SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE ARYLINDIUM HALIDES, $(C_6H_5)_n InX_{3-n}$ (X = Cl, Br, I)

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Summary

The complete series of arylindium halides, $(C_6H_5)_n InX_{3-n}$ (n = 1, 2; X = Cl, Br, I), have been prepared using previously unreported oxidative arylation of the indium(I) halide with various mercurials, and also several published routes. Infrared and Raman spectroscopy, ^{115}In nuclear quadrupole resonance spectroscopy, mass spectrometry and conductivity data were gathered for the purpose of structural characterization in the solid state. The compounds of stoichiometry $(C_6H_5)_2 InX$ (X = Cl, Br, I) are best described as adopting a polymeric lattice with multiply-associated halogen atoms linking together nearly linear $(C_6H_5)_2 In$ groups. The compounds $C_6H_5 InX_2$ also adopt the polymeric lattice when X = Cl, Br, but $C_6H_5 InI_2$ is more consistent with the associated ionic formulation, $(C_6H_5)_2 In^+ InI_4^-$. The dioxanate complexes, $(C_6H_5)_n InCl_{3-n} \cdot$ dioxane (n = 0-3), do not contain multiply-associated chlorine atoms and aid in the characterization of the base-free compounds. The polymeric structures of the arylindium halides are more comparable to the structures of the arylthallium halides than to the arylgallium halides.

Introduction

Interest in aluminum and thallium organometallic compounds has been extensive [1,2] and is fueled by synthetic and catalytic applications in a number of cases. By comparison the other Group IIIB metals, gallium and indium have been far less extensively studied. For all of these metals the majority of the work deals with the alkyl derivatives rather than the aryl compounds. In the case of the arylindium halides, past synthetic efforts have included reaction of the triaryl compound with molecular halogens [3,4] and the Grignard reaction with InX_3 [5-8]. However, some conflicts exist as to the properties of the resulting compounds [3,4] because CO_2 was used as an atmosphere and the melting points were not determined in an air and moisture free environment [3]

Structural variations among the organo halides from boron to thallium are

pronounced as a result of the various means by which the Group IIIB elements react to attain a fully coordinated valence shell. For example, the aryl-aluminum and -gallium halides seem to adopt a dimeric structure [9,10] in which the halogen atoms bridge, while the arylthallium halides become polymeric with multiply associated halogen atoms [2]. It is not known what structures the arylindium halides adopt and only in the case of $C_6F_5InCl_2 \cdot$dioxane has any structure been proposed in the solid state [11]. There does appear to be considerable structural sensitivity to the nature of both the organic group and the halide in other organoindium halides, however. In benzene solution bis(α-naphthyl)indium bromide is monomeric [5], whereas $(C_6F_5)_2InBr$ [7], $(CH_3)_2InCl$ [12] and $(CH_3)_2InI$ [12] are dimeric. Based on the nuclear quadrupole resonance spectra, $(CH_3CH_2)_2InBr$ [13] and $(CH_3)_2InX$ (X = F, Cl, Br, I) [14] behave as highly associated compounds in the solid state, but CH_3InBr_2 and $CH_3CH_2InI_2$ appear to be dimeric [14]. CH_3InI_2 is unusual in that it adopts the salt-like formulation, $(CH_3)_2In^+InI_4^-$ [14-17]. In light of these structural variations, we have examined by IR, Raman and [115]In nuclear quadrupole resonance spectroscopy, mass spectrometry and solution conductance, the aryl series of indium halides for comparison and classification into the overall structural scheme of the organo-Group IIIB halides. A previously unreported synthetic route to these compounds involving oxidative arylation reactions of the indium(I) halides with organomercurials is also developed.

Experimental

Solvents and materials

Hydrocarbons were refluxed for one hour over P_2O_5 while being degassed with N_2 and then distilled. Ethers were refluxed over $LiAlH_4$ while being degassed with N_2 and then distilled. Metal halides were prepared immediately before use so as to insure their purity.

Syntheses

The reactivity of these compounds toward air and moisture necessitates Schlenk tube and dry-box work for manipulations. All reactions were run under an N_2 atmosphere. Table 1 compiles the compounds prepared in this work along with their melting points and the class of reaction used. Indium-(I) and -(III) halides were prepared according to the methods described in Brauer [18]. The mercurials were prepared as described previously [19]. Diphenylcadmium was synthesized by the Grignard method from $CdCl_2$ as suggested by Gilman and Nelson [20].

