was readily purified by distillation and might possibly be a useful starting material for making semiconductor films, an attempt was made to synthesize $InNpMe_2$ from $InNpCl_2$ and LiMe in a 1:2 mol ratio in Et_2O at -78°C. After the reaction was complete, removal of the last traces of Et_2O proved difficult. The organoindium product was then partially separated from LiCl by pentane extraction. However, the liquid product so obtained was observed to produce small amounts of solid LiCl upon standing at 25°C. This observation suggests the presence of $LiInNpMe_2Cl \cdot nEt_2O$. Repeated pentane extractions produced a colorless liquid from which more LiCl formed. Vacuum distillation was then used to separate a volatile organoindium compound from LiCl. However, ^1H NMR spectra demonstrated that the ratio of neopentyl to methyl groups was not one to two as required by the formula $InNpMe_2$. Thus, it was not possible to obtain a pure sample of $InNpMe_2$ by using this preparative procedure. A redistribution/symmetrization reaction as shown by equation 2 apparently occurred during distillation. Thus, it is of

$$2InNpMe_2 \longrightarrow InNp_2Me + InMe_3 \qquad (2)$$

significance that we were able to distill $InNp_2Me$ and obtain an analytically pure product. Either $InNp_2Me$ does not redistribute/symmetrize or the appropriate experiment which might define the occurrence of a redistribution/symmetrization reaction has not been investigated.

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Supplementary Material Available. A table of thermal parameters (1 page); a list of observed and calculated structure factor amplitudes (pages). Ordering information is given on any current masthead page.

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Table I

Crystal Data and Summary of Intensity Data Collection and Structure Refinement

Cmpd	$[In(CH_2CMe_3)Cl_2]_x$
Color/Shape	Colorless/parallelepiped
For. wt.	256.9
Space group	$P2_12_12_1$
Temp., °C	20
Cell Constants[a]	
a, Å	6.717(4)
b, Å	12.217(4)
c, Å	22.658(7)
Cell vol, $Å^3$	1859
Formula units/unit cell	8
D_{calc}, g cm^{-3}	1.84
μ_{calc}, cm^{-1}	28.3
Diffractometer/Scan	Enraf-Nonius CAD-4/θ-2θ
Range of relative transm. factors, %	75/100
Radiation, graphite monochromator	MoKα(λ=0.71073)
Max crystal dimensions, mm	0.15x0.25x0.70
Scan width	$0.80 + 0.35\tan\theta$
Standard reflections	600; 0,12,0; 0,0,16
Decay of standards	±3%
Reflections measured	1908
2θ range, deg	$2 \leq 2\theta \leq 50$
Range of h,k,l	+8, +14, +26
Reflections observed $[F_o \geq 5\sigma(F_o)]$[b]	1584
Computer programs[c]	SHELX[12]
Structure solution	Heavy atom techniques
No. of parameters varied	145
Weights	$[\sigma(F_o)^2]^{-1}$
GOF	12.6
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.062
R_w	0.063
R inverse configuration	0.062
Largest feature final diff. map	1.0 $eÅ^{-3}$

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 21°$.

[b] Corrections: Lorentz-polarization and absorption (empirical, psi scan).

[c] Neutral scattering factors and anomalous dispersion corrections from ref 13.

Table II

Final Fractional Coordinates for $[In(CH_2CMe_3)Cl_2]_x$

Atom	x/a	y/b	z/c	B(eqv)[a]
In(1)	1.0012(3)	0.3314(1)	0.39877(6)	2.80
In(2)	0.5052(2)	0.4876(1)	0.40981(7)	2.89
Cl(1)	0.8335(8)	0.4727(5)	0.3414(3)	3.62
Cl(2)	1.1686(7)	0.4372(4)	0.4736(2)	3.08
Cl(3)	0.6677(8)	0.3400(5)	0.4652(3)	3.56
Cl(4)	0.3341(8)	0.3962(5)	0.3314(3)	3.40
C(1)	1.028(3)	0.162(1)	0.380(1)	3.83
C(2)	0.928(3)	0.121(2)	0.324(1)	3.83
C(3)	0.996(6)	0.178(2)	0.2704(8)	4.41
C(4)	0.970(5)	-0.005(2)	0.323(1)	5.51
C(5)	0.701(3)	0.133(2)	0.333(1)	5.04
C(6)	0.528(4)	0.657(1)	0.437(1)	4.48
C(7)	0.436(3)	0.739(2)	0.396(1)	3.44
C(8)	0.521(7)	0.734(2)	0.334(1)	6.41
C(9)	0.206(3)	0.715(2)	0.392(1)	4.96
C(10)	0.491(7)	0.850(2)	0.426(1)	8.04
H(1)[C(1)]	0.978	0.123	0.414	(iso)
H(2)[C(1)]	1.165	0.147	0.376	(iso)
H(1)[C(6)]	0.665	0.674	0.441	(iso)
H(2)[C(6)]	0.465	0.664	0.475	(iso)

[a] B(eqv) = 4/3[a*a*B11 + b*b*B22 + c*c*B33 + a*b*cosγ*B12 + a*c*cosβ*B13 + b*c*cosα*B23].

