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Three new indium compounds which contain two different organic substituents, $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$, $\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}$, and $(\text{Me}_3\text{CCH}_2)(\text{Me}_3\text{SiCH}_2)\text{InPEt}_2$ have been prepared, purified and characterized. All compounds were characterized by partial elemental analysis (C, H and P as appropriate), cryoscopic molecular weight studies in benzene solution as well as NMR and IR spectroscopic studies. All compounds exist as dimeric molecules in solution. NMR spectral data were consistent with the presence of mixtures of cis and trans isomers in solution. $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ crystallizes in the centrosymmetric triclinic space group $\text{P}\bar{1}$ (C_1^1; No. 2) with $a = 6.1000(10)$, $b =$				
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10.337(3), $c = 12.190(3)\text{\AA}$, $\alpha = 77.28(2)$, $\beta = 84.41(2)$, $\gamma = 84.50(2)^\circ$, $V = 744.0(3)\text{\AA}^3$ and $Z = 1$. Diffraction data (Mo K α , $2\theta = 5-50^\circ$) were collected on a Siemens R3m/V automated four-circle diffractometer and the structure was solved and refined to $R = 5.39\%$ and $wR = 7.65\%$ for those 1752 unique data with $|F_o| > 4 (|F_o|)$ ($R = 8.30\%$ for all 2629 data). Distances within the centrosymmetric dimeric molecule in the trans conformation include $\text{In-CH}_2\text{CMe}_3 = 2.140(13)\text{\AA}$, $\text{In-CH}_2\text{SiMe}_3 = 2.125(12)\text{\AA}$ and $\text{In-Cl(bridging)} = 2.572(3)$ and $2.659(3)\text{\AA}$. There is some slight disorder of CH_2CMe_3 and CH_2SiMe_3 ligands ($\sim 73\%:27\%$) and there are weak intermolecular $\text{In}\cdots\text{Cl}$ interactions at $3.528(3)\text{\AA}$ along the a -direction. Attempts to prepare the related organogallium compounds, $\text{Ga(Me)(CH}_2\text{CMe}_3)\text{Cl}$ and $\text{Ga(CH}_2\text{CMe}_3)(\text{CH}_2\text{CMe}_2\text{Ph)Cl}$, were unsuccessful. Ligand redistribution reactions led to the formation and subsequent isolation of mixtures of the appropriate symmetrized products.



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Crystal Structure of $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$, An Interesting Case of
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and Charles H. Lake

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State University of New York at Buffalo
Buffalo, New York 14214

Indium Compounds Which Contain Two Different
Organic Substituents. Crystal Structure of
[In(CH₂CMe₃)(CH₂SiMe₃)Cl]₂, An Interesting Case
of Partial Ligand Disorder In the Solid State.

by

O. T. Beachley, Jr.^{*}, John D. Maloney, Melvyn Rowen Churchill^{*}
and Charles H. Lake

Summary: Three new indium compounds which contain two different organic substituents, In(CH₂CMe₃)(CH₂SiMe₃)Cl, In(CH₂CMe₃)(C₆H₅)Cl, and (Me₃CCH₂)(Me₃SiCH₂)InPet₂ have been prepared, purified and characterized. All compounds were characterized by partial elemental analysis (C, H and P as appropriate), cryoscopic molecular weight studies in benzene solution as well as NMR and IR spectroscopic studies. All compounds exist as dimeric molecules in solution. NMR spectral data were consistent with the presence of mixtures of cis and trans isomers in solution.

Abstract

Three new indium compounds which contain two different organic substituents, $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$, $\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}$, and $(\text{Me}_3\text{CCH}_2)(\text{Me}_3\text{SiCH}_2)\text{InPEt}_2$ have been prepared, purified and characterized. All compounds were characterized by partial elemental analysis (C, H and P as appropriate), cryoscopic molecular weight studies in benzene solution as well as NMR and IR spectroscopic studies. All compounds exist as dimeric molecules in solution. NMR spectral data were consistent with the presence of mixtures of cis and trans isomers in solution.

$[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (C_i^1 ; No. 2) with $a = 6.1000(10)$, $b = 10.337(3)$, $c = 12.190(3)\text{\AA}$, $\alpha = 77.28(2)$, $\beta = 84.41(2)$, $\gamma = 84.50(2)^\circ$, $V = 744.0(3)\text{\AA}^3$ and $Z = 1$. Diffraction data (Mo K α , $2\theta = 5-50^\circ$) were collected on a Siemens R3m/V automated four-circle diffractometer and the structure was solved and refined to $R = 5.39\%$ and $wR = 7.65\%$ for those 1752 unique data with $|F_o| > 4\sigma(|F_o|)$ ($R = 8.30\%$ for all 2629 data). Distances within the centrosymmetric dimeric molecule in the trans conformation include $\text{In}-\text{CH}_2\text{CMe}_3 = 2.140(13)\text{\AA}$, $\text{In}-\text{CH}_2\text{SiMe}_3 = 2.125(12)\text{\AA}$ and $\text{In}-\text{Cl}(\text{bridging}) = 2.572(3)$ and $2.659(3)\text{\AA}$. There is some slight disorder of CH_2CMe_3 and CH_2SiMe_3 ligands ($\sim 73\%:27\%$) and there are weak intermolecular $\text{In}\cdots\text{Cl}$ interactions at $3.528(3)\text{\AA}$ along the a -direction. Attempts to prepare the related organogallium compounds, $\text{Ga}(\text{Me})(\text{CH}_2\text{CMe}_3)\text{Cl}$ and $\text{Ga}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{CMe}_2\text{Ph})\text{Cl}$, were unsuccessful. Ligand redistribution reactions led to the formation and subsequent isolation of mixtures of the appropriate symmetrized products.

