Relationships in the Stabilities of the Bonds formed between Compounds of the Group III Elements and Ligand Molecules

By P. H. BIRD and M. G. H. WALLBRIDGE

(*Department of Chemistry, The University, Sheffield*)

IT has been shown that in the 1 : 1 adducts formed between aluminium borohydride and various ligands, $L \rightarrow Al(BH_4)_3$ (I) where L = ligand, the ligand atom (*e.g.*, N, P, As, O, S) is bonded to the aluminium atom.[1-3] Excess of those ligands containing N or P (*e.g.* NMe_3, NEt_3, and PMe_3) reacts further, at 25°, successively cleaving the $Al-H_2-B$ bridges yielding, finally, derivatives of borane ($H_3B \leftarrow L$, where L = ligand) and aluminium hydride ($H_3Al \leftarrow L$).[2] In view of the interest in the comparative stability of $X_3M \leftarrow L$ (where X = H or alkyl, M = B, Al, Ga, etc.) compounds,[4,5] we now report our results for (I).

The relative stabilities for (I), deduced from quantitative displacement reactions using the 1 : 1 adducts, show $N \approx P > As$, and $O > S$, when the ligand alkyl is the donor. The N–P relationship appears to be anomalous, since for the aluminium alkyls $N > P > As$,[5] and for aluminium hydride $N > P$,[4] a result which we have confirmed independently. Re-investigation of the compounds formed between aluminium borohydride and trimethylamine, and trimethylphosphine, shows that at −78°, in the absence of solvent, the crystalline 1 : 1 adducts $Me_3N,Al(BH_4)_3$ (II) and $Me_3P,Al(BH_4)_3$ (III) on treatment with excess of

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[1] H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, *J. Amer. Chem. Soc.*, 1940, **62**, 3421.
[2] P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc.*, 1965, forthcoming.
[3] J. K. Ruff, *Inorg. Chem.*, 1963, **2**, 515.
[4] N. N. Greenwood, E. J. F. Ross, and A. Storr, *J. Chem. Soc.*, 1965, 1400.
[5] For review see "Organometallic Compounds" by G. E. Coates, Methuen and Co., Ltd., London, 1960, pp. 88—163.

ligand take up only 1 mole more forming stable involatile solids. When the 2 : 1 adducts, $(Me_3N)_2Al(BH_4)_3$ (IV) and $(Me_3P)_2,Al(BH_4)_3$ (V) are allowed to warm slowly to 25°, then at this temperature, under dry nitrogen, (IV) decomposes slowly (or rapidly at $\sim \pm 20°$ *in vacuo*), while (V) remains stable, and decomposes only slowly *in vacuo* (Found: Al, 12·1%; hydrolysable H, 5·38%; B, 15·5%. $C_6H_{30}B_3P_2Al$ requires Al, 12·1%, H, 5·37%; B, 14·5%). The reaction conditions described for (V) prevent cleavage of the $Al-H_2-B$ bridges, but under less well controlled conditions, *e.g.* reaction at 25°, (V) contains the 1 : 1 adduct, (III), and cleavage products, *e.g.* H_3B, PMe_3. (V) is decomposed by reaction with excess of ligand, at 25°, yielding derivatives of borane and aluminium hydride. The infrared spectrum of (V) is similar to that of the 1 : 1 adduct (III) and shows that (V) contains no cleavage products (*e.g.* H_3B, PMe_3), indicating (V) is a single compound. The Al–P bond frequency appears to lie outside the range of the spectrum (4000—400 cm.$^{-1}$). Decomposition in organic solvents has prevented any reliable nuclear magnetic resonance spectra being obtained.

The reactions involving ligands containing N or P [where similar products, *i.e.* $HAl(BH_4)_2, NMe_3$ (or PMe_3); H_3B, PMe_3 (or NMe_3), were always obtained irrespective of which ligand was used for the displacement reaction] are therefore consistent with the initial formation of a mixed complex $Me_3N,Al(BH_4)_3,PMe_3$. Indeed the 1 : 1 adduct (II) absorbed only 1 mole of trimethylphosphine at −78°, in the presence of an excess of the latter, yielding a solid which decomposed at $\sim -10°$, *in vacuo*, to the products given above, indicating a stability between that of (IV) and (V). A similar mixed derivative has been proposed recently for gallium hydride,[4] *i.e.* Me_3P,GaH_3,NMe_3, and this is also unstable at room temperature. The trend in stability of the 2 : 1 adducts is the reverse of that observed for the 1 : 1 adducts of all other aluminium compounds, and, apparently, the first report for compounds of the Group III elements, excluding diborane, in which the stability of the compound formed with phosphorus (as the ligand atom) exceeds that of nitrogen.[5]

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