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Some adducts of aluminium and phosphines

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ngen berekende. Ook
ltelijk te dissociëren.
en van enige microgolf-

, C_6H_5; X= Cl, Br, I) is
weergegeven. Pogingen
eren mislukten; in een
Cl_3 zijn geen aanwijzin-
an $(C_6H_5)_3PAlCl_3$.
sterktes van moleculen
ektronenstuwende of
uimte die zij inneemt,
verklaren. Uit onze
resultaten van andere
betere acceptor is als
oor sommige auteurs
leidt tot tegenstrijdig-
een acceptor (en voor
voeren.
t.o.v. elkaar, in mole-
aan de hand van een
noleculaire afstanden,
Deze laatsten ontleen-
een molecuul $AlCl_3$.
van de experimentele
ning van de potentiële
laire afstanden) onge-
dat we de vormings-
kunnen berekenen;
ening van de dipool-
r_3 uit van dezelfde
e zeer goed overeen-
n.
, niet-polariseerbare
otentiële energie van
donor; M= metaal;
oor de voorkeur van
tot D_2MX_4. Veel
ebben een ciscon-

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

$$(C_2H_5)_3P + (C_2H_5)_3PAlX_3 \rightleftharpoons \{(C_2H_5)_3P\}_2AlX_3 \text{ (X = Cl, Br)}.$$
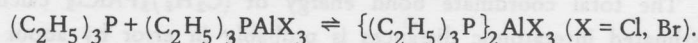
in benzene and toluene solutions are determined. The stability constant of $\{(C_6H_5)_3P\}_2AlX_3$ appeared to be very small. If dihalomethanes are used as solvents, the solvent reacts with the excess of donor.

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 $(C_6H_5)_3POSbCl_5$ 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.

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The isolation of compounds R_3PAlX_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 $(C_6H_5)_3PAlCl_3$.

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 $(C_2H_5)_3PAlCl_3$ 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 $(C_2H_5)_3PAlCl_3$ 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.