(1). Reaction of indium(I) halide with phenylmercuric halide. Into a 50 ml Schlenk flask were placed 0.01 mol of indium(I) halide and 0.01 mol of phenylmercuric halide. Diethyl ether (30 ml) was added and the mixture refluxed with stirring for 24 h. The reaction mixture rapidly acquired a grey color resulting from the formation of mercury metal and little additional change occurred after the first eight hours. The reaction mixture was cooled, filtered, and the resulting colorless filtrate evaporated to dryness under reduced pressure. Near the end of the evaporation, colorless crystals of the arylindium dihalide·etherate formed which melted if allowed to warm to room temperature. The product was heated

TABLE 1

COMPOUNDS PREPARED AND PERTINENT SYNTHETIC INFORMATION

Compound	Reaction	Recrystallizing solvent	Yield (%)	M.p. (°C)	Lit. m.p. (°C)
$C_6H_5InCl_2$	1, 3, 4	Dioxane	81-90	233-235	
$C_6H_5InBr_2$	1, 3, 4	o-Xylene	71-96	203-205	>300[a]
$C_6H_5InI_2$	3	Benzene	88	120-122	>300[a]
$(C_6H_5)_2InCl$	2, 4	Toluene	64-66	268-270	
$(C_6H_5)_2InBr$	2, 4	Toluene	77-84	255-257	>300[a,b]
$(C_6H_5)_2InI$	2	Cyclohexane	92	187-189	>300[a]
$(4-FC_6H_4)_2InBr$	2	Benzene	73	220-222	
$(4-FC_6H_4)InBr_2$	3	Toluene	82	190-192	
$(4-CH_3C_6H_4)_2InBr$	2	Benzene	95	225-227	
$(4-CH_3C_6H_4)_2InBr_2$	3	Benzene	94	194-196	
$C_6H_5InCl_2 \cdot dioxane$				205-207	
$(C_6H_5)_2InCl \cdot dioxane$				258-260	
$(C_6H_5)_3In \cdot dioxane$				209-211	

[a]Ref. 3. [b]Ref. 5.

to 70°C under vacuum for two hours to remove the remaining ether, and then boiled with the solvent listed in Table 1. Upon filtering and cooling crystals of the arylindium dihalide appeared. These were washed with hexane and dried.

(2). Reaction of indium(I) halide with diarylmercury. Indium(I) halide (0.02 mol) and 0.02 mol of diarylmercury were refluxed in 50 ml of diethyl ether and purified as described for reaction 1.

(3). Reaction of indium(I) halide with diarylmercury and mercury(II) halide. Indium(I) halide (0.02 mol), 0.01 mol of diarylmercury and 0.01 mol of mercury(II) halide were refluxed in 50 ml of diethyl ether and purified in the same manner as described for reaction 1.

(4). Reaction of indium metal with diarylmercury and mercury(II) halide. A mixture of 0.033 mol of indium metal, 0.033 mol of diarylmercury and 0.0165 mol of mercury(II) halide in 100 ml of diethyl ether were refluxed for 24 h and purified as described for reaction 1.

(5). Redistribution reaction of triphenylindium and indium(III) bromide: synthesis of diphenylindium bromide. A mixture of 2.00 g (0.0578 mol) of triphenylindium and 1.02 g (0.0289 mol) of indium(III) bromide was placed in a 50 ml Schlenk flask with 30 ml of benzene. After refluxing for 8 h the solution was filtered while hot and allowed to cool, whereupon diphenylindium bromide crystallized. The chunky, colorless crystals were washed with hexane and recrystallized.

This same reaction, when conducted with no solvent at 220°C gave only biphenyl and indium(I) bromide, the thermal decomposition products of diphenylindium bromide.

Phenylindium diiodide. A mixture of 10.0 g (0.0289 mol) of triphenylindium, 50 ml of benzene and 14.7 g (0.0578 mol) of iodine was placed in a 100 ml Schlenk flask. The solution was stirred for ten minutes and the solvent removed under reduced pressure at 40°C. The addition of 40 ml of hexane produced a yellow oil which gradually solidified into light yellow powder. This

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precipitate was filtered and then warmed with 20 ml of benzene until dissolved. Care was taken not to melt the product by heating excessively. After filtering, large, bright yellow crystals of phenylindium diiodide precipitated.

Dioxane adducts. Approximately one gram of the arylindium chloride was mixed with one to two ml of hexane. 1,4-Dioxane was added dropwise until complete dissolution was achieved. The solution was warmed, additional hexane added, and then allowed too cool until crystalline product appeared.

Weighed samples of each adduct were decomposed by heating in vacuo at 100°C for several hours to determine their stoichiometry. With the exception of indium trichloride-dioxanate, all were found to be 1/1 adducts. Indium trichloride-dioxanate was determined to be a 1/2 adduct.

Analyses

Because of the extreme air and moisture sensitivity of the organometallics synthesized here, the facilities available for elemental analyses proved unreliable in many cases. For this reason, high resolution mass spectrometry and the achievement of sharp constant melting points on multiply recrystallized samples were extensively relied upon for evidence of synthesis and purity. For some compounds an exact mass for the parent ion was established. Each spectrum was carefully examined for impurities, particularly in the mercurial region, and found to be uncontaminated. Carbon and hydrogen analyses were adequate for a number of compounds, although the hydrogen analyses are not greatly valuable because hydrogen represents only a small percentage of the total sample mass. Anal. Found: C, 47.69; H, 3.32. $(C_6H_5)_2InCl$ calcd.: C, 47.34; H, 3.31%. Found: C, 19.10; H, 1.23. $(4\text{-}F\text{-}C_6H_4)InBr_2$ calcd.: C, 19.49; H, 1.09%. Found: C, 41.39; H, 3.03. $(C_6H_5)_2InBr$ calcd.: C, 41.31; H, 2.89%. Found: C, 36.72; H, 2.81. $(C_6H_5)_2InI$ calcd.: C, 36.40; H, 2.55%. Found: C, 16.10; H, 1.42. $C_6H_5InI_2$ calcd.: C, 16.17; H, 1.31%.

