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ORGANOINDIUM CHEMISTRY
II. DERIVATIVES OF DIMETHYLINDIUM(III) AND METHYLINDIUM(III)

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SUMMARY

The synthesis and stereochemistry of several classes of organoindium derivatives are described. Four-coordination about indium, in a distorted tetrahedral stereochemistry, is most common, and occurs in a series of 1 : 1 complexes of Lewis bases with dimethylindium halides and in two organoindium anions, dimethylindium dichloride and tetramethylindate. These new organoindium derivatives are similar to analogous aluminum and gallium compounds.

1 : 1 Complexes of dimethylindium halides with bidentate ligands (1,10-phenanthroline, 2,2'-bipyridine) were synthesized and probably contain five-coordinate indium.

Several methylindium dichloride derivatives were synthesized and the parent compound is compared to the gallium and thallium analogues.

INTRODUCTION

The first paper in this series[1] described the synthesis and stereochemistry of dimethylindium halides and of some other dimethylindium(III) derivatives including certain 1 : 1 complexes with Lewis bases. All of these derivatives appear to have a tetrahedral configuration about indium and are thus similar in structure to analogous aluminum and gallium compounds, but differ from the few related thallium compounds which are six coordinate. The dimethylindium compounds so far described contain unidentate ions or molecules [*e.g.* Cl^- or $P(C_6H_5)_3$], or bidentate ions (*e.g.* *o*-nitrophenoxide ion) as ligands. Related derivatives containing neutral chelating ligands, such as ethylenediamine, might well contain more highly coordinated indium atoms. We have therefore synthesized representative examples of several new classes of dimethylindium(III) compounds with the hope of finding coordination numbers greater than four. During this study, we have also obtained methylindium dichloride and a number of other methylindium(III) derivatives. These are of some interest and may be compared with the recently reported[2-4] methylthallium(III) derivatives, and related methylgallium(III) compounds[5].

EXPERIMENTAL

The techniques used for preparing and studying derivatives were described in

Part I[1]. Carbon and hydrogen analyses were performed by Dr. A. B. Gygli, Toronto, or Dr. A. Bernhardt, Mülheim, Germany.

Melting points (°C, uncorrected) were measured in sealed tubes in a Hoover capillary melting point apparatus. In numerous instances, compounds did not have distinct melting points but appeared to soften or partially melt over a wide temperature range. Beachley, Coates, and Kohnstam[6] have described phase transitions observed for compounds of the series $[(CH_3)_2M{-}N(CH_3)_2]_2$, (where M is aluminum, gallium, or indium). At room temperature these are crystalline solids, but at higher temperatures (50–75°) they are transformed into glasses, which then "melted" over a temperature range of several degrees (in the region of 150–175°). Therefore it is possible that some of the organoindium derivatives reported here and in Part I exhibit this type of phase transition. Alternatively, compounds, particularly addition complexes, may be decomposing over a wide temperature range and not actually melting.

Lewis base adducts

These derivatives were prepared by mixing dimethylindium chloride or iodide with an equivalent of the Lewis base in solution.

(*a*) *Dimethylindium chloride triphenylphosphine oxide* was recovered as a gum from ether/chloroform solution. It was recrystallized from the ternary solvent system chloroform/ether/petroleum ether (80–100°). The compound softened at 55° and melted at 95°. (Found: C, 51.60; H, 4.53; mol. wt., 435. $C_{20}H_{21}ClInOP$ cald.: C, 52.38; H, 4.62%; mol. wt., 458.6.)

(*b*). *Dimethylindium chloride triphenylarsine oxide* also formed a gum upon concentration of an ether/chloroform solution. It crystallized upon trituration. The compound was recrystallized from ether/chloroform/petroleum ether (80–100°) yielding colorless needle-like crystals. It is soluble in methanol and benzene. The complex softened at 63° and melted at 97–99°. (Found: C, 47.29; H, 4.06; mol. wt., 533. $C_{20}H_{21}AsClInO$ calcd.: C, 47.81; H, 4.21%; mol. wt., 502.5.)