Introduction

The chemistry of organoindium compounds is important for gaining a more complete understanding of the reactions involved in the organometallic chemical vapor deposition process for making InP, an important electronic material. The most common organoindium compounds¹ employed in producing InP are InMe_3 ² and InEt_3 ^{3,4}, although a variety of other simple homoleptic trialkylindium compounds including $\text{In}(\text{n-Pr})_3$ ⁴, $\text{In}(\text{i-Pr})_3$ ⁴, $\text{In}(\text{n-Bu})_3$ ⁴, $\text{In}(\text{sec-Bu})_3$ ⁴, $\text{In}(\text{t-Bu})_3$ ⁵, $\text{In}(\text{CH}_2\text{CMe}_3)_3$ ⁶ and $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ ⁷ are known. In contrast, only a few heteroleptic organoindium compounds including InMe_2Et ⁸, InEt_2Me ⁸, $\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ ⁶ and $\text{InMe}_2(\text{C}_5\text{H}_5)$ ⁹ have been reported. It is regrettable that none of these compounds have been proven by appropriate structural studies to exist as pure compounds. Variable temperature ¹H NMR studies¹¹ have shown that rapid ligand redistribution reactions occur in solutions of InMe_2Et . Consequently, the existence of InMe_2Et as a single compound has been questioned.¹¹ A distillation¹¹ of InMe_2Et in vacuo provided initial fractions of crystalline InMe_3 contaminated with traces of ethyl-containing material. Subsequent less volatile fractions contained increased Et/Me ratios according to ¹H NMR spectral studies. In contrast, a sample of $\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ was distilled to give an analytically pure sample.⁶ However, no experimental data proved that $\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Me}$, a liquid at room temperature, existed as a single species. The solid, $\text{InMe}_2(\text{C}_5\text{H}_5)$ might be expected to exist as a pure compound with a structure analogous to that observed for $\text{GaMe}_2(\text{C}_5\text{H}_5)$ ¹² and $\text{AlMe}_2(\text{C}_5\text{H}_5)$ ¹³. The X-ray structural studies of these compounds identify a polymer with four coordinate metal atoms. The cyclopentadienyl group through its 1 and 3 positions bridges two metal atoms.

In this paper, we report the synthesis of the first fully characterized organoindium compound which contains two different simple alkyl substituents, $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$. The compound was characterized by physical properties, partial elemental analyses (C,H), cryoscopic molecular weight data, infrared as well as ^1H and ^{13}C spectroscopic data and an X-ray structural study. The related compounds $\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}$ and $(\text{Me}_3\text{SiCH}_2)-(\text{Me}_3\text{CCH}_2)\text{InPEt}_2$ have also been prepared and partially characterized (no X-ray structural studies).

EXPERIMENTAL

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or under a purified argon atmosphere. The compounds $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$,⁷ $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$,⁷ $\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$,⁶ $\text{LiCH}_2\text{CMe}_3$,¹⁴ LiPEt_2 ,¹⁵ GaMe_2Cl ,¹⁶ $\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$,¹⁷ $\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})\text{Cl}_2$ ¹⁸ and $\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_2\text{Cl}$ ¹⁸ were prepared and purified by literature methods. Solvents were dried by conventional procedures. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, 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), vw (very weak), sh (shoulder). The ^1H spectra were recorded at 300 MHz by using a Varian Gemini-300 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to SiMe_4 at δ 0.00 ppm and C_6D_6 at δ 7.15 ppm. The proton-decoupled ^{13}C NMR spectra was recorded at 161.9 MHz on a Varian VXR-400 spectrometer. Proton-decoupled ^{31}P NMR spectra are referenced to 85% H_3PO_4 at δ 0.00 ppm. All samples for NMR spectra were contained in sealed NMR tubes. 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 Drezdson.¹⁹

Synthesis of $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$. (Methathesis Reaction). A side-arm dumper charged with 0.754 g (9.65 mmol) of $\text{LiCH}_2\text{CMe}_3$ was attached to a 100-mL two-neck flask charged with 2.634 g (9.650 mmol) of $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$. After the reactants were dissolved in approximately 25 mL of Et_2O , the system was cooled to -78°C . The $\text{LiCH}_2\text{CMe}_3$ was then slowly added with stirring to $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$. After the reaction mixture was warmed to room temperature and stirred for 8 h, the Et_2O was removed by vacuum distillation. The product $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$ was finally separated from the LiCl by extraction with 30 mL of pentane. Cooling the pentane solution to -20°C produced crystals of the desired product, $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$ (2.721 g, 8.819 mmol, 91.4 %).

$\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$: (Sample recrystallized from pentane): Colorless solid; mp $89-91^\circ\text{C}$; sublimes at 70°C , 0.01 mm. ^1H NMR (C_6D_6 , δ): 0.18 (s, 9.0 H, Si-Me₃), 0.20 (s, 10.7 H, Si-Me₃), 0.25 (s, 2.0 H, In-CH₂-Si), 0.27 (s, 2.3 H, In-CH₂-Si), 1.03 (s, 10.3 H, C-Me₃), 1.08 (s, 9.3 H, C-Me₃), 1.53 (s, 2.3 H, In-CH₂-C), 1.56 (s, 2.0 H, In-CH₂-C). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , δ): 1.75 (s, Si-Me₃), 1.86 (s, Si-Me₃), 9.71 (s, CH₂-Si), 10.36 (s, CH₂-Si), 31.93 (s, CH₂-C), 32.11 (s, CH₂-C), 34.18 (s, C-Me₃), 34.28 (s, C-Me₃), 46.07 (s, C), 46.68 (s, C). Anal. Calcd.: C, 35.02; H, 7.19. Found: C, 35.23; H, 7.45. Cryoscopic molecular weight, benzene solution, formula weight 308.55 (observed molality, obsd. mol. wt., association): 0.0673, 634, 2.05; 0.0481, 624, 2.02; 0.0332, 617, 2.00. IR (Nujol mull cm^{-1}): 2710 (vw), 1298 (w), 1256 (sh), 1243 (s), 1122 (w), 1112 (w), 1087 (w), 1011 (w), 995 (sh), 979 (m), 965 (sh), 847 (s), 825 (vs), 751 (s), 747 (sh), 716

(s), 682 (m), 609 (vw), 588 (w), 573 (w), 515 (vw), 494 (w). The ^1H NMR spectrum of a sample sublimed after recrystallization and dissolved in C_6D_6 was identical to that observed for a sample purified by recrystallization.

Synthesis of $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$. (Ligand Redistribution Reaction in Benzene.) A 100 mL Schlenk flask was charged with 0.468 g (1.44 mmol) of $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ and 0.422 g (1.44 mmol) of $\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ and the components were dissolved in 30 mL of benzene. After the reaction mixture was stirred for 92 h at ambient temperature, the benzene was removed to leave 0.833 g of $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$ (2.70 mmol, 93.7 %) as a colorless solid.

