

Notes

Synthesis and Characterization of Benzylindium Compounds

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A series of organoindium compounds which incorporate the benzyl ligand, $\text{In}(\text{CH}_2\text{Ph})_x\text{Cl}_{3-x}$ ($x = 1-3$), has been prepared and characterized by elemental analyses, molecular weight data, n.m.r., i.r., and mass spectroscopy, and Lewis acid-base studies. The parent compound $\text{In}(\text{CH}_2\text{Ph})_3$ was prepared from InCl_3 and 3 equivalents of $\text{MgBr}(\text{CH}_2\text{Ph})$ in diethyl ether solution. It is a crystalline solid which exists as a monomeric three-co-ordinate species in solution and in the vapour phase. Benzylindium chloride compounds were prepared from $\text{In}(\text{CH}_2\text{Ph})_3$ by means of exchange reactions with InCl_3 , or elimination reactions with NHMe_3Cl . The compounds $[\text{In}(\text{CH}_2\text{Ph})_2\text{Cl}]_2$ and $[\text{In}(\text{CH}_2\text{Ph})\text{Cl}_2]_x$ are crystalline solids, and presumably have chloride-bridged structures. The benzylindium compounds are compared to their methyl analogues.

Despite their possible use in the production of Group 13-15 semiconductors by metal organic chemical vapour deposition (m.o.c.v.d.), there are surprisingly few organoindium compounds reported in the literature.¹ In part this may be due to their often low thermal stability and high reactivity towards air and moisture. The use of non- β -hydrogen-containing alkyl groups to stabilize transition-metal organometallic compounds is well documented, and should be applicable to organoindium compounds. The most commonly used alkyl ligands without β -hydrogens are methyl, neopentyl (CH_2CMe_3), (trimethylsilyl)methyl (CH_2SiMe_3), and benzyl (CH_2Ph), of which all but the benzyl derivatives have been reported for indium.¹⁻³

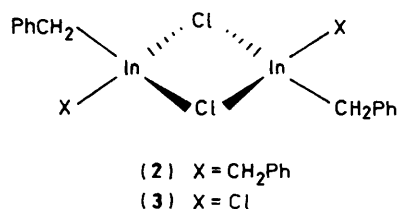
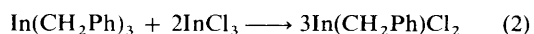
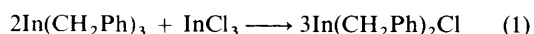
In this paper the synthesis of some benzyl derivatives of indium are reported, and their physical properties are compared to their methyl analogues.

Results and Discussion

A series of benzylindium compounds, $\text{In}(\text{CH}_2\text{Ph})_x\text{Cl}_{3-x}$ ($x = 1-3$), has been prepared and fully characterized. The simplest compound in the series, $\text{In}(\text{CH}_2\text{Ph})_3$ (1), is prepared in ca. 80% yield by the reaction of 3 equivalents of benzyl Grignard with InCl_3 in Et_2O solution. In contrast to the preparation of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, in which a 13% excess of the Grignard reagent is necessary to obtain a high yield,² the use of an excess of Grignard reagent does not improve the yield of (1). A reflux period of 2 h was required to maximize the yield of (1), however.

A variety of reaction conditions was explored in order to maximize the yield of $\text{In}(\text{CH}_2\text{Ph})_3$. The use of InBr_3 or InI_3 yielded only minor quantities of compound (1), and changing the solvent to tetrahydrofuran (thf) resulted in the isolation of the solvent adduct, $\text{In}(\text{CH}_2\text{Ph})_3 \cdot \text{thf}$, from which the thf could not be completely removed. Molecular weight measurements and mass spectral data are indicative of a three-co-ordinate indium compound, both in solution and the vapour phase.

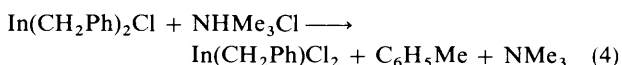
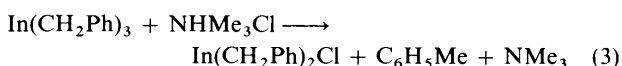
The chloro-substituted derivatives, $\text{In}(\text{CH}_2\text{Ph})_2\text{Cl}$ (2) and $\text{In}(\text{CH}_2\text{Ph})\text{Cl}_2$ (3), are readily prepared from (1) by using appropriate stoichiometric quantities of InCl_3 in exchange reactions (1) and (2). The data suggest that both (2) and (3) exist



as dimers. For instance, molecular weight measurements are consistent with a dimeric formulation for (2); unfortunately, the low solubility of (3) precludes an accurate molecular weight determination. The mass spectra of (2) and (3) each contain peaks consistent with the formation of dimers. It is reasonable to assume that compounds (2) and (3) both contain two chloro bridges.