(*c*). *Dimethylindium iodide triphenylphosphine oxide* was prepared as a white gummy substance from ether solution. The infrared spectrum was similar to that of the gummy form of dimethylindium chloride triphenylphosphine oxide. The compound was dissolved in ethanol and silver nitrate solution added, causing precipitation of silver iodide. The solvent was removed *in vacuo* leaving a gummy substance containing nitrate, dimethylindium, and triphenylphosphine oxide species according to the infrared spectrum.

(*d*). *Dimethylindium iodide* is very soluble in acetonitrile, but the solvent is readily removed *in vacuo* and the iodide is recovered unchanged. The chloride absorbs tetrahydrofuran vapor exothermally, yielding a liquid at room temperature. The tetrahydrofuran may be removed *in vacuo*. Both dimethylindium chloride and iodide are very soluble in ether and can be recrystallized from this solvent.

Ammonia adducts

Complexes of ammonia were studied tensimetrically. A known amount of dried ammonia (measured by pressure, volume and temperature) was admitted to a vessel containing dimethylindium iodide or chloride. The pressure of the ammonia was recorded when it had apparently reached equilibrium. The time for equilibration varied between a few minutes when the ratio of halide to ammonia was less than 1 : 1, to a few days at a ratio of 1 : 2. At higher pressures (*i.e.* at higher ammonia to halide ratios) the measured pressure was very temperature dependent. A plot of pressure of ammonia against moles of ammonia was made for the empty reaction vessel (Fig. 1, dashed line). Details of properties and tensimetric results are given in Table 1 and Fig. 1.

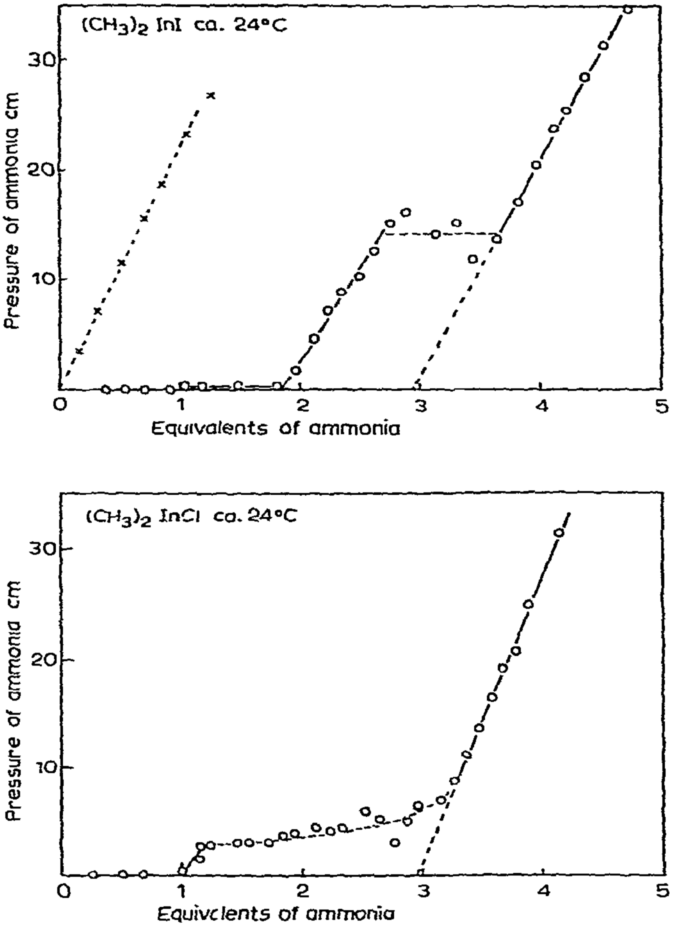

Fig. 1. Tensimetric titration of dimethylindium chloride and iodide with ammonia.