$\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$: mp = 93-94 °C. The ^1H NMR spectrum (C_6D_6) was identical to the spectrum previously described.

Synthesis of $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$. (Ligand Redistribution Reaction Without Solvent.) A tube equipped with a 20 mm Solv-Seal joint was charged with stoichiometric quantities of $\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ (0.182 g, 0.622 mmol) and $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ (0.202 g, 0.622 mmol) and was heated to 110 °C. After the two solids had melted (approximately 10 minutes), heating was stopped. The liquid solidified to a colorless crystalline solid.

$\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$: mp = 94-96 °C. ^1H NMR (C_6D_6 , δ): The ^1H NMR spectrum (C_6D_6) was identical to the spectrum previously described.

Synthesis of $\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}$. A solution of $\text{Li}(\text{C}_6\text{H}_5)$ (4.1 mL, 1.8 M, 7.4 mmol) in cyclohexane/ Et_2O was added slowly at 0 °C to 30 mL of a solution of $\text{In}(\text{CH}_2\text{CMe}_3)\text{Cl}_2$ (1.862 g, 7.492 mmol) in Et_2O . The reaction mixture was stirred for 18 h at ambient temperature and then the solvent was removed by vacuum distillation. The product $\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}$ was separated from the LiCl by extraction by using 30 mL of pentane and then washed with 10 mL of pentane at -15 °C to obtain 1.658 g (5.553 mmol, 76.60%

based on $\text{In}(\text{CH}_2\text{CMe}_3)\text{Cl}_2$ of $\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}$ as a colorless solid. The product then was recrystallized from methylcyclohexane at -15°C .

$\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}$. mp $126-131^\circ\text{C}$; sublimes at 90°C , 0.01 mm. ^1H NMR (C_6D_6 , δ): 0.94 (s, 9.6 H, CMe_3), 1.01 (s, 10.0 H, CMe_3), 1.51 (s, 2.0 H, CH_2), 1.55 (s, 2.0 H, CH_2), 7.12, 7.14, 7.16, 7.17, 7.19, 7.22, 7.23, 7.25, 7.57, 7.58, 7.73, 7.74 (phenyl protons, no integration due to interfering solvent). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , δ): 31.40 (s, CH_2), 32.05 (s, CMe_3), 33.91 (s, CH_2), 34.58 (s, CMe_3), 126.96 (s, Ph), 127.30 (s, Ph), 127.34 (s, Ph), 127.39 (s, Ph), 127.42 (s, Ph), 127.86 (s, Ph), 128.80 (s, Ph), 129.32 (s, Ph). Anal. Calcd.: C, 44.26, H, 5.40. Found: C, 44.41; H, 5.34.

Cryoscopic molecular weight, benzene solution, formula weight 298.51 obsd molality, obsd mol wt, association): 0.0515, 633, 2.12; 0.0350, 632, 2.12; 0.0271, 634, 2.13. IR (Nujol mull cm^{-1}): 3068 (m), 3050 (m), 2715 (vw), 1948 (vw), 1872 (vw), 1565 (vw), 1477 (m), 1425 (vs), 1330 (w), 1297 (w), 1259 (s), 1236 (m), 1090 (s), 1068 (s), 1017 (vs), 995 (m), 905 (w), 892 (w), 856 (m), 800 (vs), 725 (vs), 690 (vs), 658 (w), 597 (vw), 578 (vw), 472 (w), 446 (m), 390 (w), 330 (m).

Synthesis of $(\text{Me}_3\text{CCH}_2)(\text{Me}_3\text{SiCH}_2)\text{InPEt}_2$. A side-arm dumper was charged with 0.378 g (3.94 mmol) of LiPEt_2 , and attached to a 100-mL two-neck flask which was charged with 1.215 g (3.937 mmol) of $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$. After the indium reagent was dissolved in 25 mL of Et_2O , the solution was cooled to -78°C and the LiPEt_2 was slowly added with stirring. After the reaction mixture was stirred for 8 h at room temperature, the Et_2O was removed by vacuum distillation. The product $(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{InPEt}_2$ was separated from the LiCl by extraction by using 30 mL of pentane. The resulting thick, colorless oil solidified upon standing to a tacky, colorless, semicrystalline material. The product was purified by

sublimation to yield 1.157 g (3.193 mmol, 81.10%) of

$(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{InPEt}_2$.

$(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{InPEt}_2$: mp 45-50 °C; sublimes at 100 °C, 0.01 mm. ^1H NMR (C_6D_6 , δ) (see Results and Discussion): -0.38 (br, 2.0 H, $\text{CH}_2\text{-Si}$), 0.04, 0.05, 0.06, 0.062, 0.07 (s, 9.2 H combined, SiMe_3), 0.87 (p, $J = 7.2$ Hz, 6.8 H, $-\text{CH}_3$), 0.98, 0.99, 1.00, 1.01, 1.02 (s, 12.2 H combined, CH_2 and CMe_3), 1.62 (br, 4.0 H, P-CH_2 -). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , δ): -47.28 (s, 1.0), -48.74 (s, 3.0), -49.85 (s, 2.3), -50.10 (s, 1.4), -50.20 (s, 1.3), -51.26 (s, 3.5), -52.37 (s, 1.2). Anal. Calcd.: C, 43.09; H, 8.90; P, 8.55. Found: C, 42.83; H, 8.97; P, 8.15. Cryoscopic molecular weight, benzene solution, formula weight 362.27 (obsd molality, obsd molecular wt, association): 0.0776, 780, 2.15; 0.0593, 771, 2.13; 0.0489, 773, 2.13. IR (Nujol mull cm^{-1}): 2730 (vw), 2710 (vw), 1415 (m), 1357 (m), 1285 (w), 1252 (m), 1240 (vs), 1234 (sh), 1107 (w), 1093 (w), 1083 (m), 1022 (m), 1010 (m), 995 (m), 948 (s), 850 (vs), 820 (vs), 745 (vs), 719 (s), 680 (s), 605 (vw), 572 (m), 555 (m), 475 (w), 447 (w), 380 (vw).

Collection of X-Ray Diffraction Data for $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$.