Table III

Lewis Acidity Studies of $InNp_3$ and $InNp_{3-n}X_n$

	Lewis Base			
Compound	Et_2O	THF	NMe_3	TMEDA
$InNp_3$	no	no	1:1	1:1
$InNp_2Cl$	no	no	no	no
$InNpCl_2$	no	no	1:1	1:1
$InNp_2Me$	no	1:1	1:1	1:1,2:1

Table IV

^{1}H NMR Study of Various Mixtures of Neopentyl Indium Compounds

$$\mathrm{InNp_3 + InNpCl_2} \xrightarrow[\text{R.T}]{\text{benzene}} \mathrm{2InNp_2Cl}$$

Reagents	^{1}H NMR lines observed			
	CH_3	CH_3	CH_2	CH_2
$InNp_3$		1.11		1.07
$InNpCl_2$	0.89		1.46	
$InNp_3/InNpCl_2$ (1:1)	1.08		1.57	

Conclusion: Ligand redistribution to form $InNp_2Cl$ occurred readily.

$$\mathrm{InNp_2Cl + InNpCl_2} \xrightleftharpoons[\text{benzene}]{} \text{No apparent reaction}$$

Reagents	^{1}H NMR lines observed			
	CH_3	CH_3	CH_2	CH_2
$InNp_2Cl$		1.10		1.59
$InNpCl_2$	0.89		1.46	
$InNp_2Cl/InNpCl_2$ (1:1)	0.93	1.00	1.41	1.61
$InNp_2Cl/InNpCl_2$ (2:1)	0.93	1.03	1.41	1.60
$InNp_2Cl/InNpCl_2$ (1:2)	0.93	1.00	1.41	1.61

Conclusion: Rapid ligand redistribution of neopentyl groups did not occur.

Table V

Bond Distances (Å) and Angles (deg) for $[\mathrm{In(CH_2CMe_3)Cl_2}]_x$

Atoms	Distance	Atoms	Distance
In(1) -- Cl(1)	2.436(5)	In(1) -- Cl(2)	2.410(5)
In(1) -- Cl(3)	2.700(6)	In(1) -- Cl(4)a	2.821(6)
In(1) -- C(1)	2.12(2)	In(2) -- Cl(1)	2.701(6)
In(2) -- Cl(2)b	2.752(5)	In(2) -- Cl(3)	2.452(5)
In(2) -- Cl(4)	2.393(6)	In(2) -- C(6)	2.17(2)
C(1) -- C(2)	1.52(3)	C(2) -- C(3)	1.47(3)
C(2) -- C(4)	1.56(3)	C(2) -- C(5)	1.55(3)
C(6) -- C(7)	1.50(3)	C(7) -- C(8)	1.52(3)
C(7) -- C(9)	1.58(3)	C(7) -- C(10)	1.56(3)

Atoms	Angle	Atoms	Angle
Cl(1) -- In(1) -- Cl(2)	102.2(2)	Cl(1) -- In(1) -- Cl(3)	83.4(2)
Cl(2) -- In(1) -- Cl(3)	88.5(2)	Cl(1) -- In(1) -- Cl(4)a	83.1(2)
Cl(2) -- In(1) -- Cl(4)a	82.0(2)	Cl(3) -- In(1) -- Cl(4)a	161.5(2)
Cl(1) -- In(1) -- C(1)	128.8(6)	Cl(2) -- In(1) -- C(1)	128.5(6)
Cl(3) -- In(1) -- C(1)	102.6(6)	Cl(4)a-- In(1) -- C(1)	95.7(6)
Cl(1) -- In(2) -- Cl(2)b	163.0(2)	Cl(1) -- In(2) -- Cl(3)	83.1(2)
Cl(2)b-- In(2) -- Cl(3)	86.1(2)	Cl(1) -- In(2) -- Cl(4)	86.3(2)
Cl(2)b-- In(2) -- Cl(4)	83.8(2)	Cl(3) -- In(2) -- Cl(4)	104.5(2)
Cl(1) -- In(2) -- C(6)	99.9(7)	Cl(2)b-- In(2) -- C(6)	96.9(7)
Cl(3) -- In(2) -- C(6)	121.7(6)	Cl(4) -- In(2) -- C(6)	133.8(6)
In(1) -- Cl(1) -- In(2)	96.8(2)	In(1) -- Cl(2) -- In(2)a	97.7(2)
In(1) -- Cl(3) -- In(2)	96.5(2)	In(1)b-- Cl(4) -- In(2)	96.3(2)
In(1) -- C(1) -- C(2)	116(1)	C(1) -- C(2) -- C(3)	114(2)
C(1) -- C(2) -- C(4)	105(2)	C(3) -- C(2) -- C(4)	113(2)
C(1) -- C(2) -- C(5)	107(2)	C(3) -- C(2) -- C(5)	112(3)
C(4) -- C(2) -- C(5)	106(2)	In(2) -- C(6) -- C(7)	116(2)
C(6) -- C(7) -- C(8)	113(2)	C(6) -- C(7) -- C(9)	108(2)
C(8) -- C(7) -- C(9)	108(3)	C(6) -- C(7) -- C(10)	102(2)
C(8) -- C(7) -- C(10)	110(2)	C(9) -- C(7) -- C(10)	115(3)

