*Journal of Organometallic Chemistry*
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# OXIDATIVE ADDITION REACTIONS OF GROUP III METALS IN LOW OXIDATION STATES

## III*. REACTIONS OF INDIUM MONOHALIDES WITH ALKYL HALIDES

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(Received April 7th, 1972)

## SUMMARY

Alkylindium dihalides may be synthesised by the oxidation of indium monobromide and indium monoiodide with alkyl halides. The eight compounds, $RInX_2$ ($X = Br, I$; $R = Me, Et, Pr, Bu$) were synthesised and their vibrational, $^1H$ NMR and mass spectra recorded. The vibrational spectra are interpreted in terms of a dimeric formulation for the solid compounds $RInI_2$ for $R = Et$, Pr and Bu. For $MeInI_2$ an ionic formulation, $InMe_2^+InI_4^-$ is proposed.

In the bromide series evidence is presented in support of polymeric structures for $MeInBr_2$ and $EtInBr_2$.

Mass spectra indicate that in the vapour phase all compounds are dimeric, apart from $EtInBr_2$ which is at least tetrameric.

## INTRODUCTION

In previous papers[1,2] we described the oxidative addition reactions of gallium(I) (in the "gallium dihalides") and alkyl halides. We showed that for the methyl halide series oxidative addition occurred as shown: $MeX + Ga_2X_4 \rightarrow MeGa_2X_5$. A new series of methylgallium halides ($X = Cl, Br, I$) was formed.

For the reactions with higher alkyl halides, apart from the $EtBr/Ga_2Br_4$ reaction in which $EtGa_2Br_5$ was formed, the reaction was of little synthetic value since extensive decomposition occurred due to the further reaction of the strong Lewis acid with excess alkyl halide. Since indium(III) halides are weaker Lewis acids than their gallium analogues it was thought that (provided oxidative addition reactions occurred between lower valent indium compounds and alkyl halide) the products would be less reactive towards alkyl halide, and therefore isolable.

We have previously reported the reaction between $InBr_2$ and methyl bromide[3], we showed that whilst oxidative addition occurred with the formation of $MeInBr_2$ and $InBr_3$ the method was of little value in the synthesis of alkylindium dihalides since the products are not readily separable. In order to overcome this problem we

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* For part II see ref. 2.

used the indium monohalides (InBr and InI) and the success of the InBr/MeBr reaction has been reported in a preliminary communication[4].

Reactions between indium monochloride and alkyl halides were not attempted since our experience with analogous $Ga^I$ systems showed that alkyl chlorides were unreactive and that with alkyl bromides and iodides extensive halogen exchange occurred.

Previous work on oxidative addition reactions of indium(I) has been confined to its insertion into metal–metal bonds, metal–halogen bonds[5], and sulphur–sulphur bonds[6].

## RESULTS AND DISCUSSION

The reactions investigated were those between InX and RX for X = Br, I and R = Me, Et, Pr, Bu. The nature of the reactions in the two series (Br and I) differ considerably and will be first considered separately.

### *Reactions between alkyl bromides and indium monobromide*

These reactions are complex. Excess alkyl bromide was shaken with InBr at room temperature. For methyl and ethyl bromide the reactions took about one week and were monitored by Raman spectra. The first stage of the reactions involved the formation of an orange intermediate (unidentified) which was insoluble in alkyl bromide. This then further reacted and finally gave the pure white crystalline product, which analysed as $RInBr_2$, in 100% yield.

The reactions at room temperature between InBr and propyl and butyl bromides were much slower and took about four weeks to reach completion. The initial stages of the reactions were similar to those already described in that orange intermediates were first formed. These then slowly reacted to give a white insoluble compound which gave a strong Raman band at 197 $cm^{-1}$ and a white crystalline compound which was soluble in the excess alkyl bromide. The soluble compounds corresponded to the expected products, *i.e.* $PrInBr_2$ and $BuInBr_2$, whilst the insoluble one was readily identified as $InBr_2$.

Reactions at 50° were much more rapid (3 days) and in the case of the propyl reaction a 100% yield of propylindium dibromide was obtained. Small amounts of $InBr_2$ were still produced in the butyl bromide reaction at this temperature but a good yield of butylindium dibromide was obtained.

The reaction pathways are clearly very complex and we are presently investigating the intermediates formed in these reactions.

### *Reactions between alkyl iodides and indium monoiodide*

These were much more rapid and appear to be much less complex than their bromide analogues. In all cases reactions were complete in 24 h. The final products were similar to those described above and the reactions may be represented as:

$$RI + InI \rightarrow RInI_2$$

The oxidative addition reactions of indium monobromide and monoiodide thus provide very convenient synthetic routes to the alkylindium dihalides. Attempts to extend these reactions to aryl halides were unsuccessful.