The crystal selected for the diffraction study (dimensions 0.6 x 0.2 x 0.25) was sealed into a thin walled capillary under anaerobic conditions and was aligned on a Siemens R3m/V diffractometer with its extended direction (a) close to a coincident with the ϕ -axis. Details of data collection appear in Table 1.

The crystal belongs to the triclinic system, possible space groups being the non-centrosymmetric $P1$ and the centrosymmetric $P\bar{1}$. Intensity statistics favored the choice of $P\bar{1}$; this was confirmed by the successful solution of the structure. All data were corrected for Lorentz and

polarization effects and for absorption. 5258 reflections were collected (a complete shell for $2\theta = 5-50^\circ$ for Mo K α radiation) and merged ($R_{\text{int}} = 1.36\%$) to a unique set of 2629 reflections.

Solution and Refinement of the Structure of $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$.

All crystallographic calculations were carried out with use of the Siemens SHELXTL PLUS program set.²⁰ The analytical scattering factors for neutral atoms were corrected for both components ($\Delta f'$ and $i\Delta f''$) of anomalous dispersion.²¹

The structure was solved by a combination of automatic Patterson search and direct methods. Positional and anisotropic thermal parameters of all non-hydrogen were refined. Hydrogen atoms were not located directly, but were input in calculated positions with $d(\text{C-H}) = 0.96\text{\AA}$ ²² and the appropriate staggered tetrahedral geometry. Refinement of the ordered model converged with $R = 5.15\%$ and $wR = 7.86\%$ for 110 parameters refined against those 1503 reflections with $|F_o| > 6\sigma(|F_o|)$, and $R = 8.69\%$ for all 2629 reflections.

A careful survey of our structure led to the following observations.

(1) The R-factors seemed high when compared to the internal consistency of the data collected (i.e., $R_{\text{int}} = 1.36\%$ for averaging 2629 equivalent pairs of reflections).

(2) The thermal parameters for all atoms were high. Those for the external methyl groups were higher than any that we had even encountered in an ordered structure, with U_{equ} values of $0.150-0.445\text{\AA}^2$ ($B_{\text{equ}} = 11.8-35.1\text{\AA}^2$).

(3) The thermal ellipsoids of C(Me) atoms appeared to represent a

"wagging" motion of the CMe_3 system, in a direction perpendicular to the $\text{In-C}(\alpha)\text{-[C(B) or Si]}$ plane, in addition to the more normal libration about the $\text{C}(\alpha)\text{-[C(B) or Si]}$ axis.

(4) The thermal parameters for $\text{Si}(1)$ were much larger than those for the bonded inner atom $\text{C}(11)$ ($U_{\text{equ}} = 0.148\text{\AA}^2$ vs $0.107\text{\AA}^2$), while those for $\text{C}(22)$ were much smaller than those for the bonded inner atom $\text{C}(21)$ ($U_{\text{equ}} = 0.090\text{\AA}^2$ vs $0.127\text{\AA}^2$).

(5) One C-Me bond was alarmingly short [$\text{C}(22)\text{-C}(25) = 1.18(5)\text{\AA}$] even though it clearly could be increased by a "riding" correction for librational motion.

Since the CH_2CMe_3 and CH_2SiMe_3 ligands are very similar in size and shape, we decided to check on possible disorder of these ligands in the crystal lattice, even though this had not been indicated by difference-Fourier maps. We therefore refined an atom at the site of $\text{Si}(1)$ as a composite silicon and carbon atom (respective occupancies x and $1-x$) and an atom at the site of $\text{C}(22)$ as a composite carbon and silicon atom (occupancies y and $1-y$). Refinement led to the independent values of $x = 0.724(26)$ and $y = 0.729(37)$, indicating that, while the net composition of the material is secure, there is a minor scrambling ($\sim 73\%:27\%$) of CH_2CMe_3 and CH_2SiMe_3 ligands at the two crystallographically unique ligand sites.

This disordered model yielded $R = 4.88\%$ and $wR = 5.28\%$ for the 1503 reflections with $|F_o| > 6\sigma(|F_o|)$ and $R = 8.30\%$ for all 2629 reflections.

The previously anomalous features of the structure were all improved.

U_{equ} values for methyl carbons are now $0.161\text{--}0.344\text{\AA}^2$ ($B_{\text{equ}} = 12.7\text{--}27.2\text{\AA}^2$), the orientations of the ellipsoids are now closer to those expected for librational motion, U_{equ} values for α and β atoms are more internally consistent, and the $\text{C}(22)\text{-C}(25)$ bond length is now acceptable at $1.490(25)\text{\AA}$:

The largest features on a final difference Fourier map were in the range $-0.51 \rightarrow +0.81 \text{ e/\AA}^3$. (In the ordered structure these were little different at $-0.71 \rightarrow +0.81 \text{ e/\AA}^3$.)

Final atomic coordinates are listed in Table 2.

Results and Discussion

Three new indium compounds containing two different organic substituents, $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$, $\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}$ and $(\text{Me}_3\text{CCH}_2)-(\text{Me}_3\text{SiCH}_2)\text{InPet}_2$ have been prepared, purified and characterized. The identity of the first compound in the above series as a dimer, $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$, was confirmed by an X-ray structural study. The elemental analyses (C, H and P, as appropriate) of purified samples of all three compounds were consistent with the above formulae. Cryoscopic molecular weight measurements in benzene solutions of all three compounds identified the existence of dimeric molecules in solution. Spectroscopic NMR spectral data were consistent with the presence of cis and trans isomers. Attempts to prepare the related organogallium compounds, $\text{Ga}(\text{Me})(\text{CH}_2\text{CMe}_3)\text{Cl}$ and $\text{Ga}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{CMe}_2\text{Ph})\text{Cl}$, were unsuccessful. Ligand redistribution reactions led to the formation and subsequent isolation of mixtures of the appropriate symmetrized products.

The compounds, $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$ and $\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}$, were synthesized by metathetical reactions between $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$ or $\text{In}(\text{CH}_2\text{CMe}_3)\text{Cl}_2$ and the appropriate organolithium compounds in Et_2O solutions. In addition, $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$ was prepared by ligand redistribution reactions between $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$, either neat at 110°C or in benzene at room temperature. The products were purified by recrystallization and/or sublimation. The partial elemental

analyses, melting points and the X-ray structural study of $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$ confirm the purified products to be single compounds in the solid phase. Furthermore, samples of $\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}$ prepared by different routes and/or purified by different methods gave samples with essentially identical NMR spectra.