Bidentate ligand derivatives of dimethylindium halides

These derivatives were prepared by the same method used to synthesize the 1 : 1 adducts of monodentate Lewis bases and dimethylindium halides. The reactants were mixed in a stoichiometrical ratio of 1 : 1 in solution, and the products purified by recrystallization.

(*a*). *Dimethylindium chloride phenanthroline* was isolated from an ether solution of dimethylindium chloride and dried, sublimed phenanthroline. Crystallization occurred slowly after the solution had been concentrated. Yield 80%. Melting point 207–210° with decomposition. (Found: C, 46.48; H, 3.78; Cl, 9.96. $C_{14}H_{14}ClInN_2$ calcd.: C, 46.64; H, 3.91; Cl, 9.83%.)

TABLE 1

PHYSICAL PROPERTIES OF AMMONIA COMPLEXES OF DIMETHYLINDIUM CHLORIDE AND IODIDE

$(CH_3)_2InX \cdot n(NH_3)$		"Melting point"[a] (°C)	Dissociation pressure at 24° (cm)	Comments
X	n			
Cl	0.5	< 20	0.05	Sticky gum, probably dimethylindium chloride dissolved in the 1 : 1 adduct
Cl	1	46–54	0.05	Colorless crystals, soluble in ether
Cl	2	37–55	2.7	White powder; infrared spectrum similar to that of 1 : 1 adduct
Cl	3	42–73	3–5	Bulky white powder; soluble in large excess of ammonia; dissociates under nitrogen
I	1	< 20	0.00	Clear colorless liquid; soluble in ether
I	2	87–115	0.1	White powder; scarcely soluble in ether or nitromethane; relatively stable under nitrogen
I	3	100–119	12–15	Bulky white powder; soluble in ammonia; readily dissociates under nitrogen

[a] These derivatives appeared to soften and liquefy over a wide temperature range.

(*b*). *Dimethylindium chloride 2,2'-bipyridine* formed a gummy precipitate when the reactants were mixed in ether solution. This crystallized upon concentration of the solution and trituration. The compound slowly melted over the range 109–115°. (Found: C, 44.28; H, 4.32. $C_{12}H_{14}ClInN_2$ calcd.: C, 42.84; H, 4.19%.) These data could not be improved after several recrystallizations and hence solvent is apparently retained. An attempt to prepare this compound from methanol solution yielded some methylindium dichloride bipyridine.

(*c*). *Dimethylindium iodide 2,2'-bipyridine* was isolated from a methanol solution of the iodide and bipyridine, following evaporation of the solvent *in vacuo*. The light yellow compound was recrystallized from a chloroform/toluene mixture. It was also prepared fom an ethereal solution of the two reactants, yielding a light yellow-green precipitate. Melting point 122–125°. (Found: C, 33.63; H, 3.42. $C_{12}H_{14}IInN_2$ calcd.: C, 33.68; H, 3.30%.)

(*d*). *Dimethylindium chloride ethylenediamine* was prepared by mixing dimethylindium chloride in slight excess with ethylenediamine in methanol solution. The compound was recrystallized from methanol/chloroform. It was also recovered from concentrated methanol solution by successive treatment with petroleum ether causing precipitation of the complex. The compound began to melt and decompose in the range 135–145°. (Found: C, 19.92; H, 5.44; Cl, 14.92. $C_4H_{14}ClInN_2$ calcd.: C, 19.99; H, 5.87; Cl, 14.75%.) An unidentified byproduct of low solubility in methanol/chloroform was produced during recrystallization. A slight excess of ethylenediamine resulted in a different product, likely a solvate, which had additional absorptions in the infrared spectrum compared to the spectrum of the 1 : 1 adduct. Typical analyses for this product were: C, 21.07; H, 6.17; Cl, 13.35, 14.38, 12.78, 15.86%. This complex was also obtained by adding ethylenediamine to an ether solution of dimethylindium chloride, causing precipitation of a white solid.