Vibrational spectra

Infrared spectra were measured on a Perkin—Elmer Model 180 double-beam grating spectrophotometer between 1200-180 cm^{-1}. Samples were run as Nujol mulls suspended between CsI plates and were prepared in a dry-box. Raman spectra were obtained on compounds sealed inside Kimex capillary tubes using a Spex Ramalog 1401 double-monochrometer spectrometer. A CRL Model 54 Ar$^+$ laser was used for excitation and operated at 150 mW power and 4880 Å. Frequency errors are estimated to be about ±2 cm^{-1}.

Mass spectrometry

Electron impact mass spectra were obtained with a CEC (DuPont) 21-110B mass spectrometer. Low resolution spectra were taken at 70 eV ionizing voltage, 6 kV accelerating voltage, and a resolution of ~1000 (10% valley). Methane chemical ionization spectra were obtained with the CEC spectrometer previously modified for high pressure operation [21,22]. The reagent gas pressure was typically 0.7-1.0 Torr, the accelerating voltage 6 kV, the ionizing voltage 400-600 eV, and the repeller voltage zero volts. The samples were introduced into the source with a Mass Spectrometer Accessories all glass direct insertion probe which has an independent temperature monitoring and control system. With

this probe the sample temperature is independent of the source block temperature which was typically 200-300°C. Probe temperature were those necessary for sample volatilization.
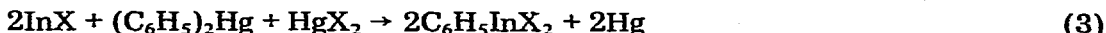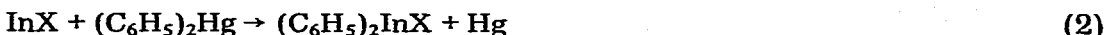
NQR spectra

The nuclear quadrupole resonance data were obtained with a spectrometer and frequency measurement system described before [23]. All spectra were recorded at room temperature and the errors in the frequency measurement are mostly those of improperly selecting the center line of the resonance multiplet. However, for ^{115}In, which is an $I = 9/2$ nucleus, four signals corresponding to $\nu_1 = \pm1/2 \rightarrow \pm3/2$, $\nu_2 = \pm3/2 \rightarrow \pm5/2$, $\nu_3 = \pm5/2 \rightarrow \pm7/2$, and $\nu_4 = \pm7/2 \rightarrow \pm9/2$ can be observed. The two unknowns of interest in NQR spectroscopy are the nuclear quadrupole coupling constant, e^2Qq/h, in MHz and the electric field gradient asymmetry parameter, η. These two unknowns can be redundantly solved by using the four known frequencies [24] and yield several independent checks as to whether or not the center line of each resonance multiplet was correctly chosen. The error in coupling constant was established to be ±0.08 MHz and the asymmetry parameter is ±0.001.

Conductivity measurements

A Beckman 16B2 conductivity bridge operating with a cell temperature of 25.0°C was used to determine the conductivity of several compounds in nitrobenzene. The range of conductivity for 1/1 electrolytes in nitrobenzene is 20-30 ohm^{-1} cm^{-2} mol^{-1} [25].

Syntheses and properties

Indium(I) halides do not insert directly into aryl halide bonds [16], but do insert into the alkyl halides [15,16]. We find that oxidative arylation does occur with the indium(I) halides and the aryl mercurials in a manner similar to the germanium(II) [26] and tin(II) [27] halides, although the tin reaction produces some redistribution products as well [27]. For example, the following reactions (eqns. 1-3) in ether successfully produce the arylindium halides:

$$InX + C_6H_5HgX \rightarrow C_6H_5InX_2 + Hg \tag{1}$$

$$InX + (C_6H_5)_2Hg \rightarrow (C_6H_5)_2InX + Hg \tag{2}$$

$$2InX + (C_6H_5)_2Hg + HgX_2 \rightarrow 2C_6H_5InX_2 + 2Hg \tag{3}$$

Elemental indium also produces the same compounds when a mixture of the diarylmercurial and mercury(II) halide is used (eqn. 4). Although usually run for

$$2In + n(C_6H_5)_2Hg + (3 - n)HgX_2 \rightarrow 2(C_6H_5)_nInX_{3-n} + 3Hg \ (n = 1,2) \tag{4}$$

