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ORGANOINDIUM CHEMISTRY
I. A CONVENIENT PREPARATION OF DIMETHYLINDIUM(III) DERIVATIVES*

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INTRODUCTION

In comparison with other group III metals, the organometallic chemistry of indium has received scant attention. The tetrameric nature[1] of trimethylindium[2] is well-known, and other triorganoindium(III) derivatives have been reported[3-7]. Very few diorganoindium(III) derivatives, R_2InX, are known and no systematic exploration has been made of the stereochemical possibilities of these and related compounds. Diphenyl-[3,5] and di-1-naphthylindium bromide[5] and diphenylindium iodide[3] are known, and also the tetrameric dimethylindium cyanide[8]. Additionally, by reaction of trimethylindium with the appropriate amine, phosphine, or arsine, derivatives of the type $[(CH_3)_2In{-}MR_2]_x$ where M = N, P or As; R = CH_3 or C_6H_5 have been obtained[9-11], with the elimination of methane. Dimethylindium methoxide and the acetylacetonate are known[9], while recently bis(pentafluorophenyl)indium bromide has been described[12]. The dimeric compounds $[(C_6H_5)_3C{-}O{-}In(CH_3)_2]_2$ and $[(C_6H_5)_3Si{-}O{-}In(CH_3)_2]_2$ have also been prepared[13] from trimethylindium.

Our interest in organoindium chemistry has developed from our previous studies of organotin[14,15] and organoantimony[16] compounds, of the types R_3SnX, R_2SnX_2 and R_3SbX_2. These have established the non-ionic and frequently polymeric structures of such compounds, and have explored the nature of the strong interaction between the organometallic and anionic species. In contrast, similar studies of organothallium derivatives, R_2TlX, indicate the considerable stability and wide occurrence of R_2Tl^+ ions[17-20]. A more direct comparison can be made of, say, $(CH_3)_2InX$ with $(CH_3)_3SnX$ compounds. The present work was initiated in order to make such a comparison, and simultaneously to further develop the general organometallic chemistry of indium.

EXPERIMENTAL

All operations (except conductance and molecular weight studies) were carried out in a glass vacuum system, or under nitrogen in a dry box or glove bag. All chemicals and solvents were dried by standard methods, and glassware was oven-dried. The

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methyllithium (Foote Mineral Co.) was prepared from methyl chloride, and hence was free of halide. Infrared spectra were taken on a Beckman IR 10 spectrophotometer (4000–300 cm^{-1}, calibrated against polystyrene) in nujol or halocarbon oil mulls between potassium bromide or cesium iodide plates. Molecular weights were measured in benzene solution on a Mechrolab Vapor Phase Osmometer model 301A. Conductance studies were done in methanol using an Industrial Instruments Conductivity Bridge and a conductivity cell with cell constant 0.100/cm. Melting points were measured in sealed tubes in a Hoover capillary melting point apparatus. Carbon and hydrogen analyses were by Dr.Alfred Bernhardt. Chloride analyses were by the dichlorofluorescein adsorption indicator method after oxidation of a sample with aqueous hydrogen peroxide and removal of indium as the hydroxide. All products were white crystalline solids unless otherwise stated.

Trimethylindium

Indium trichloride (1.2 g, 5.5 mmoles) was mixed with methyllithium (10 ml at 1.67 *M*, 16.7 mmoles) in 10 ml ether. After the vigorous reaction was complete, the ether and trimethylindium were condensed into a $-196°$ trap *in vacuo*, while the reaction vessel was heated to 100° to increase the rate of transfer of the final product. Due to the difficulty of separating trimethylindium quantitatively from ether, fractionation was not attempted. Identification of trimethylindium was made by comparison of the infrared spectrum with that given by Oswald[21]. Virtually no indium remained in the involatile residue, hence the yield was nearly quantitative.

Preparation of dimethylindium(III) halides

Dimethylindium(III) chloride. Dried indium trichloride (1.5 g, 6.8 mmoles) was mixed with methyllithium (8.1 ml at 1.67 *M*, in ether, 13.6 mmoles) in 20 ml of ether and shaken for two days. Volatiles were removed *in vacuo*, and the product purified by sublimation at 110° *in vacuo* to a 15° cold finger, forming a white powder or colorless crystals. Yield 1.0 g, 81%; m.p. 218–219°; molar conductance at 1.31×10^{-3} *M*, 69. (Found: C, 13.67; H, 3.51; Cl, 19.22; mol.wt., 385. C_2H_6ClIn calcd.: C, 13.32; H, 3.35; Cl, 19.66%; mol.wt. of dimer, 360.)