(*e*). *Dimethylindium iodide ethylenediamine* was prepared likewise, although purification was again difficult due to the formation of a solvate. The complex softened and melted with decomposition in the range 172–184°. (Found: C, 16.77, 15.91; H, 5.24, 4.94. $C_4H_{14}IInN_2$ calcd.: C, 14.48; H, 4.25%.) The data suggest that excess ethylenediamine could not be satisfactorily removed.

Other derivatives

(*a*). *Dimethylindium trifluoroacetate* was prepared from trimethylindium and trifluoroacetic acid in ether solution. It is soluble in warm ether but forms needle-like crystals when a solution is concentrated and cooled. It sublimes rapidly at 100° *in vacuo*. Melting point 220–222°. (Found: C, 18.98; H, 2.33; F, 22.05. $C_4H_6F_3InO_2$ calcd.: C, 18.83; H, 2.34; F, 22.10%.)

(*b*). *Methylindium oxide* is the final product of the decomposition of trimethylindium in ether solution when exposed to moist air. It is an involatile, insoluble white powder which may be decomposed by dilute mineral acids. The compound decomposed slightly at 255° but did not melt. (Found: C, 8.05; H, 1.85. CH_3InO calcd.: C, 8.23; H, 2.07%.)

Organoindium anions

(*a*). *Lithium tetramethylindate*(III) was synthesized by condensing trimethylindium on to methyllithium in ether. The compound, a white solid, is very sensitive to oxidation and hydrolysis, and this may explain the poor analyses. (Found: C, 25.07; H, 6.40. $C_4H_{12}InLi$ calcd.: C, 26.42; H, 6.65%.)

(*b*). *Tetraphenylarsonium dimethylindium dichloride* slowly crystallized when an ether/chloroform solution of tetraphenylarsonium chloride and dimethylindium chloride was concentrated. Melting point 148–152°. (Found: C, 51.81; H, 4.55; Cl, 11.88. $C_{26}H_{26}AsCl_2In$ calcd.: C, 52.13; H, 4.37; Cl, 11.83%.)

(*c*). *Tetraethylammonium dimethylindium dichloride* was similarly prepared from methanol solution. It precipitated as a white solid upon addition of ether. In cold ether it is a white solid, but on warming in ether it becomes a white gummy substance. The compound softened and melted over the range 41–62°. (Found: C, 32.74, 32.78; H, 7.39, 7.23; Cl, 21.56. $C_{10}H_{26}Cl_2InN$ calcd.: C, 34.71; H, 7.57; Cl, 20.49%.) Repeated recrystallizations did not lead to better analytical data.

Methylindium dichlorides and derivatives

Methylindium dichloride was prepared by two routes, (*a*) and (*b*).

(*a*). Trimethylindium in ether and two equivalents of anhydrous hydrogen chloride were sealed in a Carius tube and stored for two days. Ether and methane were removed *in vacuo* leaving a white solid after extensive pumping and heating to 80° to remove the last of the ether. This solid was extracted with hot toluene to isolate the compound.

(*b*). Indium trichloride and dimethylindium chloride were mixed in a 1:1 molar ratio in ether and stored for a day. The trichloride slowly dissolved, and methylindium dichloride was formed quantitatively. Melting point 165°. (Found: C, 6.06; H, 1.91, 2.45; Cl, 34.38. CH_3Cl_2In Calcd.: C, 5.98; H, 1.51; Cl, 35.32%.)

(c). Methylindium dichloride 2,2′-bipyridine was obtained from the dichloride and 2,2′-bipyridine in ether solution. It precipitated as a fine white powder. The compound was also obtained from dimethylindium chloride (0.68 g, 3.8 mmoles) and bipyridine (0.30 g, 1.9 mmoles) in methanol solution. It slowly precipitated as white, needle-like crystals (0.31 g, 0.8 mmoles). It started to melt at 197° and decomposed about 224°. (Found: C, 36.90, 37.02; H, 3.12, 3.43; Cl, 19.81. $C_{11}H_{11}Cl_2InN_2$ calcd.: C, 37.02; H, 3.11; Cl, 19.86%.)