24 h to insure completeness, the reactions often appeared to be complete after a few hours. Qualitatively, the rate as a function of X judged by mercury metal formation is Cl > Br > I. The rate of formation of the arylindium dihalides is faster than that of the diarylindium halides. The reaction of InX with the mercurials is to be contrasted with the behavior of thallium in the analogous reac-

tion. For indium:

$$InX + (C_6H_5)_2Hg \rightarrow (C_6H_5)_2InX + Hg \tag{5}$$

but because of the instability of Tl(III), the reaction according to eqn. 6 is ob-

$$(C_6F_5)_2TlX + Hg \rightarrow (C_6F_5)_2Hg + TlX \tag{6}$$

served [28]. Redistribution of triarylindium and the indium trihalides was also used to produce a number of mixed arylindium halides:

$$n(C_6H_5)_3In + (3 - n)InX_3 \rightarrow 3(C_6H_5)_nInX_{3-n} \tag{7}$$

It proved easiest to prepare $C_6H_5InI_2$ by reaction of $(C_6H_5)_3In$ with I_2 because the mercurial route produced a yellow oil which was extremely difficult to purify. With the exception of $C_6H_5InI_2$, which is yellow, all of the arylindium halides are colorless, high melting, air and moisture sensitive compounds having low solubility in non-complexing solvents. The trend in solubilities is, however, Cl < Br < I and $C_6H_5InX_2$ < $(C_6H_5)_2InX$. In complexing solvents, such as ethers and ketones, the compounds are quite soluble but are, of course, somewhat different molecules in that they probably exist as donor-acceptor complexes.

The $(C_6H_5)_2InX$ (X = Cl, Br, I) and $C_6H_5InI_2$ decompose when held at their melting points to produce colors characteristic of the corresponding indium(I) halide. On further examination the decomposition products were found to be the indium(I) halide and biphenyl with some indium(III) halide also present in the case of $C_6H_5InI_2$.

Structural information

In Table 2 the low frequency IR and Raman frequencies are compiled. These data serve to determine whether the arylindium halides adopt the dimeric molecular structures characteristic of the organo-aluminum and -gallium halides or the polymeric lattice found for the organothallium halides. Vibrational data below 1200 cm^{-1} were obtained, but since only skeletal modes leading to structural information about the C—In—X framework were of interest, the modes above 700 cm^{-1} are not reported. In this lower range the only purely C—C mode routinely observed was the in-plane ring deformation [29] in the 610-630 cm^{-1} region. It is not included in Table 2 because it is unimportant to the discussion. A number of other phenyl modes involving some indium motion absorb in this region and these can be readily identified by comparing the spectra to other monosubstituted benzene systems [29-31]. In several instances the modes were confirmed by noting the frequency shift for the *para* substituted analogues.

$(C_6H_5)_2InX$

No pure indium—carbon motions exist in these compounds because of coupling with the C—C modes. Figure 1 shows the nature of the important modes involving indium and initial identification of these greatly simplifies the spectral interpretation. The symmetric in-plane stretch (Mode A) at 648-660 cm^{-1} in the Raman and IR is perhaps closest to an In—C stretching mode and deserves some comment. A mode at about the same frequency is observed in

TABLE 2

VIBRATIONAL SPECTRA OF ARYLINDIUM HALIDES AND RELATED COMPOUNDS[a]

Compound	Modes[b] (cm^{-1})					
	A	B	C	D	E	In—X[c]
$(C_6H_5)_2InCl$	648 vs[d]	445 vw	392 vw	205 s 209 m 220 mw	169 mw	184 mw
$(C_6H_5)_2InBr$	650 vs	438 vw	392 vw	204 m 212 s 220 m	169 s	159 m
$(C_6H_5)_2InI$	650 s	453 vw	394 vw	199 mw 211 s 217 mw	167 ms 177 mw	141 s
$C_6H_5InCl_2$[e]	654 w	435 s[f]				243 w
$C_6H_5InBr_2$	654 m	430 vw		210 vw	170 w	185 vs
$C_6H_5InI_2$	654 m[g]	439 vw		200 w	167 w	137 vs[g] 177 mw
$(4-FC_6H_4)InBr_2$	572 m	508 vw	304 w	223 vw 243 vw	207 vw	178 vs
$(4-CH_3C_6H_4)InBr_2$	576 w	478 w	396 w	229 w 240 w	208 w	178 ms
$(4-CH_3C_6H_4)_2InBr$	564 w	479 w		225 w 260 w	184 m	145 vs
$(C_6H_5)_2Cd$	645 s	433 vw	391 vw	197 s 202 s	167 s 175 s	
$(C_6H_5)_3In$	646 s	438 vw	387 vw 395 vw	205 vs 248 w 257 w	163 ms 178 ms	
$(C_6H_5)_3In \cdot C_4H_8O_2$	650 s	454 w		205 s	169 m	
$(C_6H_5)_2InCl \cdot C_4H_8O_2$[h]	651 s	457 w	400 w	199 s 223 m	180 w	251 s
$C_6H_5InCl_2 \cdot C_4H_8O_2$[h]	660 m	435 m[f]	402 w	200 m[f]	163 m	327 m 323 m[f]
$InCl_3 \cdot (C_4H_8O_2)_2$[h]						312 vs[f] 304 vs[f] 280 vs

[a] All frequencies are from the Raman spectra of powders unless otherwise indicated. [b] See Fig. 1. [c] Only in the case of the dioxanates is In—X proposed to be terminal. [d] Polarized in H_2O solution. [e] Sample undergoes some decomposition in laser beam. [f] IR frequency in Nujol mull. [g] Polarized in C_6H_6 solution. [h] Very strong bonds also appear at 138-141 cm^{-1}.