This experiment was repeated with the same quantities of indium trichloride and methyllithium, but all volatiles were removed immediately after the vigorous reaction ceased (approx. 30 min). The product was trimethylindium. No dimethylindium chloride was formed, but the involatile residue contained indium. The trimethylindium was recombined with the residue and dimethylindium chloride was recovered after two days.

Dimethylindium(III) iodide. Indium trichloride (1.0 g, 4.5 mmoles), methyllithium (5.4 ml at 1.67 *M*, 9.0 mmoles), and lithium iodide (0.6 g, 4.5 mmoles) were mixed in 20 ml of ether and shaken for two days. After removal of all volatiles, the product was purified by sublimation *in vacuo* as above. Yield, 0.9 g, 73%; m.p. 212–218°; molar conductance at 1.70×10^{-3} *M*, 87. (Found: C, 9.09; H, 2.49; mol.wt., 577. C_2H_6IIn calcd.: C, 8.84; H, 2.23%; mol.wt. of dimer, 543.)

Dimethylindium(III) iodide (0.2 g, 0.73 mmoles) and methyllithium (0.5 ml at 1.67 *M*, 0.83 mmoles) were mixed in ether. Following vacuum fractionation, trimethylindium was identified by its infrared spectrum.

Dimethylindium(III) bromide. Trimethylindium (*ca.* 5.4 mmoles) in ether was solvolyzed with dry methanol to yield dimethylindium methoxide[9] in solution. Hydrogen bromide (4.6 mmoles) was condensed into the solution and all volatiles were then pumped off. The product was purified by subliming twice *in vacuo* at 110°. (Found: C, 10.1; H, 2.65. C_2H_6BrIn calcd.: C, 10.7; H, 2.69%.)

Dimethylindium(III) fluoride. Boron trifluoride etherate (0.26 g, 1.8 mmoles) in ether was slowly added to trimethylindium (*ca.* 5.4 mmoles) in ether. Effervescence was observed. The white precipitate was filtered, sublimed (yield 0.5 g, *ca.* 50%), recrystallized twice from methanol and resublimed. M.p. 295° (decomp.). (Found: C, 14.87; H, 3.81; F, 11.98. C_2H_6FIn calcd.: C, 14.67; H, 3.70; F, 11.60%.)

Dimethylindium(III) derivatives from trimethylindium in ether

Numerous derivatives were prepared by adding an equivalent of the appropriate reagent to an ethereal solution of trimethylindium.

Dimethylindium(III) acetylacetonate[9] was prepared from acetylacetone, and purified by sublimation *in vacuo* after the volatiles were pumped off. Molar conductance at 4.68×10^{-3} *M*, 26 (increasing with time, apparently due to decomposition). (Found: C, 35.12; H, 5.66; mol.wt., 302. $C_7H_{13}InO_2$ calcd.: C, 34.47; H, 5.37%; mol.wt., 243.)

Dimethylindium(III) 8-hydroxyquinolinate precipitated, with effervescence, as a bright yellow solid when 8-hydroxyquinoline in ether was added to trimethylindium. M.p. 260° (decomp.); molar conductance at 0.72×10^{-3} *M*, 2.9. (Found: C, 46.16; H, 4.58. $C_{11}H_{12}InNO$ calcd.: C, 45.7; H, 4.18%.) The compound is completely air-stable.

Dimethylindium(III) o-nitrophenoxide precipitated slowly from an ethereal solution of trimethylindium and *o*-nitrophenol as a bright orange solid. M.p. 190° (decomp.). (Found: C, 33.81; H, 3.89. $C_8H_{10}InNO_3$ calcd.: C, 33.9; H, 3.56%.)

Dimethylindium(III) acetate precipitated with effervescence from acetic acid and trimethylindium in ether, and was purified by sublimation *in vacuo* at 130°. It was too insoluble in benzene for a molecular weight determination. (Found: C, 23.17; H, 4.29. $C_4H_9InO_2$ calcd.: C, 23.56; H, 4.55%.)

Dimethylindium(III) 1,1-bis(trifluoromethyl)ethoxide was prepared from trimethylindium and hexafluoroacetone in ether, as a clear colorless liquid. Proton magnetic resonance showed two signals in the ratio of 2 : 1 at $\tau = 9.91$ ppm [$In(CH_3)_2$] and at $\tau = 8.48$ ppm [$C(CF_3)_2CH_3$], ^{19}F magnetic resonance showed a singlet at 81 ppm upfield from $CFCl_3$. (Found: C, 21.3; H, 2.51; F, 33.19. $C_6H_9F_6InO$ calcd.: C, 22.1; H, 2.78; F, 35.0%.)