TABLE 1

VIBRATIONAL SPECTRA OF THE ALKYLINDIUM DIBROMIDES ($cm^{-1}$)[a]

| *Compound* | *ν(In–C)* | | *ν(In–Br)* <br> *Raman* |
|---|---|---|---|
| | *Raman* | *IR* | |
| $MeInBr_2$ | 524 s | 523 s | 196 s, 148 m, 97 m, 85 w |
| | 517 w | 516 m | |
| $EtInBr_2$ | 502 m | 496 m | 213 s, 200 s, 187 s, |
| | 494 s | 491 m | 135 w, 91 m |
| $PrInBr_2$ | 584 m (br) | 578 m (br) | 188 s (br) |
| | 495 m (br) | 490 m (br) | |
| $BuInBr_2$ | 584 w (br) | 583 s (br) | 232 w, 189 s |
| | 493 s (br) | 496 s (br) | |

[a] Raman spectra were recorded on solid samples; IR spectra were recorded on hexachlorobutadiene mulls.

TABLE 2

VIBRATIONAL SPECTRA OF THE ALKYLINDIUM DIIODIDES ($cm^{-1}$)[a]

| *Compound* | *ν(In–C)* | | *ν(In–I)* <br> *Raman* |
|---|---|---|---|
| | *Raman* | *IR* | |
| $MeInI_2$ | 484 s (sym) | 555 s (asym) | 196 w, 185 m, 141 s, |
| | | | 118 w, 65 m |
| $EtInI_2$ | 489 s | 484 s | 250 w, 171 m, 144 s |
| $PrInI_2$ | 574 s (br) | 572 s (br) | 196 w, 167 m, 145 s |
| | 485 s (br) | 482 m (br) | |
| $BuInI_2$ | 577 m (br) | 576 s (br) | 184 m, 168 m, 143 s |
| | 487 m (br) | 482 m (br) | 87 w |

[a] See footnote Table 1.

### *The vibrational spectra and structure of alkylindium dihalides*

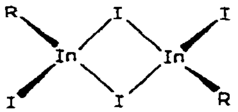
The vibrational spectra of these compounds in the indium–carbon and indium–halogen regions are given in Tables 1 and 2. Of the compounds, $MeInI_2$ has a very different spectrum in the In–C region and this will be discussed first. We have previously reported this work in a communication[7] and here this is summarised and extended. The mutual exclusion of the symmetric and asymmetric In–C bands in the Raman and IR spectra together with the large difference in their magnitudes strongly suggests that there are two methyl groups attached to an indium atom arranged linearly. Further the bands at 141 and 185 $cm^{-1}$ are consistent with the $InI_4^-$ ion[8]. The compound may thus be formulated $InMe_2^+InI_4^-$. It is very likely that the linear ion is weakly bonded to bridging iodide atoms and the weak band at 196 $cm^{-1}$ may arise from this interaction.

We also found during the course of the MeI/InI reaction that if excess methyl iodide was removed from the reaction mixture shortly after the reaction had commenced an additional band appeared at 512 $cm^{-1}$ in the Raman spectrum. This may be due to the initial formation of the expected form of $MeInI_2$ in which one methyl group is attached to each indium atom. Rearrangement of this may then occur to give the more stable form.

The spectra of the other compounds are difficult to interpret since it was not possible to determine their molecular weights due to their insolubility in solvents such as benzene. However by analogy with the structures of the indium(III) halides it might be expected that in the solid state the alkylindium diiodides would be dimers; higher coordination, resulting in polymerised systems, might be expected for the bromides. Certain features of the spectra are consistent with these models.

The Raman spectrum of dimeric $In_2I_6$ above 100 $cm^{-1}$ contains a strong band at 134 $cm^{-1}$ [9] due essentially to a bridging vibration ($\nu_2$)[10] and a medium band at 187 $cm^{-1}$ associated mainly with symmetric In–I terminal stretching ($\nu_1$).

Each of the iodide compounds contains a strong band in the region 143–145 $cm^{-1}$ and these we tentatively assign to the bridging mode. In addition the medium bands between 167–184 $cm^{-1}$ we assign to terminal modes.



(I)

It would be expected, by analogy with other Group III alkylmetal dihalides[11], that the *trans* form (I) of the dimeric species would be the most stable. Since this form is centrosymmetric, in the In–C region two bands should be observed, $\nu_{sym}$ in the Raman and $\nu_{asym}$ in the IR. However it is doubtful whether strong coupling would occur for such a bridging species with heavy indium and iodine atoms. Indeed for the dimethyl and diethylindium monoiodides coupling is absent[12,13]. Under these circumstances one band would be expected in the IR and Raman spectrum and this is observed for $EtInI_2$. For $PrInI_2$ and $BuInI_2$ two strong broad bands are observed in both the IR and Raman spectrum of each compound. Superficially these may be assigned to symmetric and asymmetric modes of $R_2In$ systems. However there are two objections against these assignments:

(*a*), the bands are broad and their relative intensities remain approximately the same in both the IR and Raman;

(*b*), the higher frequency bands are greater than those observed for $Me_2InX$[12] and $Et_2InX$[13] whereas it would be expected that these should be lower.

