Dimeric Di(*tert*-butyl)haloalanes and a Monomeric Di(*tert*-butyl)phosphino-di(*tert*-butyl)alane

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The di(*tert*-butyl)aluminum halides, $t\mathrm{Bu_2AlX}$ (X = Br, I) have been prepared in yields ranging from 55 to 64 % from $\mathrm{AlX_3}$ and Li*t*Bu in a 1 : 2 molar ratio in pentane. In the crystal these pyrophoric compounds are dimeric featuring Al–X–Al bridges. The reaction of $\mathrm{AlCl_3}$ with Li*t*Bu in diethyl ether produced a volatile solvate of composition $t\mathrm{Bu_3Al–Cl–Al}t\mathrm{Bu_2(OEt_2)}$. Reaction of this species with $\mathrm{AlCl_3}$ at 120 °C yielded a separable mixture of $t\mathrm{Bu_2AlCl}$ and $t\mathrm{Bu_2AlCl(OEt_2)}$. $t\mathrm{Bu_2AlCl}$ and $t\mathrm{Bu_2GaCl}$ react with $t\mathrm{Bu_2PLi}$ to produce the monomeric compounds $t\mathrm{Bu_2E–P}t\mathrm{Bu_2}$ (E = Al, Ga). The aluminum compound decomposes at 111 °C to give a mixture of the *cis*/*trans*-isomers of $[t\mathrm{Bu(H)Al–P}t\mathrm{Bu_2}]_2$ while at 200 °C only the *trans*-isomer is formed.

Key words: Di(*tert*-butyl)aluminum Halides, Chloro Penta(*tert*-butyl)dialuminum Diethyl Ether, Di(*tert*-butyl)phosphino-di(*tert*-butyl)alane, NMR Spectra, Crystal Structures