Lewis base adducts

Dimethylindium iodide/pyridine adduct. Dimethylindium iodide was dissolved in pyridine. Excess pyridine was pumped off and the product purified by sublimation *in vacuo* at 60°. M.p. 72–75°. (Found: C, 24.17; H, 3.10. $C_7H_{11}IInN$ calcd.: C, 23.96; H, 3.16%.)

Dimethylindium chloride/pyridine adduct. Pyridine was added to dimethylindium chloride in ether. The product was purified by washing with ether. M.p. 82–84.5°, molar conductance at 3.44×10^{-3} *M*, 55. (Found: C, 31.88; H, 4.31; Cl, 14.6. $C_7H_{11}ClInN$ calcd.: C, 32.41; H, 4.27; Cl, 13.67%.)

Dimethylindium iodide/triphenylphosphine adduct. Dimethylindium iodide (0.14

g, 0.52 mmoles) was mixed with triphenylphosphine (0.13 g, 0.52 mmoles) in ether, and the solvent pumped off. The product was washed with a little ether and with petroleum ether. (Found: C, 44.86; H, 3.82; mol.wt., 459. $C_{20}H_{21}IInP$ calcd.: C, 44.98; H, 3.96%; mol.wt., 534.)

Bis(dimethylindium chloride)/triphenylphosphine. Dimethylindium chloride (0.25 g, 1.4 mmoles) and triphenylphosphine (0.18 g, 0.7 mmoles) were dissolved in 25 ml of ether. The solvent was pumped off and the white product washed with a little ether, and petroleum ether. M.p. 130–138°; molar conductance at 1.57×10^{-3} *M*, 111. (Found: C, 41.79; H, 4.30. $C_{22}H_{27}Cl_2In_2P$ calcd.: C, 42.4; H, 4.37%.)

DISCUSSION

Previous preparations of trimethylindium have utilized dimethylmercury[2], methylmagnesium chloride in ether[5], aluminum alkyls[6], or the reaction of methylbromide with magnesium/indium alloy[7]. Not surprisingly, trimethylindium can also be obtained from indium trichloride and methyllithium. When this reaction is carried out, using a 2 : 1 molar ratio of methyllithium to indium trichloride, the final product is determined by length of time allowed for reaction. If the reaction mixture is fractionated as soon as the initial vigorous reaction is complete (*ca.* 30 minutes), trimethylindium is obtained in good yield. If reaction is allowed to continue for two days, dimethylindium chloride, $(CH_3)_2InCl$, is obtained in excellent yield. Clearly, the longer reaction period allows equilibrium to be established.

$$2\,(CH_3)_3In + InCl_3 \rightleftharpoons 3\,(CH_3)_2InCl$$

$$(CH_3)_3In + LiCl \rightleftharpoons (CH_3)_2InCl + LiCH_3$$

The second equilibrium lies well to the left, however, and must be less important That lithium halide is involved is further shown by the reaction of methyllithium with lithium iodide and indium trichloride (in a 2 : 1 : 1 ratio) in diethyl ether. With short reaction times (*ca.* 30 minutes) trimethylindium is again the principal product but with reaction times of 2–3 days, $(CH_3)_2InI$, but no $(CH_3)_2InCl$, is obtained in greater than 70% yield. This must be due to the reaction:

$$(CH_3)_2InCl + LiI \rightarrow (CH_3)_2InI + LiCl$$

the occurrence of which will be favored by the solubility order $LiCl < LiI < (CH_3)_2InI$. As might be expected, dimethylindium(III) iodide with excess methyllithium in diethyl ether, is converted to trimethylindium. The considerable advantage of these reactions lies in the fact that dimethylindium chloride and iodide can be readily obtained by a single-step reaction through suitable control of the molar ratio of reactants, and of the reaction period. Moreover, the use of a highly toxic reagent such as dimethylmercury is avoided. The method also allows the rapid preparation of trimethylindium with no interference from other reaction products, as is the case when aluminum alkyls are used[6]. It is interesting that this preparation of $(CH_3)_2InX$ (X = Cl or I) is similar to the formation[12] of $(C_6F_5)_2InBr$ by a competitive halogen exchange in the reaction of $InCl_3$ with C_6F_5MgBr. In contrast, the reported preparation of $(C_6H_5)_2InX$ (X = Br or I) requires two steps, the initial preparation of $(C_6H_5)_3In$, followed by direct halogenation.