Diethyl ether does not form an adduct with compound (1) at room temperature, but a stable 1:1 adduct is formed with thf. The relative stability of the thf adduct of (1) as compared to that observed for $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ ² is not unexpected due to the decreased steric bulk of the benzyl ligand. A 1,4-dioxane adduct of (1) has also been prepared. It is formulated as $[\text{In}(\text{CH}_2\text{Ph})_3]_2 \cdot 1,4\text{-diox}$ from ¹H n.m.r. spectroscopy, suggesting that 1,4-dioxane acts as a bridging ligand between two $\text{In}(\text{CH}_2\text{Ph})_3$ molecules.

Neither (2) nor (3) formed a stable adduct with the bases NMe_3 , 1,4-dioxane, thf, or Et_2O . Indeed, it is possible to synthesize (2) and (3) by the reaction of NHMe_3Cl with (1) and (2) respectively; no incorporation of amine is observed [equations (3) and (4)]. It is noteworthy that $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ and $\text{In}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$ also do not form stable Lewis-base adducts.²



Compounds (1)-(3) have physical properties very similar to the corresponding methyl derivatives; for instance, their relative solubilities, Lewis acidities, and melting points [$86-87^\circ\text{C}$ for (1) vs 89°C for InMe_3 ,⁴ $215-217^\circ\text{C}$ for (2) vs 218°C for

InMe_2Cl ,⁵ and 171–172 °C for (3) vs. 165 °C for InMeCl_2 ,⁶] are comparable.

In light of physical and chemical similarities, it is reasonable to propose solid-state structures for $\text{In}(\text{CH}_2\text{Ph})_3$, $\text{In}(\text{CH}_2\text{Ph})_2\text{Cl}$, and $\text{In}(\text{CH}_2\text{Ph})\text{Cl}_2$ that are similar to those of the methyl analogues.^{4–6} Unfortunately, crystals of (1)–(3) were not suitable for X-ray crystallographic studies to confirm this proposal.

Conclusions

Physical and spectroscopic data suggest that benzylindium derivatives are isostructural to the methyl analogues. Although methyl and benzyl are sterically distinct, they are electronically similar.⁷ This would suggest that electronic, not steric, factors predominate in the structural chemistry of organoindium compounds.

Experimental

All manipulations were carried out under nitrogen or *in vacuo*. Solvents were dried, distilled, and degassed before use. Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were performed by MultiChem Laboratories Inc., Lowell, Massachusetts. Molecular weight measurements were made in benzene or dichloromethane, using an instrument similar to that described by Clark.⁸ Mass spectra were recorded on a Kratos mass spectrometer, i.r. spectra (Nujol mulls, CsI) on a Perkin-Elmer 598 spectrometer, and proton n.m.r. spectra on a Bruker AM-250 spectrometer. Chemical shifts are referenced to SiMe_4 (external).

Synthesis of $\text{In}(\text{CH}_2\text{Ph})_3$.—To a stirred suspension of InCl_3 (4.0 g, 18.1 mmol) in diethyl ether (60 cm^3) at room temperature in the dark was added $\text{MgBr}(\text{CH}_2\text{Ph})$ (34.0 cm^3 of 1.63 mol dm^{-3} solution in Et_2O , 55.4 mmol) dropwise. On completion of the addition the mixture was refluxed for 2 h. The solvent was then removed under vacuum, the residue washed with pentane ($2 \times 10 \text{ cm}^3$) and then extracted with benzene ($2 \times 50 \text{ cm}^3$). Removal of the solvent *in vacuo* resulted in a white powder which was recrystallized from Et_2O : yield 5.82 g (83%), m.p. 86–87 °C (Found: C, 65.1; H, 5.45. Calc. for $\text{C}_{21}\text{H}_{21}\text{In}$: C, 64.9; H, 5.45%). Molecular weight (C_6H_6): Found: 394. Calc. for $\text{In}(\text{CH}_2\text{Ph})_3$: 388.2. Mass spectrum (m/z): 388(M^+), 297($M^+ - \text{C}_7\text{H}_7$), and 206($M^+ - \text{C}_{14}\text{H}_{14}$). I.r.: 3 060s, 1 945w, 1 860w, 1 800w, 1 730w, 1 590s, 1 485s, 1 415w, 1 300w, 1 255m, 1 200s, 1 185w, 1 150w, 1 080sh, 1 025s, 990m, 890w, 795s, 745s, 690s, 615w, 545m, and $\nu(\text{In}-\text{C})$ 430 cm^{-1} . Proton n.m.r. (C_6D_6): 7.02 (m, 15 H, Ph) and 2.13 (s, 6 H, CH_2).