$(C_6H_5)_3In$ and has been assigned to this motion on the basis of a normal coordinate analysis [32]. The mode is considerably higher in frequency, however, than the relatively pure In—C modes of $(CH_3)_2InX$ which lie at ca. 500 cm^{-1} in the Raman and 550 cm^{-1} in the IR [12,15,16,33-35], and very much higher than the In—C modes in $(C_5H_5)_3In$ found [36] at 338 cm^{-1}. The spread of frequencies in these compounds is not unreasonable because the C_5H_5—In bond is likely to be rather weak, and coupling of the In—C motion with the C—C motion of the phenyl ring should greatly increase its frequency relative to $(CH_3)_2$-InX. Other In—C modes include the following: out-of-plane bending at 430-454 cm^{-1} (Mode B), which is weak in the Raman, but strong in the IR; in-plane stretching at 387-403 cm^{-1} (Mode C) which is weak in the Raman, but strong in
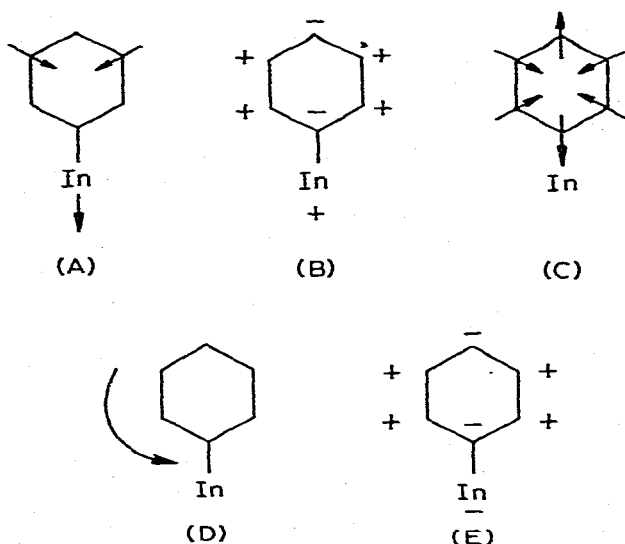
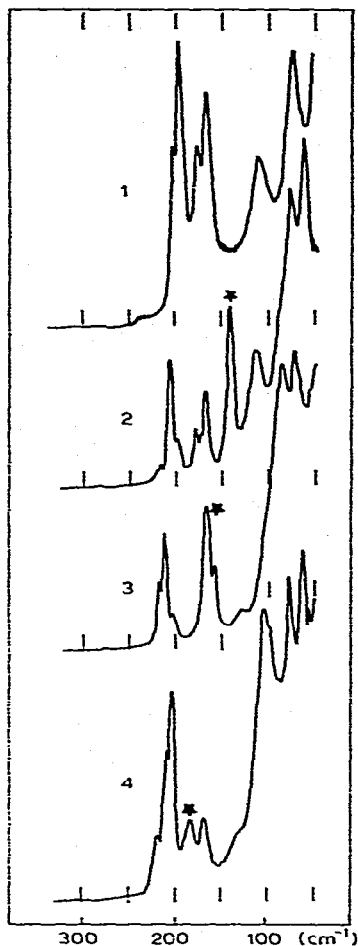Fig. 1. Relative carbon—metal motions in the low frequency region [30].

Fig. 2. Raman spectra of $(C_6H_5)_2Cd$ (1), $(C_6H_5)InI$ (2), $(C_6H_5)InBr$ (3), and $(C_6H_5)InCl$ (4). (Removal of the starred band which is associated with the halogen motion reveals that the $(C_6H_5)_2M$ group is very similar for all systems.)

the IR; in-plane ring rotation in the 200-250 cm^{-1} region (Mode D) which was often assigned to split modes particularly when more than one phenyl ring was present; and out-of-plane bending at 160-180 cm^{-1} (Mode E).

The only other low frequency modes found in these compounds show a distinct frequency progression as a function of the halogen. Fig. 2 shows the Raman spectra of $(C_6H_5)_2InX$, (X = Cl, Br, I) and $(C_6H_5)_2Cd$. The spectra are quite similar after the In—X modes at 184, 159 and 141 cm^{-1} for X = Cl, Br and I, respectively, are identified. For these three modes a progressive increase in intensity is noted which is consistent with the trend in bond polarizability of In—I > In—Br > In—Cl. The comparatively low frequency of these modes, however, strongly intimates that these compounds contain no "terminal" halogens. For example, "terminal" In—Cl modes in neutral complexes occur in the 290-