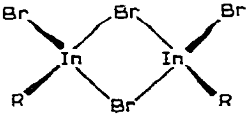
We propose that these two broad bands in each compound are due to the presence in the crystal of mixtures of the two internal torsional *trans* and *gauche* forms. Similar forms have been observed for $Pr_4Sn$ by Taimsulu and Wood[14] and our assignments are based on this work. In the similar thallium compounds $Pr_2TlX$ and $Bu_2TlX$ only the *trans* forms have been observed[15].

In summary then, the vibrational spectra of the iodide series provide evidence in support of the dimeric structure (I).

The spectra of the alkylindium dibromide systems are more complex and for the methyl and ethyl compounds two closely separated bands are observed in both their IR and Raman spectra. For these two compounds dimeric *trans* structures are unlikely since it is doubtful whether strong enough coupling between the alkyl groups would occur to give observably different asymmetric and symmetric vibrational frequencies; compare the analogous gallium compounds:

$Me_2Ga_2Cl_4$, $\nu(Ga\text{–}C)_{sym}$ 603 $cm^{-1}$; $\nu(Ga\text{–}C)_{asym}$ 608 $cm^{-1}$ [11]
$Me_2Ga_2Br_4$ $\nu(Ga\text{–}C)_{sym}$ 595 $cm^{-1}$; $\nu(Ga\text{–}C)_{asym}$ 591 $cm^{-1}$ [1]
$Et_2Ga_2Cl_4$, $\nu(Ga\text{–}C)_{sym}$ 568 $cm^{-1}$; $\nu(Ga\text{–}C)_{asym}$ 570 $cm^{-1}$ [11].

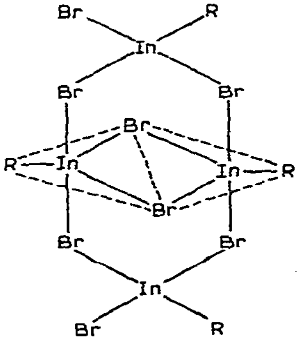
In absence of such coupling a spectrum similar to that observed for the methyl compound might be expected if both *cis* (II) and *trans* (I) isomers were present.



(II)

We do not consider this to be likely since *cis* forms are expected to be less stable than *trans*[16]. It is also seen that for $EtInBr_2$ additional bands are observed which are not common to both the IR and Raman spectra.

The most likely explanation of these complex spectra is that the compounds are polymeric and that the alkyl groups are attached to indium atoms in different coordination sites. Indeed the mass spectra of the ethyl compound (discussed below) indicate that in the vapour phase tetrameric species are present. There are several structural possibilities for polymeric species containing mixed coordination sites. One such possibility for a tetrameric unit with 5- and 4-fold coordination is shown in (III).

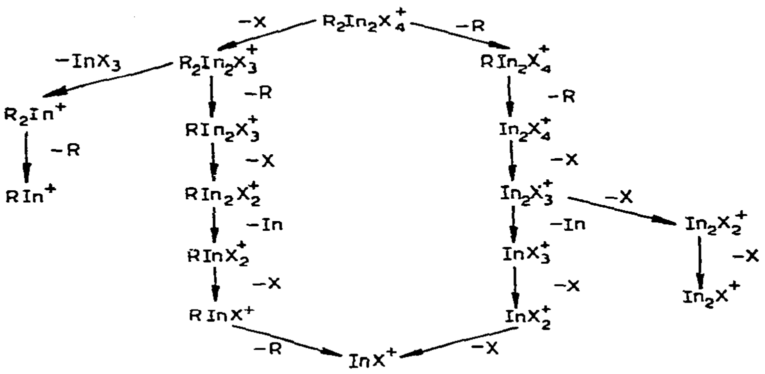


(III)

The spectra of the propyl and butylindium dibromides are very similar to their iodide analogues and it may be that in these cases the molecules are dimeric; further polymerisation being inhibited by the size of the attached alkyl groups.

### *Mass spectra*

All of the compounds studied, apart from $EtInBr_2$, have mass spectra which are consistent with a dimeric structure. Proposed fragmentation patterns are shown below:



In the mass spectrum of $EtInBr_2$ significant additional peaks appeared at mass numbers corresponding to the ions: $In_4Br_5Et^+$, $In_4Br_4^+$, and $In_3Br_5Et_3$. These results suggest that in the vapour phase tetramers or even higher polymers are present and it is to be expected that these will also exist in the solid state. Surprisingly no peaks corresponding to higher polymeric species were observed for $MeInBr_2$ and it appears that the dimeric form is the stable form for this compound in the vapour phase.