(*d*). Methylindium dichloride-2,2′, 2″-terpyridine precipitated as a fine yellow powder from an ether solution of the dichloride and 2,2′,2″-terpyridine. It was recrystallized from methanol. The compound did not melt below 260°. (Found: C, 43.43; H, 3.48; Cl, 15.97. $C_{16}H_{14}Cl_2InN_3$ calcd.: C, 44.28; H, 3.25; Cl, 16.37%.)

(*e*). Methylindium dichloride bis(pyridine) was synthesized from methylindium dichloride and excess pyridine in ether solution. It was recrystallized from ether. This derivative is much more soluble in ether than indium trichloride tris(pyridine). It softened at 75°, and turned to a cloudy gum by 116°. (Found: C, 37.30; H, 4.24; Cl, 19.85. $C_{11}H_{13}ClInN_2$ calcd.: C, 36.81; H, 3.65; Cl, 19.76%.)

DISCUSSION

In an extension of the previously described preparation of adducts of dimethylindium halides with pyridine and triphenylphosphine, similar adducts of dimethylindium(III) chloride with triphenylphosphine oxide and triphenylarsine oxide have now been obtained. These are monomeric in nitromethane solution, and the conductivity of the triphenylphosphine oxide adduct in nitromethane (molar conductance at a concentration of 1.59×10^{-3} *M*, 7.9) suggests that it is only slightly ionized. The conductivity of the triphenylarsine oxide adduct is somewhat greater (molar conductance at 1.96×10^{-3} *M*, 13.6) so that dissociation must be a little more extensive. The infrared spectra of these adducts show bands at 1145 cm^{-1} attributable to coordinated triphenylphosphine oxide[7] [ν(P=O)], and at 878 and 860 cm^{-1} assigned to coordinated triphenylarsine oxide[8], as well as ligand absorptions in the same region (475–540 cm^{-1}) as the In–C stretching vibrations.

The behavior of the dimethylindium halides as Lewis acids was further demonstrated by the ready dissolution in coordinating solvents such as diethyl ether, acetonitrile and tetrahydrofuran, the process of dissolution being noticeably exothermic in the latter solvent.

The formation of ammonia adducts of the dimethylindium halides was best studied tensimetrically (Fig. 1 and Table 1). The results show that the chloride and iodide form 1:1, 1:2, and 1:3 adducts with ammonia, with the 1:2 adduct of the chloride giving only a small break in the tensimetric titration curve. Under nitrogen, the monoammines are relatively stable but the chloride diammine and both triammines dissociate under nitrogen. All ammonia could be removed from all of the complexes by prolonged pumping *in vacuo*. The infrared spectra of the adducts, which exhibited differences between the 1:1, 1:2, and 1:3 complexes, showed peaks which could be assigned to coordinated ammonia[9–11]. However, it was not possible to decide unambiguously whether or not the ammino group $-NH_2$, or the NH_4^+ ion, were also present. The 1:1 adducts are probably neutral, tetrahedral complexes similar to the pyridine adducts already described, while the 1:2 adducts could be neutral, five-coordinate species or ionic, $NH_4^+[(CH_3)_2InCl(NH_2)]^-$ or $[(CH_3)_2In(NH_3)_2]^+Cl^-$ Although the former structure was suggested by Coates[12] for the analogous dimethylgallium chloride diammoniate, Shriver and Parry[13] have since presented evidence that the latter structure is correct.