340 cm^{-1} region [37-39]. "Terminal" In—Br modes in neutral complexes appear to lie in the 190-240 cm^{-1} region [37,39], and "terminal" In—I modes of neutral complexes appear to lie in the 160-220 cm^{-1} region [37,39]. Bridging iodide motions have been assigned in the 140 cm^{-1} region [15,37] as have modes for InI_4^- [40] so the spectrum of $(C_6H_5)_2InI$ is less decisive than those of the chloride and bromide. The range of these frequencies is still good evidence for the existence of multiply associated halogen atoms in these compounds, however. Only one In—X mode is reported in Table 2 because modes below 120 cm^{-1} cannot be readily distinguished from those of the lattice and may be coupled in a complicated fashion in these polymeric-type lattices. The mode referred to here as In—X may actually be the strongly Raman active breathing mode of the polymeric framework:
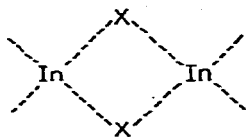
It should be mentioned that stretching modes for $InCl_3$ (279 R, 255 IR) [41, 42] and $InBr_3$ (180 IR, 171 R) [41,42] are proposed to result from highly polymeric lattices and are greater than or about equal to the In—X frequencies in the arylindium chloride and bromide compounds.

The ^{115}In NQR spectrum of $(C_6H_5)_2InCl$ gives further structural information and the data are shown in Table 3. The very large coupling constant for indium is consistent with the *trans* arrangement of aryl groups and the asymmetry parameter of 14-17% is also suggestive of an approximately axially symmetric site for indium, albeit somewhat distorted. $(CH_3)_2InCl$ [14], $(CH_3CH_2)_2InCl$ [13] and $(CH_3CH_2)_2InBr$ [13] have similar NQR parameters and also adopt this basic arrangement in the solid state. Ruled out by the large coupling constant and small asymmetry parameter is the dimeric geometry in which indium is tetrahedrally coordinated. From the NQR data, two crystallographically inequivalent formula units are clearly present in the unit cell of $(C_6H_5)_2InCl$. It is not surprising that many of the vibrational modes in Table 2 are split in light of this.

The mass spectra give additional supportive evidence of a polymeric crystal lattice. Since all $(C_6H_5)_2InX$ compounds gave similar spectra they will not be reproduced in total here. As a representative example, the 70 eV electron impact spectrum for $(C_6H_5)_2InBr$ at a probe temperature of 290°C contains the follow-

TABLE 3

NUCLEAR QUADRUPOLE RESONANCE DATA IN MHz FOR DIORGANOINDIUM CHLORIDES

	ν_1	ν_2	ν_3	ν_4	$e^2Qq/h(^{115}In)$	$\eta(^{115}In)$
$(C_6H_5)_2InCl^a$	54.28	90.95	139.10	185.87	1117.0	0.142
	58.00	91.17	140.40	187.80	1129.2	0.171
$(CH_3)_2InCl^b$	54.03	98.85	149.70		1200.16	0.096
$(CH_3CH_2)_2InCl^c$	52.90	92.45	142.13		1142.7	0.164

^{a}This work at 298 K. ^{b}Room temperature determination in Ref. 14. ^{c}77 K in Ref. 13.

$(C_6H_5)_2InBr^+$

$-Br$ $-HBr$ $-C_6H_5$

$(C_6H_5)_2In^+$ $(C_6H_5)_2In-1^+$ $C_6H_5InBr^+$

$-C_6H_5$

$C_6H_5In^+$
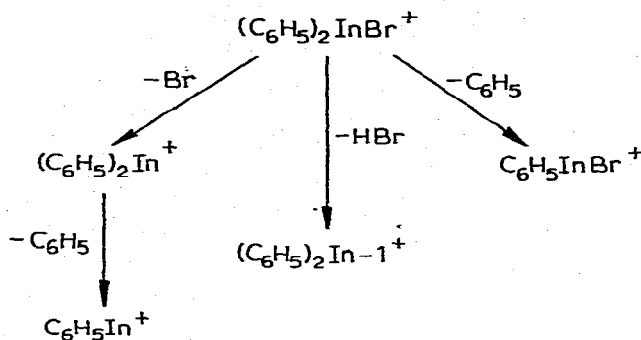
Fig. 3. The partial fragmentation pattern of $(C_6H_5)_2InBr$ based on observed metastable species.

ing important ions: $(C_6H_5)_2InBr^+$ (0.48), $(C_6H_5)_2In - 1^+$ (0.47), $C_6H_5InBr^+$ (14.47), $C_6H_4InBr^+$ (0.09), $(C_6H_5)_2In^+$ (7.00), $(C_6H_5)_2In-1^+$ (5.40), $C_6H_5In^+$ (1.35), M^+ (23.98), $C_{12}H_{10}^+$ (7.22), $C_6H_6^+$ (8.04), $C_6H_5^+$ (11.73). The parenthetical numbers are the percentage of total ionization and are corrected for the ^{13}C isotope contribution. The isotope contribution of other atoms is summed. The biphenyl in the spectrum is a pyrolysis product of $(C_6H_5)_2InBr$ at this temperature. The benzene present comes from hydrolysis at the time of sample introduction. In all cases the most stable metal containing fragments, other than In^+, are $(C_6H_5)_2In^+$ and $C_6H_5InX^+$ which have stable isoelectronic analogues in cadmium. Metastables for the reactions shown in Fig. 3 were observed and thus verify this scheme as the fragmentation pathway.

