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## Some adducts of aluminium and phosphines

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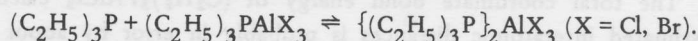
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## SUMMARY

In this thesis some investigations concerning reactions of aluminium halides with solutions of phosphines are described. These investigations mainly deal with the formation of adducts  $(R_3P)_nAlX_3$  ( $R = C_2H_5, C_6H_5$ ;  $X = Cl, Br$ ;  $n = 1, 2$ ). Some experiments with other trialkylphosphines and (thio)phosphoryl compounds as donors or with  $AlI_3$  as acceptor were also performed. The usefulness of electrostatic calculations for understanding some of our results is investigated.

In chapter I an introduction is given in which some experimental work of other authors and some general ideas relevant to this study are mentioned.

NMR measurements of  $^{27}Al$  and  $^{31}P$  nuclei in mixed solutions of aluminium halides and phosphines are described in chapter II. From the results of these measurements the equilibrium constants of the equilibria



in benzene and toluene solutions are determined. The stability constant of  $\{(C_6H_5)_3P\}_2AlX_3$  appeared to be very small. If dihalomethanes are used as solvents, the solvent reacts with the excess of donor.

Preliminary NMR experiments on solutions of aluminium halides and other phosphines and (thio)phosphoryl compounds are also reported in chapter II.

In chapter III dielectric measurements on mixed solutions of aluminium halides and  $(C_2H_5)_3P$  or  $(C_6H_5)_3P$  are described. The dipole moments of  $R_3PAlX_3$  ( $R = C_2H_5, C_6H_5$ ;  $X = Cl, Br$ ) and of  $(C_6H_5)_3POSnCl_4$  are determined. From measurements of the dielectric constant of solutions of  $R_3P$  and  $AlX_3$  with a concentration ratio  $> 1$  it can be concluded that in addition to  $R_3PAlX_3$  adducts  $\{(C_2H_5)_3P\}_2AlX_3$  are formed in solution, but no  $\{(C_6H_5)_3P\}_2AlX_3$ . The complexes  $\{(C_2H_5)_3P\}_2AlX_3$  appear to have small dipole moments and we conclude that they have trigonal bipyramidal structures with the phosphine donors in the axial positions. Stability constants calculated from our dielectric measurements are in good agreement with those found from our NMR measurements.  $\{(C_6H_5)_3PS\}_2SnCl_4$  is also found to be partly dissociated in benzene solution.

Microwave titrations of aluminium bromide solutions with some phosphines are also reported in chapter III.

The isolation of compounds  $R_3PAIX_3$  ( $R = C_2H_5, C_6H_5$ ;  $X = Cl, Br, I$ ) is described in chapter IV. Their IR spectra are reported. Attempts to isolate a compound  $\{(C_6H_5)_3P\}_2AlCl_3$  failed; the melting point diagram of mixtures of  $(C_6H_5)_3P$  and  $AlCl_3$  gives no indications for the existence of any other compound than  $(C_6H_5)_3PAI_3$ .

In chapter V the donor strengths of the molecules  $R_3P$  and the acceptor strength of the molecules  $AlX_3$  are discussed. Steric requirements of the group R and its electron releasing properties can satisfactorily explain the relative donor strengths of  $R_3P$ . In agreement with the results of other authors,  $AlBr_3$  appears to have an equal or better acceptor strength than  $AlCl_3$ . The concept of reorganization energy, as used by some authors in the discussion of acceptor strength, leads to conflicting conclusions. We think it more satisfactory to discuss acceptor strength in terms of 'resistance to reorganization' of an acceptor.

The coordinate bond energies of  $Al_2Cl_6$  and  $AlCl_4^-$  are calculated from an electrostatic model, using interatomic distances, polarizabilities and Born repulsion parameters derived from a calculation on  $AlCl_3$ ; the results deviate from experimental data by only 1 and 2 percent, respectively.

The total coordinate bond energy of  $(C_2H_5)_3PAI_3$  calculated with estimated interatomic distances is probably in error by about 5 percent, which means that the enthalpy of adduct formation cannot be calculated with any accuracy (even the sign is incorrect). However, the dipole moments of  $(C_2H_5)_3PAI_3$  and of  $(C_2H_5)_3PAlBr_3$  calculated from the same data are in close agreement with those derived from our dielectric measurements.

Electrostatic calculations were performed on models of trans- and cis- $D_2MX_4$  and of 'trans'- and 'cis'- $D_2MX_3$  built from hard non-polarizable spheres ( $D =$  donor;  $M =$  metal;  $X =$  halogen); these calculations offer an explanation for the preference of  $D_2MX_3$  for a 'trans' configuration, while many complexes  $D_2MX_4$  have a cis configuration.

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