Synthesis of $\text{In}(\text{CH}_2\text{Ph})_2\text{Cl}$.—*Method 1.* The compound $\text{In}(\text{CH}_2\text{Ph})_3$ (0.67 g, 1.73 mmol) dissolved in benzene (50 cm^3) was added to InCl_3 (0.19 g, 0.85 mmol). The reaction mixture was refluxed gently until all the solid dissolved (12 h). On cooling, fine needles were deposited from solution: yield 0.81 g, 95%.

Method 2. To a solution of $\text{In}(\text{CH}_2\text{Ph})_3$ (0.23 g, 0.59 mmol) in Et_2O (30 cm^3) was added solid NHMe_3Cl (0.056 g, 0.59 mmol). After stirring for 5 h, the solvent was removed under vacuum and the white residue was recrystallized from hot benzene. Yield 0.25 g (64%), m.p. 215–217 °C (Found: C, 51.1; H, 4.15. Calc. for $\text{C}_{14}\text{H}_{14}\text{ClIn}$: C, 50.6; H, 4.25%). Molecular

weight (CH_2Cl_2): Found: 679. Calc. for $[\text{In}(\text{CH}_2\text{Ph})_2\text{Cl}]_2$: 665.0. Mass spectrum (m/z): 664($2M^+$), 332(M^+), 241($M^+ - \text{C}_7\text{H}_7$), and 150($M^+ - \text{C}_{14}\text{H}_{14}$). I.r.: 3 080w, 1 950w, 1 875w, 1 805w, 1 720w, 1 600s, 1 490s, 1 325w, 1 260w, 1 215m, 1 180w, 1 155w, 1 090m, 1 050m, 900m, 805m, 755s, 715m, 690s, 570w, 550w, and $\nu(\text{In}-\text{C})$ 445 cm^{-1} . Proton n.m.r. (CD_2Cl_2): 7.15 (m, 10 H, Ph) and 2.57 (s, 4 H, CH_2).

Synthesis of $\text{In}(\text{CH}_2\text{Ph})\text{Cl}_2$.—*Method 1.* To InCl_3 (0.61 g, 2.76 mmol) and $\text{In}(\text{CH}_2\text{Ph})_3$ (0.54 g, 1.39 mmol) was added benzene (40 cm^3). The reaction was refluxed for 5 h. After cooling, a white solid precipitated, which was filtered off and dried under vacuum. Yield 1.03 g, 90%.

Method 2. Solid NHMe_3Cl (0.11 g, 1.15 mmol) was added to a solution of $\text{In}(\text{CH}_2\text{Ph})_2\text{Cl}$ (0.39 g, 1.17 mmol) in Et_2O (30 cm^3). After stirring for 5 h the volatiles were removed under vacuum and the residue recrystallized from Et_2O (20 cm^3). Yield: 0.18 g (57%), m.p. 171–172 °C (Found: C, 30.8; H, 2.60. Calc. for $\text{C}_7\text{H}_7\text{Cl}_2\text{In}$: C, 30.4; H, 2.55%). Mass spectrum (m/z): 552($2M^+$), 461($2M^+ - \text{C}_7\text{H}_7$), 276(M^+), and 185($M^+ - \text{C}_7\text{H}_7$). I.r.: 3 020w, 1 950w, 1 870w, 1 800w, 1 765w, 1 595m, 1 410w, 1 255s, 1 090s, 1 040sh, 1 015s, 845w, 795s, 755m, 725m, 690m, 565m, $\nu(\text{In}-\text{C})$ 445w, 390w, 295m, and 270 cm^{-1} . Proton n.m.r. (CD_2Cl_2): 7.10 (m, 5 H, Ph) and 2.49 (s, 2 H, CH_2).

Lewis Acidity Studies.—The Lewis acidities of the benzylindium compounds were determined by treating neat base (1,4-dioxane, thf, or Et_2O) with a weighed quantity of compounds (1)–(3). The reaction mixture was stirred at room temperature for 1 h. The excess of base was then removed under vacuum. If a stoichiometric quantity of base was retained the product was characterized by ^1H n.m.r. spectroscopy (C_6D_6): $\text{In}(\text{CH}_2\text{Ph})_3 \cdot \text{thf}$ (4), 7.05 (m, 15 H, Ph), 2.96 [q, $J(\text{H}-\text{H}) = 6.5$, 4 H, OCH_2], 2.20 (s, 6 H, CH_2), and 0.99 [q, $J(\text{H}-\text{H}) = 6.5$ Hz, 4 H, OCH_2CH_2]; $[\text{In}(\text{CH}_2\text{Ph})_3] \cdot 1,4\text{-diox}$, (5), 7.10 (m, 30 H, Ph), 2.88 (s, 8 H, OCH_2), and 2.12 (s, 12 H, CH_2).

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