Rather than using these EI spectra, much more solid-state structural information can be obtained from the temperature dependence of the $(C_6H_5)_2InBr$ mass spectrum. The data compiled in Table 4 show that as the sample temperature increases, the number of high molecular weight fragments increases. Such a phenomenon can be explained only by the presence of a highly associated crystal lattice in which ever larger fragments are volatilized as the temperature in-

TABLE 4

TEMPERATURE DEPENDENCE OF $(C_6H_5)_2InBr$ ELECTRON IMPACT SPECTRUM[a]

Ion	Temperature (°C)					
	300	290	280	270	240	180
$(C_6H_5)_2In_3Br^+$[b]	14	10	3	0	0	0
$(C_6H_5)_4In_2Br_2^+$[b]	25	17	5	0	0	0
$(C_6H_5)_3In_2Br_2^+$[b]	4	2	0	0	0	0
$(C_6H_5)_2InBr^+$	29	24	17	7	3	0
$(C_6H_5)_2InBr - 1^+$	34	23	14	6	2	0
$(C_6H_5)_2In^+$	473	366	204	93	27	3
$(C_6H_5)_2In - 1^+$	442	338	220	96	32	2
$C_6H_5InBr^+$	899	726	488	237	61	6

[a] Since total spectrum was not tabulated, raw peak heights in mm are given. [b] Stoichiometry not absolutely certain because of the similar mass of Br and C_6H_5.

TABLE 5

REPELLER VOLTAGE STUDY OF $(C_6H_5)_2InBr$

Volts	Ratios				
	Trimer[+]	Dimer[+]	Monomer[+]	$(C_6H_5)_2In^+$	$C_6H_5InBr^+$
0	0.017	0.028	0.033	0.54	1.00
5	0.018	0.030	0.034	0.56	1.00
10	0.020	0.032	0.037	0.56	1.00
20	0.017	0.029	0.032	0.53	1.00

creases. In order to demonstrate that these higher mass ions are primarily fragments and not products of ion-molecule reactions, a repeller voltage study was done. The ratio of ions formed by ion-molecule reactions occurring in the source of the spectrometer to ions formed by primary ionization and fragmentation processes is a function of the concentration of neutral species and the residence time of the primary ions in the source. Application of a repeller voltage markedly reduces the residence time of the ions in the source and it follows that a sharp drop in the abundance of the ions formed by ion-molecule reactions would accompany an increase in the repeller voltage. Table 5 shows that changes in the repeller voltage have essentially no effect on the relative abundances of the higher mass ions. These higher mass ions are thus not products of ion-molecule reactions. It can be concluded that they are primary ions and are a further indication of extensive association of the compound in the solid state.

Evidence is thus very strong that compounds of the stoichiometry $(C_6H_5)_2$-InX (X = Cl, Br, I), are made up of polymeric lattices in which the halogen atoms are highly associated and the diarylindium fragment is approximately linear.
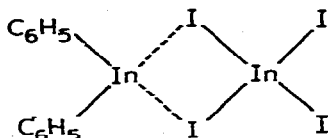
$C_6H_5InX_2$

The ring modes in these compounds are considerably weaker in intensity than the diaryl compounds and the in-plane ring rotation region is not as complicated. Not all bands for $C_6H_5InCl_2$ could be located in the Raman because of sample decomposition in the laser beam.

In addition to the expected phenyl modes tabulated in Table 2, modes appear at 243 and 185 cm^{-1} for X = Cl and Br, respectively. For X = I, two new modes at 137 and 177 cm^{-1} are clearly apparent. The higher frequency of the In—X modes for X = Cl and Br in this stoichiometry compared to $(C_6H_5)_2InX$ is suggestive of somewhat stronger indium—halogen interaction although the frequencies are still considerably less than those characteristic of terminal In—X bonds (vide supra). This frequency increase is most probably a consequence of lesser charge neutralization at indium by the one phenyl ring compared to the diaryl case such that stronger In—X association can occur. Comparison of the vibrational spectrum of $C_6H_5InBr_2$ with that of $C_6H_5GaBr_2$ [43], for which evidence is very strong that molecular dimers exist [10,18,43], reveals no similarity at all in the low frequency region of the IR and Raman spectra. Considering these facts the $C_6H_5InX_2$ compounds (X = Cl, Br) are best reconciled with their spectra and insoluble nature if a polymeric lattice exists in the solid state.

Unfortunately, the mass spectra of the $C_6H_5InX_2$ compounds (X = Cl, Br) are not very useful because pyrolysis is extensive before an ion current is produced. Few metal-containing fragments are found and it suffices to mention that the most abundant metal-containing fragments are, as anticipated, $C_6H_5InX^+$ and InX_2^+.