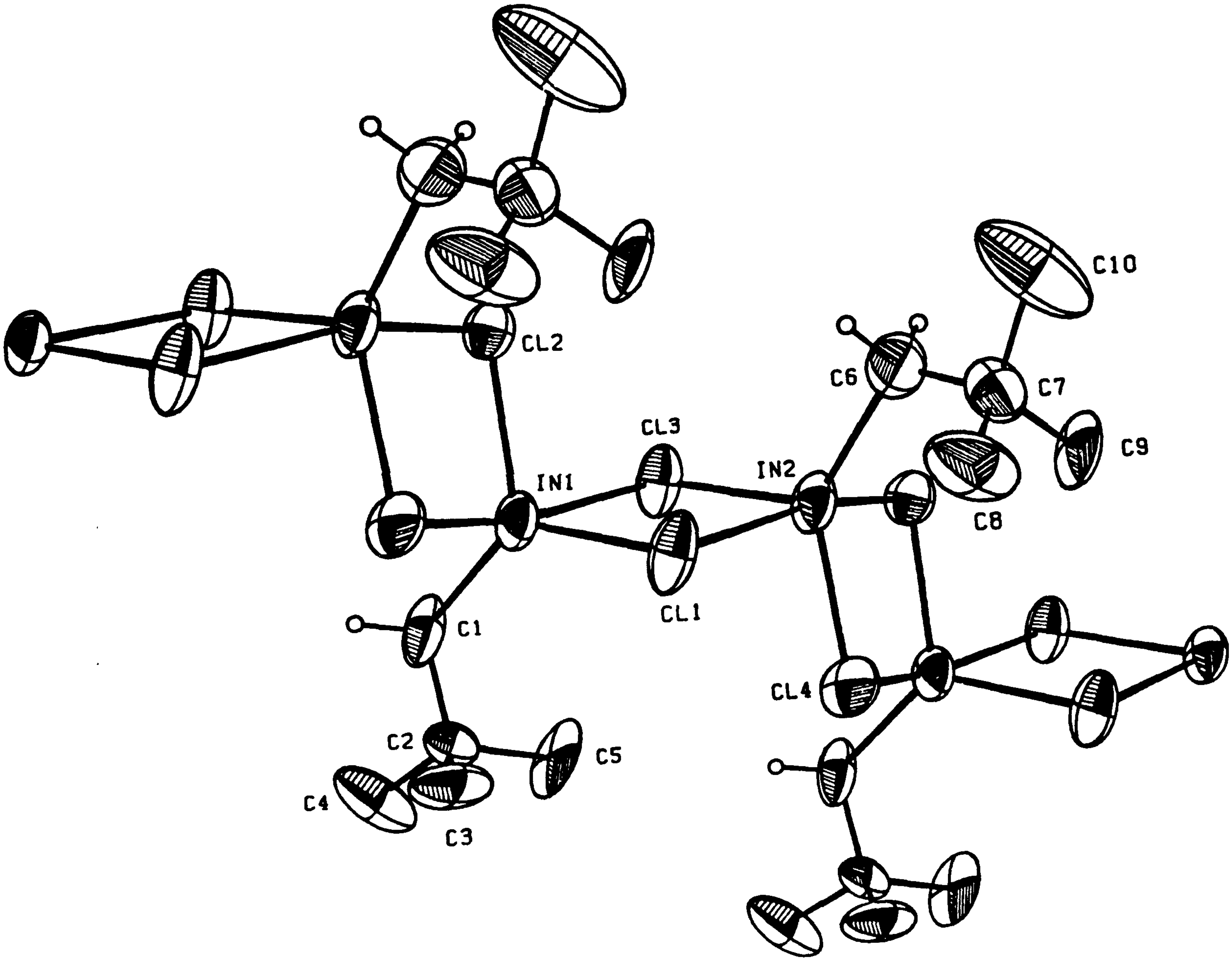
[a] Atoms related to those in Table II by 1 + x,y,z.