### $^1H$ *NMR spectra*

These were recorded on chloroform, methylene dichloride and methyl bromide solutions; details are given in the experimental section. These did not contribute any further structural evidence but did confirm that the n-propyl and n-butyl groups were present rather than their isomeric forms.

## EXPERIMENTAL

Indium monobromide was prepared by heating indium tribromide and the exact amount of indium metal at 320° for 48 h. Indium monoiodide was prepared by heating exact amounts of dried iodine and indium metal at 400° for 24 h.

The alkyl halides were purified by the method previously described[1]. All reactions were carried out *in vacuo*.

The RI/InI reactions were all complete within 24 h at room temperature and were soluble in excess alkyl halide. On removal of this excess white crystalline products were obtained.

The RBr/InBr reactions were much slower at room temperature. The methyl bromide and ethyl bromide reactions were complete after one week and 100% yields of $RInBr_2$ were obtained. For the propyl and butyl bromide/InBr systems reactions came to completion after one month at room temperature and amounts of $InBr_2$ were also formed. Separation of this mixed product was readily effected since the alkylindium dihalides are very soluble in excess alkyl halide whilst $InPr_2$ is insoluble.

At 50° the propyl and butyl reactions were much more rapid and were complete in three days. Although a small amount of $InBr_2$ was again produced in the BuBr/InBr reaction none was formed in the PrBr/InBr reaction and $PrInBr_2$ was obtained in 100% yield at this temperature. Analytical and m.p. data are given in Table 3.

TABLE 3

ANALYTICAL DATA OF $RInX_2$

| *Compound* $RInX_2$ | *Analysis* | | | | *M.p. (°C)* |
|---|---|---|---|---|---|
| | *Found (%)* | | *Calculated (%)* | | |
| | *In* | *X* | *In* | *X* | |
| $MeInBr_2$ | 39.36 | 55.15 | 39.64 | 55.17 | 168–169 |
| $EtInBr_2$ | 37.49 | 52.26 | 37.81 | 52.62 | 138–139 |
| $PrInBr_2$ | 36.06 | 49.98 | 36.14 | 50.30 | 84 (dec.) |
| $BuInBr_2$ | 34.48 | 48.21 | 34.61 | 48.17 | 70 (dec.) |
| $MeInI_2$ | 29.94 | 66.34 | 29.95 | 66.16 | 131 (dec.) |
| $EtInI_2$ | 28.80 | 63.79 | 28.88 | 63.83 | 97 (dec.) |
| $PrInI_2$ | 27.89 | 61.58 | 27.85 | 61.66 | 50 (dec.) |
| $BuInI_2$ | 26.72 | 59.60 | 26.97 | 59.63 | 45 (dec.) |

### *$^1H$ NMR spectra*

These were measured on a Varian HA 100-D spectrometer and in all cases refer to the solvent as standard.

*$MeInBr_2$*. Solvent $CH_3Br$, singlet $\delta$ −1.56 ppm.

*$EtInBr_2$*. Solvent $CH_3Br$, methylene multiplet centred at $\delta$ −1.05 ppm and methyl triplet at $\delta$ −1.24 ppm; intensity ratio 2/3.

*$PrInBr_2$*. $CH_2Cl_2$ solvent, complex methylene multiplet centred at $\delta$ −3.48 ppm and a methyl triplet at $\delta$ −4.25 ppm; intensity ratio 4/3.

*$BuInBr_2$*. Solvent $CH_2Cl_2$, complex methylene multiplet centred at $\delta$ −3.70 ppm and methyl triplet at $\delta$ −4.36 ppm; intensity ratio 6/3.

*$MeInI_2$*. Solvent $CH_2Cl$, singlet at $\delta$ −4.14 ppm.

*$EtInI_2$*. Solvent $CHCl_3$, methylene quartet centred at $\delta$ −5.28 ppm and a methyl triplet at $\delta$ −5.91 ppm; intensity ratio 2/3.

*$PrInI_2$*. Solvent $CH_2Cl_2$, methylene triplet centred at $\delta$ −3.25 ppm, complex methylene multiplet at $\delta$ −3.53 ppm and a methyl triplet at $\delta$ −4.22 ppm; intensity ratio 2/2/3.

*$BuInI_2$*. Solvent $CH_2Cl_2$, methylene triplet centred at $\delta$ −3.20 ppm, complex methylene multiplet at $\delta$ −3.70 ppm, and a methyl triplet at 4.35 ppm; intensity ratio 2/4/3.

IR and Raman spectra were recorded on Perkin–Elmer 225 and Carey 81 spectrometers respectively.

## ACKNOWLEDGEMENT

We thank the Science Research Council for an award to M.J.S.G.

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