$C_6H_5InI_2$ contains some anomalies not found in the other arylindium halides. The presence of two low frequency vibrational modes at 137 vs and 177 mw is comparable to that found for CH_3InI_2 (141 vs, 184 w) [15,16] and InI_4^- (139 v, 185 w) [40]. CH_3InI_2 has the salt-like structure $(CH_3)_2In^+InI_4^-$ [14-17]. The methane chemical ionization spectrum of $C_6H_5InI_2$ at 100°C contains the ions InI_4^+ (0.13) and $(C_6H_5)_2InI_2^+$ (1.17) that are not found in any other spectra. Few other metal-containing fragments are present because of pyrolysis. Further, the conductivity of $C_6H_5InI_2$ in nitrobenzene is 15.59 ohm^{-1} cm^{-2} mol^{-1} which is slightly lower than, but still close to, that of a 1/1 electrolyte in that solvent [25]. This conductance value is to be contrasted with a value of 5.88 for $(C_6H_5)_2InI$ determined under the same conditions. Caution should be exercised in using these conductivity data because of the uncertain relationship between the solution conductivity measurements and the solid state structures of these compounds. The available data do intimate, however, that $C_6H_5InI_2$ adopts the salt-like structure, $(C_6H_5)_2In^+InI_4^-$, similar to the methyl analogue [14-17]. The organometallic portion of the vibrational spectrum of $C_6H_5InI_2$ also compares reasonably well with those in the $(C_6H_5)_2InX$ lattice and with $(C_6H_5)_2Cd$. However, minor variations in the band intensities occur which may result from some distortion in the solid state. A plausible explanation for such differences is the *gem* diphenyl structure:

The diphenylindium cation has not been characterized previously, although $(CH_3)_2In^+$ has received considerable attention [13,14-17,33-35]. In light of a unit of this formulation in $(C_6H_5)_2InX$ and $C_6H_5InI_2$, it seems reasonable to now mention that its properties appear to be a straightforward extension of those of the methyl analog. The decrease in the ^{115}In coupling constant in $(C_6H_5)_2InCl$ compared to $(CH_3)_2InCl$ [14] and $(CH_3CH_2)_2InCl$ [13] is consistent with the poorer electron-donating power of the phenyl ring. The increase in vibrational frequency of Mode A upon going from $(C_6H_5)_2Cd$ to $(C_6H_5)_2In^+$ is consistent with the increased M—C bond strength as the formal charge of M increases.

$(C_6H_5)_nInCl_{3-n} \cdot dioxane$

Throughout the above discussion we have postulated multiply associated halogen atoms, but as a final test of the structural hypotheses it would be worthwhile to know what the frequency of "terminal" halogen motions actually is in these compounds. For this reason the dioxanate adducts of the $(C_6H_5)_n$-$InCl_{3-n}$ compounds were prepared. In the adducts the halogen coordination at the acceptor site should be replaced by the dioxane molecules making the In—Cl

bonds terminal. If this is the case, the In—Cl vibrational bands formerly assigned as being associated with multiply coordinated chlorine atoms should disappear and new modes in the range expected of terminal In—Cl bonds should appear. This is precisely what is observed. In—Cl modes in $InCl_3 \cdot (dioxane)_2$ appear at 315, 305 and 280 cm^{-1} in both the IR and Raman spectra. These can be compared with values for other $InCl_3 \cdot L_2$ compounds which appear at 290-340 cm^{-1} [37-39]. The IR and Raman activity of the modes suggests that the $InCl_3 \cdot (dioxane)_2$ does not contain indium with D_{3h} symmetry, however. For $C_6H_5InCl_2 \cdot$ dioxane modes appear in the IR and Raman at 327 and 323 cm^{-1} which may be the symmetric and antisymmetric indium—halogen motions. The closeness of ν_s and ν_{as} for a bent X—M—X arrangement of halogens in heavy metal halides is well documented [44]. $\nu(In—Cl)$ in $C_6F_5InCl_2 \cdot$ dioxane has been located at 330 cm^{-1} in the IR [11]. As expected, a single IR and Raman active mode at 251 cm^{-1} is found in $(C_6H_5)_2InCl \cdot$ dioxane. The In—Cl frequencies in the arylindium chlorides thus represent a 70-80 cm^{-1} decrease over their dioxanate counterparts. The appearance of terminal halogen modes in these adducts and their absence in the base-free compounds is good evidence for highly associated halogen atoms in the base-free compounds.

For $(C_6H_5)_3In \cdot$ dioxane the spectrum is similar to that of $(C_6H_5)_3In$ except that the splitting of the modes in the phenyl region does not occur. In $(C_6H_5)_3In$ significant intermolecular association between indium and the neighboring phenyl ring [45] complicates the vibrational description. This association appears to be eliminated by the presence of the dioxane molecules.

In summary, this work gives a more complete picture of the periodic trend for the aryl Group IIIB halides. The solid state structures of the arylindium halides bear strong resemblance in their polymeric motif to the arylthallium halides and are not like the dimeric aryl-aluminum and -gallium halides. Phenylindium diiodide is an exception to this structual pattern, perhaps because the large size of the iodine atoms renders five and six coordination at indium unreasonable. In this circumstance, a structure more comparable to the four-coordinate aluminum and gallium systems seems to be preferred.

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