Compounds of the type $(CH_3)_2InX(AA)$, where X is a halogen and AA is a neutral bidentate ligand, have also been synthesized. Data on the new compounds are given in Table 2. The molecular weight data indicate that in nitromethane solution these compounds are monomers, although it is interesting that in benzene solution the dimethylindium chloride bipyridine complex shows a tendency to associate with increasing concentration. Since normal 1 : 1 electrolytes such as tetraphenylarsonium chloride have conductance values of 70–80 mho·cm²·mole⁻¹ in nitromethane, the value of 6 mho·cm²·mole⁻¹ for dimethylindium chloride 1,10-phenanthroline strongly suggests that it must be an essentially un-ionized, neutral species. Hence, a neutral, five-coordinate structure is the most reasonable. Similarly, the bipyridine derivatives of dimethylindium chloride and iodide are expected to be five-coordinate monomers. In view of their slightly higher conductances, they must be ionizing to a greater degree than the phenanthroline compound. The infrared spectra show only that absorptions assignable to the ligands agree with those reported elsewhere[14] for compounds in which the ligands are bidentate. For dimethylindium chloride bipyridine and 1,10-phenanthroline, infrared absorptions around 525 and 480 cm^{-1} can be assigned to the In–C asymmetric and symmetric stretching vibrations respectively, so that the C–In–C moiety must be bent. Interestingly, the spectrum of the solid dimethylindium iodide bipyridine complex shows only a very weak absorption at 480 cm^{-1}, although in chloroform solution the same compound shows a symmetric stretching absorption of medium intensity comparable to that observed for the chloride analogue. It seems likely that in the solid iodide complex, crystal packing factors may affect the shape of the $(CH_3)_2In$ group.

TABLE 2

DIMETHYLINDIUM HALIDE BIDENTATE LIGAND DERIVATIVES

$(CH_3)_2In{\cdot}(AA)$		Molecular weight			Conductance		Infrared (cm^{-1})[d]		
X	AA	Calcd.	Found	Concn. $M \times 10^2$	Λ_m (mho cm² ·mole⁻¹)	Concn. $M \times 10^3$	In–CH_3 rock	ν_{asym}(In–C)	ν_{sym}(In–C)
Cl	phen	360.5	366	1.85[a]	6.2	0.95[a]	Obscured	522 s	483 m
			352	3.12[a]	5.8	2.27[a]			
Cl	bipy	336.5	307	3.27[a]	12.4	1.78[a]	705 vs br	529 s	481 m
			315	5.61[a]	11.7	2.33[a]			
			337	0.74[b]	51.0	2.50[c]		523 s[e]	481 m[e]
			350	1.39[b]					
			407	2.17[b]					
I	bipy	427.9	418	2.31[a]	28.2	1.09[a]	Obscured	539 s	480 vw
			431	0.97[b]	25.3	1.74[a]		525 s[e]	478 m[e]
Cl	en	240.4	*ca.* 295	0.56[a]	16.4	1.51[a]	720 vs br	515 s br	481 m br
I	en	331.8			90.7	1.35[c]	722 vs br	520 s br	491 m br

[a] In CH_3NO_2. [b] In C_6H_6. [c] In CH_3OH. [d] s = strong; m = medium; w = weak; br = broad; v = very. [e] In chloroform.

Solvates with a ligand/dimethylindium halide ratio slightly exceeding 1 : 1 precipitated readily from ether solutions of dimethylindium iodide or chloride and ethylenediamine. Recrystallization from methanol gave the 1 : 1 adducts in low yield after removal of unidentified slightly soluble by-products. The molecular weight and conductance data of Table 2 were obtained with dilute solutions, because of solubility problems, and hence may not be completely reliable.

Close comparisons cannot always be made of these $(CH_3)_2InX(AA)$ compounds with related derivatives of the other Group III metals. Dimethylthallium iodide 1,10-phenanthroline has been synthesized[15], but its structure is unknown. Dimethylthallium perchlorate 1,10-phenanthroline[16] and its bipyridine analogue[17] are known, and the structural study[18] of the former shows the effective coordination of thallium to be six. However, the infrared spectrum[15,16] and also the long thallium–oxygen distances[18] show that the interaction between the $(CH_3)_2Tl$ and ClO_4 groups is weak. Certainly these do not appear to be particularly similar to the $(CH_3)_2InX(AA)$ derivatives. In terms of stereochemistry, the latter most closely resemble the bis(pentafluorophenyl)thallium halides which give[19] derivatives $(C_6F_5)_2TlX$(1,10-phen or bipy), where X is Cl^-, Br^-, NO_3^-, or CF_3COO^-, which were assigned five-coordinate structures.