Attempts to prepare dimethylindium(III) bromide from the reaction of the chloride with potassium bromide in ether were unsuccessful but the bromide was obtained by reacting the methoxide, $(CH_3)_2InOCH_3$, with one equivalent of hydrogen bromide. Dimethylindium (III) fluoride was best prepared by the interesting reaction of boron trifluoride etherate with trimethylindium, while only trace amounts of the fluoride were obtained from reactions of trimethylindium with potassium hydrogen fluoride in ether.

The chloride and iodide are both dimeric in benzene solution, and for all the halides the infrared spectra (see Table) show both the In–C asymmetric and In–C symmetric stretching vibrations. These frequencies are higher than those reported[11] for $[(CH_3)_2In{-}MR_2]_x$ compounds, particularly for those with M = P or As, for which some π-interaction in the In–M bond has been proposed[9]. For these dimethylindium(III) halides, halogen-bridged dimers with non-linear $(CH_3)_2In$ groups are therefore the most probable structural units, although polymeric structures are also possible for the solid compounds. A crystal structure determination of the chloride is now in progress. These halides are thus very similar to diorganogallium(III) halides, such as $(CH_3)_2GaCl$ which is dimeric in the vapor[22], and quite different from the diorganothallium halides which contain linear C–Tl–C units[17–20] with an octahedrally coordinated thallium atom.

TABLE 1

INFRARED FREQUENCIES (cm^{-1}) FOR THE $(CH_3)_2In$ GROUP IN $(CH_3)_2InX$ DERIVATIVES[a]

Compound	*CH_3 deformation*	*In–CH_3 rock*	*In–C stretch*
$(CH_3)_2InCl$	1178 (m), 1160 (w)	732 (vs, bd)	558 (s), 488 (m)
$(CH_3)_2InBr$	1170 (m)	735 (vs, bd)	554 (s), 486 (w)
$(CH_3)_2InI$	1164 (m), 1150 (vw)	730 (vs, bd)	548 (s), 480 (vw)
$(CH_3)_2InF$	1180 (m), 1165 (m)	720 (vs, bd)	548 (s), 493 (m)
$(CH_3)_2In(C_5H_7O_2)$[b]	1162 (w), 1156 (w)	715 (vs, bd)	550 (s), 486 (m), 540 (s) (chelate ring)
$(CH_3)_2In$ oxinate		705 (s, bd)	530 (s), 498 (m) or 483 (m), 508 (m) (ligand)
$(CH_3)_2InOC_6H_4$-o-NO_2		730 (vs, bd)	568 (s), 550 (s), 523 (w), 497 (w)
$(CH_3)_2InOOCCH_3$	1162 (w), 1156 (w)	725 (vs, bd)	548 (s), 490 (m), (455 w, acetate?)
$[(CH_3)_2InOCH_3]_3$		705 (vs, bd)	517 (s), 495 (s), 470 (s), (two of)
$(CH_3)_2InOC(CF_3)_2CH_3$		734 (vs, bd)	540 (vs), 487 (s), (466 s, 444 m, ethoxide)
$(CH_3)_2InI\cdot py$		720 (vs, bd)	522 (s), 482 (m)
$(CH_3)_2InCl\cdot py$		720 (vs, bd)	526 (s), 488 (m)
$(CH_3)_2InI\cdot PPh_3$		724 (s)	515 (s), [495 (s)], 478 (m)
$[(CH_3)_2InCl]_2PPh_3$		730 (s)	544 (m), 515 (s), 498 (s), 492 (s)

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak, bd = broad. [b] Acetylacetonate.

Although the infrared data do not suggest any marked structural differences among the dimethylindium(III) halides, the fluoride does show some noticeable differences from the remaining three halides, notably its much higher melting point, and very low solubility in chloroform and ether. Such differences also occur between triorganotin fluorides and other triorganotin halides, and for the trimethyltin compounds are known to reflect a difference in structure. It remains to be seen from detailed studies whether dimethylindium(III) fluoride is structurally different from other dimethylindium(III) halides.