The structure of a crystal of (neopentyl)[(trimethylsilyl)methyl] indium(III) chloride grown by slow sublimation consists of dimeric units of $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ (having crystallographically imposed $\bar{1}$ (C_i) symmetry) which are associated with intermolecular $\text{In}\cdots\text{Cl}$ contacts of $3.528(3)\text{\AA}$ and a $\text{Cl}-\text{In}\cdots\text{Cl}(-1+x,y,z)$ angle of $160.4(1)^\circ$ along the a -axis (see Figure 1). Interatomic distances and angles are collected in Table 3, while an atomic labelling diagram is provided as Figure 2. It should be noted that all atoms are showing substantial "amplitudes of thermal motion", probably an artificial effect caused by disorder.

The In_2Cl_2 core is required to be strictly planar and has inequivalent $\text{In}-\text{Cl}$ distances with $\text{In}(1)-\text{Cl}(1) = \text{In}(1A)-\text{Cl}(1A) = 2.659(3)\text{\AA}$ and $\text{Cl}(1)-\text{In}(1A) = \text{Cl}(1A)-\text{In}(1) = 2.572(3)\text{\AA}$; internal angles are $\text{In}(1)-\text{Cl}(1)-\text{In}(1A) = 95.5(1)^\circ$ and $\text{Cl}(1)-\text{In}(1)-\text{Cl}(1A) = 84.5(1)^\circ$. The CH_2SiMe_3 and CH_2CMe_3 ligands are associated with indium-carbon lengths of $\text{In}(1)-\text{C}(11) = 2.125(12)\text{\AA}$ and $\text{In}(1)-\text{C}(21) = 2.140(13)\text{\AA}$ (respectively), with an interligand angle of $\angle\text{C}(11)-\text{In}(1)-\text{C}(21) = 148.1(6)^\circ$. These indium-carbon and indium-chlorine distances are similar to those observed for $[\text{In}(\text{C}_6\text{Me}_3\text{H}_2)_2\text{Cl}]_2$, the only other structurally characterized simple, four coordinate indium-chloride bridged dimer. The $\text{In}-\text{C}$ distances in $[\text{In}(\text{C}_6\text{Me}_3\text{H}_2)_2\text{Cl}]_2^{23}$ are $2.146(9)$ and $2.174(10)\text{\AA}$ whereas the $\text{In}-\text{Cl}$ distance is $2.574(3)\text{\AA}$. The other structurally characterized organoindium chloride derivatives, $\text{InMe}_2\text{Cl}^{24}$, InMeCl_2^{25} and $\text{In}(\text{CH}_2\text{CMe}_3)\text{Cl}_2^6$, involve infinite chains in the solid state

with trigonal-bipyramidal geometry about indium. The geometry of the α -carbon atom of each ligand in $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ is perturbed from the regular sp^3 angle of 109.5° with $\angle \text{In}(1)-\text{C}(11)-\text{Si}(1) = 125.1(8)^\circ$ and $\angle \text{In}(1)-\text{C}(21)-\text{C}(22) = 123.0(9)^\circ$.

The structure of $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ involves some slight disorder. The " CH_2SiMe_3 site" is occupied $\sim 73\%$ by CH_2SiMe_3 and $\sim 27\%$ by CH_2CMe_3 ; similar structures apply, mutatis mutandis, to the " CH_2CMe_3 " site. The interior "bonds" to the B-atoms, $\text{C}(11)-\text{Si}(1) = 1.704(14)\text{\AA}$ and $\text{C}(21)-\text{C}(22) = 1.552(21)\text{\AA}$ should be compared to the weighted average of their components, rather than to true C-Si and C-C bond lengths. (C-Si = $1.865 \pm 0.008\text{\AA}$ for alkylsilanes²⁶ and $\text{C}(\alpha)-\text{Si} = 1.848(9)-1.860(8)$ for the CH_2SiMe_3 ligands in $[(\text{Me}_3\text{SiCH}_2)_2\text{InPPh}_2]_2$ ²⁷; C-C = $1.541 \pm 0.003\text{\AA}$ in alkanes²⁶ and $\text{C}(\alpha)-\text{C}(\beta) = 1.478(13)-1.549(9)\text{\AA}$ for the CH_2CMe_3 ligand in $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$ ²⁸. A 73%:27% average of the bond lengths from "International Distances"²⁶ would yield theoretical $\text{C}(11)-\text{Si}(1)$ and $\text{C}(21)-\text{C}(22)$ distances of $1.78\text{\AA}$ and $1.62\text{\AA}$, respectively. Other "composite distances" observed are $\text{Si}(1)-\text{Me} = 1.676(28)-1.938(31)\text{\AA}$ and $\text{C}(12)-\text{Me} = 1.490(36)-1.520(22)\text{\AA}$.

The ^{13}C and ^1H NMR spectra of $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ are consistent with the existence in solution of an approximately equimolar mixture of cis and trans isomers. The ^{13}C NMR spectrum consists of ten lines, two sets of five lines each. One set of lines must be related to the cis isomer and the other set to the trans isomer. The (trimethylsilyl)methyl substituent exhibits two lines, whereas the neopentyl group has three lines for each isomer. None of the ten lines corresponds with the ^{13}C NMR chemical shifts of lines observed for pure samples²⁹ of $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$ ($32.43(\text{C})$, $34.69(\text{Me})$, $42.63(\text{CH}_2)$) and $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ ($2.21(\text{Me})$, $10.44(\text{CH}_2)$). Thus,

the ^{13}C NMR spectrum is inconsistent with an equilibrium between $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$, $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$. It is regrettable that it is not possible to assign a given set of lines to a specific isomer. The ^1H NMR spectrum has eight lines consisting of four pairs of lines. The two lines of a given pair are of similar intensities. These lines can be alternatively described as two sets of four lines. One set of four lines originates from the methylene and methyl protons of the neopentyl and (trimethylsilyl)methyl groups for the cis isomer; the other set is for the trans isomer. The lines due to the trans isomer have unique chemical shifts whereas the lines assigned to the cis isomer are essentially identical to those observed for $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$, as would be expected. The cis isomer by virtue of its structure has a "neopentyl group side" and a "(trimethylsilyl)methyl group side." Consequently, the interaction between substituent and solvent would be expected to be very similar to that in the corresponding diorganoindium chloride. Thus, the chemical shifts of the respective protons should be the same as that observed for the pure diorganoindium chloride dimer.