For the ethylenediamine complexes, full comparison is also not possible. Dimethylthallium perchlorate ethylenediamine has been prepared[17] but its structure is not known. Dimethylthallium halides do not form complexes with ethylenediamine, but may be recrystallized from this solvent. This inertness is presumably associated with the stability of the octahedral, halogen-bridged structures of these halides[20]. Dimethylgallium chloride ethylenediamine, on the basis of molecular weight measurements, is thought[13] to be ionic with four-coordinate gallium, $[(CH_3)_2Ga(en)]^+Cl^-$.

During the course of this work, increased interest in the chemistry of indium trihalide derivatives[21] suggested that a monoalkylindium dihalide should be synthesized in order to complete our study of R_nInX_{3-n} compounds where $n = 1$–3. The analogous dimeric methylgallium dichloride has been reported[5] but there has been considerable controversy over the existence of the methylthallium(III) moiety. Hart and Ingold[2], and Sarrach[22] were unable to isolate alkylthallium dihalides as reported by Melinkov and Gratscheva[23]. Very recently, Kurosawa and Okawara have described[3,4] the isolation and characterization of methylthallium diacetate.

TABLE 3

PROPERTIES OF METHYLINDIUM DICHLORIDE AND DERIVATIVES

Compound	Molecular weight			Conductance		Infrared (cm^{-1})[b]	
	Calcd.	Found	Concn. $M \times 10^2$	Λ_m (mho·cm·mole^{-1})	Concn. $M \times 10^3$	In–CH_3 rock	ν(In–C)
CH_3InCl_2	200.8	196	3.87[a]	13.3	3.18[a]	745 s, br 720 sh	523 m
CH_3InCl_2·bipy	356.9	375	1.38[a]	26.4	1.54[a]	Obscured	496 m, 508 vw?
CH_3InCl_2·2 py	358.9					720 sh (obscured)	512 m
CH_3InCl_2·terpy	434.0					Obscured	522 m, 510[c] w sh

[a] InCH_3NO_2. [b] s = strong; m = medium; w = weak; vw = very weak; br = broad; sh = shoulder. [c] Probably due to ligand.

Methylindium dichloride was prepared from trimethylindium and two equivalents of hydrogen chloride, or by the exchange reaction between dimethylindium chloride and indium trichloride. The dichloride appears to be monomeric in nitromethane solution (Table 3) although the conductivity indicates slight ionization.

A number of addition compounds of methylindium dichloride were synthesized. The first was obtained during an attempted preparation of dimethylindium chloride bipyridine, when the reaction of dimethylindium chloride with bipyridine in methanol caused the slow precipitation of white, crystalline methylindium dichloride bipyridine. Rearrangement has obviously occurred but the reaction 2 $(CH_3)_2InCl \rightleftarrows CH_3InCl_2 + (CH_3)_3In$ is improbable. In methanol solution, the trimethylindium should solvolyze rapidly to dimethylindium methoxide. However, such rearrangement and solvolysis has not been observed in many other preparations under similar conditions. Therefore, the exchange process probably takes place later in the reaction sequence, *e.g.* 2 $(CH_3)_2InCl(bipy) \rightleftarrows (CH_3)InCl_2(bipy)\downarrow + (CH_3)_3In(bipy)$.

Methylindium dichloride bipyridine could also be obtained directly from the dichloride and bipyridine, and likewise a pyridine adduct, methylindium dichloride bis(pyridine), and methylindium dichloride terpyridine have been obtained (Table 3).

To summarize the Lewis acid behavior of the methylindium chloride series; trimethylindium forms 1:1 adducts with monodentate ligands; dimethylindium chloride forms 1:1 complexes with both monodentate and bidentate ligands; methylindium dichloride forms a 1:2 compound with pyridine, and 1:1 complexes with a bidentate and a tridentate ligand; indium trichloride yields both 1:2 and 1:3 complexes with monodentate Lewis bases[21]. Certainly, the number of coordinated Lewis base molecules appears to increase with the number of halogen atoms, and apparently the coordination of indium in these derivatives also increases from four to five to six. The series $(CH_3)_nInCl_{3-n}$ thus exhibits chemical and stereochemical behavior similar to that observed for aluminum[24] or tin[25].