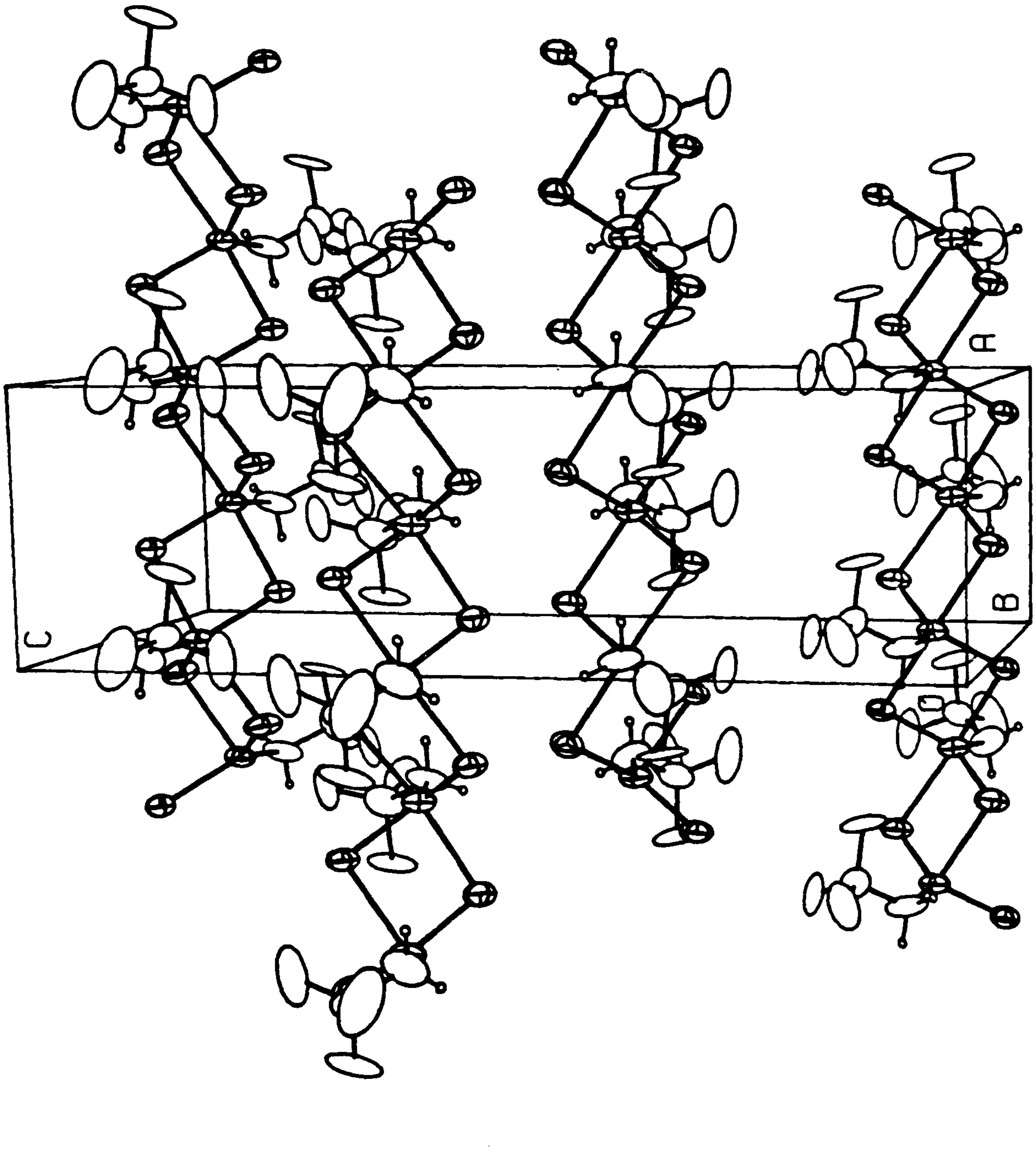
[b] x-1, y, z.

Figure Captions

Figure 1. ORTEP drawing of $[In(CH_2CMe_3)Cl_2]_x$. The thermal ellipsoids are at the 50% probability level. The hydrogen atoms for methyl groups were not located.

Figure 2. Unit cell of $[In(CH_2CMe_3)Cl_2]_x$.


C10
CL2
C6
C7
CL3
IN1
IN2
C9
C8
C1
CL1
CL4
C2
C5
C4
C3


A
B
C

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