An alternative explanation for the ^1H NMR spectrum of benzene solutions of $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ which involves an equilibrium mixture of $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$, $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ is inconsistent with a variety of experimental observations, with the literature and with the ^{13}C NMR spectrum, as previously discussed. If an equilibrium did exist, then of the observed eight ^1H NMR lines, two lines would be assigned to $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$, two to $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ and four to $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$. The molecule $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ would either have to be undergoing fast exchange on the NMR time scale in order to average the chemical shifts of the lines for the different

substituents for the cis and trans isomers or have to exist as only one isomer. When $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ were mixed in benzene solution, the four lines expected for the two reactants were observed. Fast exchange between the reactants did not occur. Similarly, fast exchange was not observed for mixtures⁶ of $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{CMe}_3)\text{Cl}]_2$. The ^1H NMR study of the equimolar mixture of $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ further revealed with time that four new lines appeared and increased in intensity and the four original lines decreased in intensity until the new and the old line in each of the four pairs of lines were of approximately equal intensity (~ 72 h). A low temperature ^1H NMR spectral study is inconsistent also with the proposal of a fast exchange between cis and trans isomers; the four "new" lines did not broaden and split as the sample was cooled. Instead, the lines for the CH_2SiMe_3 protons changed (moved and broadened) before a change was observed in the lines for the neopentyl group protons. Thus, complex rotational and/or dissociative processes (which will be discussed in a future paper) are occurring. In conclusion, the ^1H NMR spectrum is best explained by an approximately equimolar mixture of cis and trans isomers. A mixture of $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$, $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ in only one isomer conformation to give four pairs of lines of equal intensity is inconsistent with the ^{13}C NMR spectrum and seems unlikely. Such a mixture in solution would be expected to give an impure product when the solvent was removed. Instead, a pure compound was obtained.

The hypothesis, that $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ exists as a single compound in solution rather than as an equilibrium mixture with $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$, is also supported by the observation that the compound reacts with LiPEt_2 in Et_2O solution at -78°C

to form $(\text{Me}_3\text{CCH}_2)(\text{Me}_3\text{SiCH}_2)\text{InPEt}_2$ and LiCl . The indium-phosphorus product, initially isolated as a thick, colorless oil, which crystallized upon standing, was purified by sublimation at 100°C . The cryoscopic molecular weight study of the product in benzene solution identified the existence of dimeric molecules in solution. The most likely structure for the dimer would involve bridging PEt_2 groups as observed for $[(\text{Me}_3\text{SiCH}_2)_2\text{InPPh}_2]_2$,³⁰ $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$ ²⁸ and other related group 13-15 compounds.³¹ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of seven lines suggests that the species in solution must have a variety of conformations including cis and trans isomers of planar and/or puckered indium-phosphorus rings. No line had a chemical shift which was identical to that observed for $[(\text{Me}_3\text{CCH}_2)_2\text{InPEt}_2]_2$ ³² (-52.6 ppm). The observation that all lines for $[(\text{Me}_3\text{CCH}_2)(\text{Me}_3\text{SiCH}_2)\text{InPEt}_2]_2$ occurred in the narrow range of five ppm is consistent with the presence of species of only one degree of association, i.e. dimer. If planar and/or puckered rings are present, the rate of fluxionality between the conformations must be slow on the NMR time scale. The rather complex ^1H NMR spectrum is also consistent with multiple conformations and isomers.

The compound $\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}$ was prepared by reacting $\text{In}(\text{CH}_2\text{CMe}_3)\text{Cl}_2$ with $\text{Li}(\text{C}_6\text{H}_5)$ in Et_2O at 0°C . The colorless, crystalline product was purified by recrystallization from methylcyclohexane or by sublimation at 90°C . Molecular weight studies indicate that $\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}$ exists in benzene solution as dimeric molecules. The most likely structure for a dimer would involve chlorine bridges as observed for $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$. The ^1H and ^{13}C NMR spectra of the compound in benzene solution are consistent with the presence of cis and trans isomers and the absence of an equilibrium mixture of $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$, $[\text{In}(\text{C}_6\text{H}_5)_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}]_2$. Two singlets were observed for

the methylene protons, two singlets for methyl group protons as well as two sets of lines for phenyl protons. The low temperature (-85°C) ^1H NMR spectrum did not show any splitting of the original lines for methylene and methyl protons as might be expected if two of the lines were due to neopentyl group protons in $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}]_2$, as previously described. Further confirmation of the absence of an equilibrium comes from the ^{13}C NMR spectrum. The neopentyl group CH_2 and CMe_3 carbon atoms exhibit two sets of lines with none corresponding to $[\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}]_2$. It is regrettable that the ^{13}C NMR spectrum of $[\text{In}(\text{C}_6\text{H}_5)_2\text{Cl}]_2$ is not available for comparison.

The successful synthesis and characterization of organoindium compounds with two different organic substituents prompted us to attempt the preparation of related organogallium chlorine compounds. However, the synthesis of $\text{Ga}(\text{Me})(\text{CH}_2\text{CMe}_3)\text{Cl}$ and $\text{Ga}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{CMe}_2\text{Ph})\text{Cl}$ by metathesis and/or ligand redistribution reactions were unsuccessful. Our characterization data of the materials isolated after the utilization of separation and purification techniques confirmed that ligand redistribution reactions which gave symmetrical products of the types GaR_2Cl and $\text{GaR}_2'\text{Cl}$ had occurred. Thus, the more symmetrical products must be thermodynamically more stable than the unsymmetrically substituted derivatives in gallium chemistry whereas the opposite appears to be true in indium chemistry. The reasons behind these observations are currently under investigation.

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Supplementary Material Available. Anisotropic thermal parameters, calculated positions of hydrogen atoms and an F_o/F_c list for $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ (pages). For ordering information, see any current masthead page.

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Table 1.