Two organoindium anions have been synthesized, namely $[In(CH_3)_4]^-$ obtained as its lithium salt, and $[(CH_3)_2InCl_2]^-$ obtained as its tetraethylammonium and tetraphenylarsonium salts. These are white crystalline compounds, the first being

TABLE 4

PROPERTIES OF MISCELLANEOUS DERIVATIVES

Compound	Molecular weight			Conductance		Infrared (cm^{-1})^b		
	Calcd.	Found	Concn. $M \times 10^2$	Λ_m (mho·cm^2·mole^{-1})	Concn. $M \times 10^3$	In–CH$_3$ rock	ν_{asym}(In–C)	ν_{sym}(In–C)
$[(C_2H_5)_4N]^+$-$[(CH_3)_2InCl_2]^-$	346 0	201	3.72^a	83 9	2 37^a	715 vs br	512 s	483 m
		201	7.23^a					465 vw
$[(C_6H_5)_4As]^+$-$[(CH_3)_2InCl_2]^-$	599.0	341	5.75^a	71.0	2.25^a	Obscured	512 m	489 w
							511 m^c	470^{d}s
$(C_6H_5)_4AsCl$	418 8	202	5.95^a	73.3	3 82^a			
$(C_2H_5)_4NCl$	165.7	105	11.78^a	82.9	5.00^a			
$(CH_3)_2InOC$-$(O)CF_3$	257 9	276	3.24^a	2.1	1 62^a	734 vs br	564 s	518 m
								497 w

[a] In CH_3NO_2 [b] s = strong; m = medium; w = weak; v = very; br = broad, sh = shoulder. [c] In chloroform. [d] Probably ligand absorptions.

particularly sensitive to oxidation and hydrolysis. Lithium tetramethylindate(III) is soluble in ether and slightly soluble in chloroform, while the $[(CH_3)_2InCl_2]^-$ salts are insoluble in ether but very soluble in methanol and chloroform. In nitromethane, the latter compounds are highly conducting and probably behave as 1 : 1 electrolytes (Table 4).

Lithium tetramethylindate extends the series of tetraorgano Group III metal anions from boron through to indium. The $[(CH_3)_2InCl_2]^-$ salts are analogous to organothallium derivatives, *e.g.* $[(CH_3)_4N]^+[(C_6H_5)TlCl_3]^-$ and $[(CH_3)_4N]_2^+$-$[C_6H_5TlCl_4]^{2-}$ and $[Q]^+[(C_6F_5)_2TlX_2]^-$ where Q = tetraphenylarsonium or tetraethylammonium, and X is chloride or bromide[26]. Again, a close relationship between dimethylindium derivatives and (pentafluorophenyl)thallium compounds is apparent.

Various dimethylindium(III) derivatives of anions other than halides have also been studied. Dimethylindium acetate has been previously described[1] and we have now obtained the trifluoroacetate. Both are sublimable, white crystalline solids, non-conducting in nitromethane. The trifluoroacetate is monomeric in this solvent, and soluble in warm ether. The carboxyl absorption in the infrared spectrum of the trifluoroacetate is at 1620 cm^{-1}, as compared with 1780 cm^{-1} for trifluoroacetic acid, suggesting strong interaction of the carboxyl group. Hence an ionic formulation $(CH_3)_2In^+(OCOCH_3^-$ or $OCOCF_3^-)$ is improbable.

Finally, it should be noted that the decomposition of trimethylindium by moist air produces methylindium oxide, an insoluble white powder. It appeared that $(CH_3)_2InOH$ may have been produced initially in the hydrolysis reaction but within minutes this must decompose to methylindium oxide. However, a more detailed study is necessary to determine precisely the steps involved in this conversion.

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