The ease with which trimethylindium loses a CH_3 group, which thus shows considerable basicity, by reaction[9] with a donor molecule containing a reactive hydrogen atom or with an hydroxyl compound can also be utilized to prepare dimethylindium(III) derivatives, as illustrated by the preparations of dimethylindium(III) methoxide[9], acetylacetonate[9], 8-hydroxyquinolinate, and *o*-nitrophenoxide. The latter three compounds are presumably neutral, tetrahedral species, this being supported by the low molar conductances, the monomeric nature of the acetylacetonate in benzene solution, and most importantly by the observation of both the asymmetric and symmetric In–C stretching vibrations in the infrared spectra (see Table 1). Thus, in the spectrum of the acetylacetonate, the In–C asymmetric and symmetric stretching vibrations are at 550 and 486 cm^{-1} respectively, the peak at 540 cm^{-1} being due to the complexed β-diketone system[20]. It is interesting that although the diorgano halides of indium and thallium are structurally different, acetylacetonates can be readily prepared for both dimethylindium and dimethylthallium[23].

In a very similar reaction dimethylindium(III) acetate was prepared from trimethylindium and acetic acid. A similar preparation was used previously[24] to obtain dimethylgallium acetate which is dimeric in solution. The infrared spectrum of $(CH_3)_2InOOCCH_3$ shows both the asymmetric and symmetric In–C stretching vibrations, but little useful structural information can be deduced[25] from the acetate peaks. The reaction of trimethylindium with hexafluoroacetone to give dimethylindium(III) 1,1-bis(trifluoromethyl)ethoxide, also indicates the ease with which one In–C bond is cleaved.

$$(CH_3)_3In + (CF_3)_2CO \rightarrow (CH_3)_2InOC(CF_3)_2CH_3$$

The adducts $(CH_3)_2InX \cdot py$ ($X = Cl$ or I), and $(CH_3)_2InI \cdot PPh_3$ are white, sublimable solids, only slightly soluble in ether. The triphenylphosphine complex apparently dissociates quite readily, since its molecular weight in benzene solution is appreciably less than the expected value for the monomer. The infrared spectra of these adducts again show two In–C stretching vibrations, although for the phosphine complex there are interfering ligand bands. The pyridine adducts show peaks characteristic of co-ordinated pyridine[26], particularly around 430, 630 and 690 cm^{-1}, but absorptions due to In–halogen vibrations are expected to be outside the range of the instruments used. The molar conductance of $(CH_3)_2InCl \cdot py$ at a concentration of 3.44×10^{-3} *M* is appreciably less than that of the original chloride (at 1.7×10^{-3} *M*). It therefore seems clear that the pyridine complexes, and probably also $(CH_3)_2InI \cdot PPh_3$ are neutral, monomeric, tetrahedral species. This contrasts with the behavior of dimethylthallium halides[17] which can be recrystallized from pyridine and do not form stable adducts, although there is some spectroscopic evidence that in pyridine and tetramethylguanidine the linear $(CH_3)_2Tl^+$ cation is somewhat distorted presumably by solvation. Certainly a solution of $(CH_3)_2TlI$ in pyridine shows two infrared bands at 470 and 536 cm^{-1} which are consistent with a nonlinear $(CH_3)_2Tl^+$ species, although in this case the Tl atom could be three- of four-co-ordinate[27].

Although the iodide gave a simple 1 : 1 adduct with triphenylphosphine, dimethylindium chloride gave a product with the composition $[(CH_3)_2InCl]_2PPh_3$.

This gave a high conductance in methanol, in comparison with other compounds described here, and showed four infrared bands at 544, 515, 498, and 492 cm^{-1}, two of which can be assigned to In–C stretching vibrations and two vibrations of co-ordinated triphenylphosphine. A suggested formulation is $[Ph_3PIn(CH_3)_2]^+ \cdot [(CH_3)_2InCl_2]^-$ although there are other possibilities and further studies are in progress.

It is noteworthy that in all of the dimethylindium(III) derivatives so far described, a tetrahedral configuration is preferred, and there are no indications that indium achieves six-co-ordination. Dimethylindium(III) derivatives containing strong chelating ligands, such as ethylenediamine and bipyridine may well produce stereochemistries with co-ordination numbers of five or six for indium, and we are currently attempting such reactions.

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SUMMARY

A convenient method is described for the one-step synthesis of trimethylindium, or dimethylindium(III) chloride, the final product depending on the length of the reaction. The preparations of dimethylindium(III) fluoride, bromide, and iodide are described, and on the basis of molecular weights and infrared spectra, dimeric, halogen-bridged structures are proposed. Other new dimethylindium(III) derivatives include the 8-hydroxyquinolinate, the *o*-nitrophenoxide, the acetate, and the 1,1-bis(trifluoromethyl)ethoxide, these all being prepared from trimethylindium. Lewis base adducts of dimethylindium iodide and chloride with pyridine and triphenylphosphine have also been prepared.

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