STRUCTURE DETERMINATION SUMMARY

Crystal Data

Empirical Formula	$C_{18}H_{44}Cl_2In_2Si_2$
Color; Habit	Colorless
Crystal Size (mm)	0.60 x 0.25 x 0.20
Crystal System	Triclinic
Space Group	$P\bar{1}$
Unit Cell Dimensions	$a = 6.1000(10) \text{ \AA}$ $b = 10.337(3) \text{ \AA}$ $c = 12.190(3) \text{ \AA}$ $\alpha = 77.28(2)^\circ$ $\beta = 84.41(2)^\circ$ $\gamma = 84.50(2)^\circ$
Volume	$744.0(3) \text{ \AA}^3$
Z	1
Formula weight	617.3
Density(calc.)	1.378 Mg/m^3
Absorption Coefficient	1.789 mm^{-1}
F(000)	312

Data Collection

Diffractometer Used	Siemens R3m/V
Radiation	MoK α (λ = 0.71073 Å)
Temperature (K)	298
Monochromator	Highly oriented graphite crystal
2 θ Range	5.0 to 50.0°
Scan Type	2 θ - θ
Scan Speed	Constant; 2.00°/min. in ω
Scan Range (ω)	0.47° plus K α -separation
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	3 measured every 97 reflections
Index Ranges	$-7 \leq h \leq 7$, $-12 \leq k \leq 12$ $-14 \leq l \leq 14$
Reflections Collected	5258
Independent Reflections	2629 (R_{int} = 1.36%)
Observed Reflections	1503 ($F > 6.0\sigma(F)$)
Absorption Correction	Semi-empirical
Min./Max. Transmission	0.5650 / 0.6258

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)*

	x	y	z	U(eq)*
In(1)	-2206(1)	269(1)	1199(1)	76(1)
Cl(1)	2162(4)	182(3)	796(2)	94(1)
Si(1)	-1320(10)	-2340(5)	3400(4)	125(3)
C(11)	-2738(23)	-1622(12)	2255(11)	109(5)
C(12)	-233(53)	-1311(20)	4051(19)	289(23)
C(13)	1133(48)	-3337(24)	2753(33)	288(24)
C(14)	-2684(34)	-3626(19)	4318(14)	161(9)
C(21)	-2948(31)	2379(13)	879(14)	136(8)
C(22)	-2846(18)	3218(10)	1781(10)	130(6)
C(23)	-3636(53)	4680(19)	1453(25)	260(19)
C(24)	-1048(52)	2851(25)	2563(30)	269(21)
C(25)	-4553(76)	2576(41)	2631(41)	344(35)

* Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond Lengths and Bond Angles.

Bond Lengths (Å)

In(1)-Cl(1)	2.659 (3)	In(1)-C(11)	2.125 (12)
In(1)-C(21)	2.140 (13)	In(1)-Cl(1A)	2.572 (3)
Cl(1)-In(1A)	2.572 (3)	Si(1)-C(11)	1.704 (14)
Si(1)-C(12)	1.676 (28)	Si(1)-C(13)	1.938 (31)
Si(1)-C(14)	1.757 (19)	C(21)-C(22)	1.552 (21)
C(22)-C(23)	1.520 (22)	C(22)-C(24)	1.490 (36)
C(22)-C(25)	1.490 (45)		

Bond angles (°)

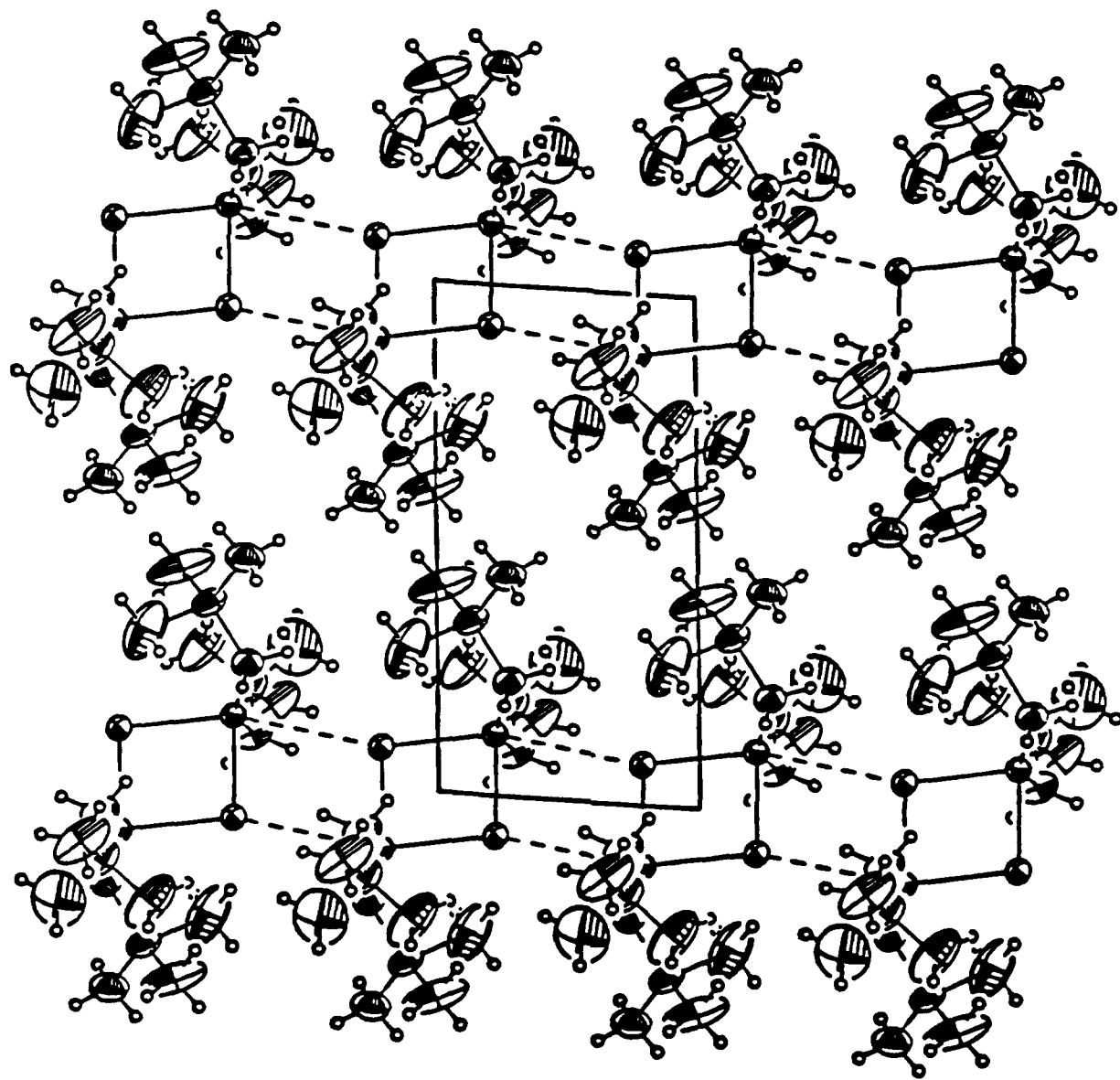
Cl(1)-In(1)-C(11)	103.1(4)	Cl(1)-In(1)-C(21)	99.7(5)
C(11)-In(1)-C(21)	148.1(6)	Cl(1)-In(1)-Cl(1A)	84.5(1)
C(11)-In(1)-Cl(1A)	102.9(4)	C(21)-In(1)-Cl(1A)	101.3(5)
In(1)-Cl(1)-In(1A)	95.5(1)	C(11)-Si(1)-C(12)	116.8(9)
C(11)-Si(1)-C(13)	102.5(12)	C(12)-Si(1)-C(13)	106.9(15)
C(11)-Si(1)-C(14)	113.0(9)	C(12)-Si(1)-C(14)	114.2(10)
C(13)-Si(1)-C(14)	101.2(10)	In(1)-C(11)-Si(1)	125.1(8)
In(1)-C(21)-C(22)	123.0(9)	C(21)-C(22)-C(23)	116.3(15)
C(21)-C(22)-C(24)	118.1(15)	C(23)-C(22)-C(24)	117.4(18)
C(21)-C(22)-C(25)	98.5(22)	C(23)-C(22)-C(25)	106.4(20)
C(24)-C(22)-C(25)	93.8(23)		

