Novel Oxidative Addition Reaction of Indium Monobromide

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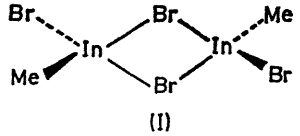
Summary Methylindium dibromide is formed in 100% yield by oxidation of indium monobromide with methyl bromide at room temperature; indium–carbon bonds are characterised by Raman and i.r. spectra, and mass spectra show that the compound is dimeric in the vapour phase.

WE have recently been interested in the ability of Group III metals in +1 oxidation states to undergo oxidative addition reactions by use of their *s* valence electrons. We have shown for example that Ga^+ readily inserts into C–halogen bonds [1,2] and that $InBr_2$ which is formulated as $In^+ InBr_4^-$, with methyl bromide undergoes similar oxidative addition reactions to form In–C bonds.[2] The products of the latter reaction are thought to be $InBr_3$ and $InBr_2Me$. As a method of synthesising pure $InBr_2Me$ this reaction is of limited value because of the difficulties involved in its separation from $InBr_3$. The use of InBr eliminates these difficulties and $InBr_2Me$ is formed in 100% yield.

Excess of dry methyl bromide was condensed on to indium monobromide *in vacuo*. A slow reaction occurred at room temperature. The red solid InBr was first transformed into an orange powder which, after about one week, further reacted to form hard white crystals which analysed as $InBr_2Me$, m.p. 169 °C.

The Raman spectrum of this crystalline product and its i.r. spectrum (Nujol mull) showed a strong band at 523 cm^{-1}, a frequency similar to that observed by Clark and Pickard[3] for $InCl_2Me$, the only other known methylindium dihalide. The presence of a single band at 523 cm^{-1} in the In–C region of the Raman and i.r. spectrum suggests that there is one methyl group attached to each indium in a non-centrosymmetric structure. The insolubility of the compound in common solvents *e.g.* benzene, indicates that in the solid state it may be polymeric owing to the preference of indium for five or six co-ordination.

Although the mass spectrum did not reveal a dimeric molecular ion peak, significant peaks occurred at mass numbers corresponding to In_2Br_4Me and $In_2Br_3Me_2$ which indicates that dimeric molecules are present in the vapour phase and it is to be expected that they have structure (I).



(I)

Preliminary work using other alkyl bromides indicates that this is a general reaction.

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[1] W. Lind and I. J. Worrall, *Chem. Comm.*, 1969, 829.
[2] W. Lind, L. Waterworth, and I. J. Worrall, to be published.
[3] H. C. Clark and A. L. Pickard, *J. Organometallic Chem.*, 1968, **13**, 61.