Captions to Figures

Figure 1. Packing diagram viewed down the 'b' axis with a vertical and c horizontal. Note the intermolecular contacts running down a.

Figure 2. Labelling of atoms in the $[\text{In}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)\text{Cl}]_2$ molecule; ORTEPII diagram with 20% probability ellipsoids and with hydrogen atoms artificially reduced.

Fig 1



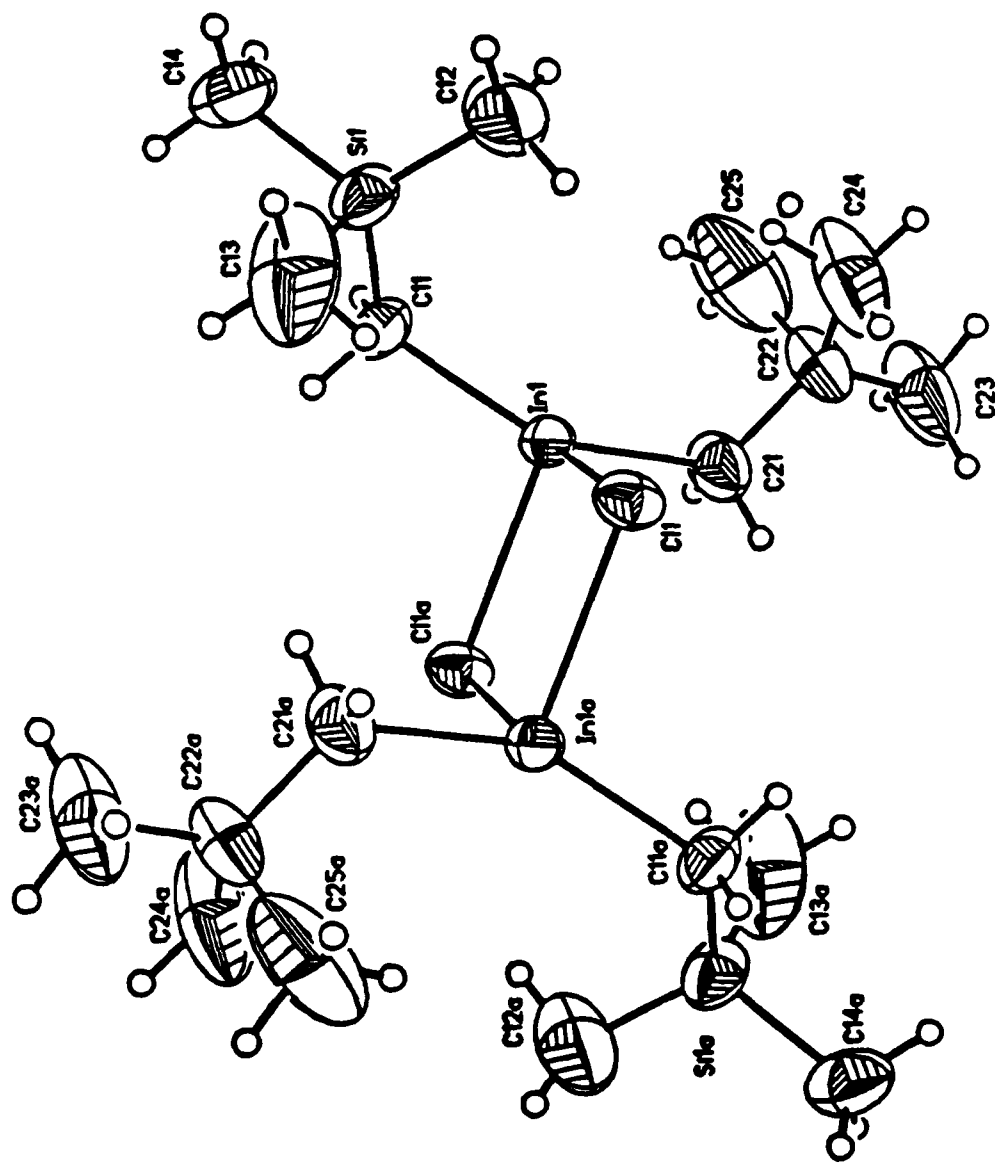


FIG 2

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