an einem Quarzkontakt bei 300° C entsprechend der Gleichung

$$3\,P_nH_{n+2} \rightarrow (n+2)\,PH_3 + (2n-2)\,P$$

quantitativ in Phosphor und Phosphin zersetzt wird. Das gebildete Phosphin wird nach Stock u. Mitarb.[4]) als Kupferphosphid zur Wägung gebracht. Die Brauchbarkeit des Verfahrens wurde durch Analysen von reinem P_2H_4 und P_2D_4 getestet. Die Methode ist zur analytischen Charakterisierung der Phosphane wesentlich genauer als die Bestimmung des Gesamtphosphors oder -wasserstoffs, deren Prozentgehalte sich bei den einzelnen Homologen nur sehr wenig voneinander unterscheiden, während die Differenzen in dem pyrolytisch gebildeten Phosphin und „Rest-Phosphor" wesentlich größer sind.

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*) Untersuchungen über Phosphorverbindungen XV. – XIV. Mitt. Baudler, M.: Z. Naturforsch **14**b, 464 (1959).

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On the Existence of Hexachlorogermanates, $M_2^IGeCl_6$

Germanium tetrachloride is known for its tendency to establish a co-ordination number of six for the germanium by the addition of various other molecules, particularly those containing nitrogen or oxygen with free electron pairs[1]). There is, however, only one recorded example of hexa-coordination achieved by the donation of two more chloride ions to the $GeCl_4$ molecule. This is the compound Cs_2GeCl_6, first prepared by Laubengayer, Billings and Newkirk[2]) in 1940. These workers have pointed out that the other alkali and earth alkaline metal ions do not undergo reactions with $GeCl_4$.

In the course of work on the acceptor strength of group IV chlorides for chloride ions in liquid anhydrous HCl[3]) we have thoroughly investigated the possibility of the formation of the complex ion, $GeCl_6^{2-}$. Surprisingly, our results indicated the absence of complex ion formation. Germanium tetrachloride is completely insoluble in liquid HCl and does not noticibly increase the self-conductance of HCl, indicating that any equilibrium concentration of $GeCl_6^{2-}$ is immeasurably small. A further proof of the absence of the $GeCl_6^{2-}$ anion, in liquid HCl, is furnished by the distinctly different behaviour of $SnCl_4$ and $GeCl_4$ in this solvent.

When $SnCl_4$ is titrated against the highly conducting solution of 0·2 m tetramethylammonium chloride ($\Lambda = 25{\cdot}0\ \mathrm{cm^2\ \Omega^{-1}\ mol^{-1}}$) in liquid HCl the conductivity drops sharply until the equivalent point corresponding to a molar ratio of the formula $(Me_4N)_2SnCl_6$ is reached. This compound can be isolated when the HCl is evaporated. On the addition of $GeCl_4$ to the same solution of 0·2 m Me_4NCl in HCl, the conductivity at first slightly increases and then remains constant throughout the titration. When the solution is allowed to warm up, to room temperature in a closed system, the $GeCl_4$ evaporates after the HCl, leaving only the tetramethylammonium hydrogen dichloride, Me_4NHCl_2, as a solid in the cell. Similar results are obtained with tetraethylammonium-chloride.

When nitrosyl chloride is condensed on $GeCl_4$ and then gradually warmed up, $GeCl_4$ and NOCl are miscible in all proportions but no compound formation occurs. Attempts by other workers[4]) to prepare $(NO)_2GeCl_6$ have also failed. Laubengayer and co-workers[2]) obtained Cs_2GeCl_6 as a flocculent yellowish white precipitate by the addition of $GeCl_4$ to a solution of caesium chloride in a mixture of ethanol and 12 N aqueous hydrochloric acid. Adoption of this technique, using tetramethylammonium chloride, tetraethylammonium chloride, triphenylchlormethane and phosphorous pentachloride as possible chloride ion donors, met with no success. The conditions were then modified systematically and the solvents methanol, ethanol, chloroform, benzene, toluene and nitrobenzene were used, in a variety of mixtures, in the presence and absence of water, and with or without the passage of dry HCl gas. Again no complex salt could be obtained.

Liquid $GeCl_4$ itself did not dissolve any of the chloride ion donors nor did it react with them. Nitrogen containing solvents of a more polar nature such as acetonitrile or pyridine cannot be employed since they form adducts with $GeCl_4$ themselves[5]),[6]).

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The Preparation of Co-Ordination Compounds of Boron with Halogen Ions as Ligands

In a recent communication[1]) concerning the preparation of vinyl- and alkyl dihalogenoboranes the possibility of the existence of complex anions of boron such as $RBX_{3-n}Y_n^-$ has been suggested. This prompts us to communicate the preparation of a number of new co-ordination compounds of boron in which BCl_3 and BF_3 have functioned as acceptors for halogen ions. The following compounds have been obtained.

Table

Compound	Analysis (%)	Description
Me_4NBCl_4	calc.: Cl = 62·5; B = 4·9 found: Cl = 62·5; B = 5·1	A white solid decomposes at 100° C into Me_4NCl and BCl_3
Et_4NBCl_4	calc.: Cl = 50·1; B = 3·8 found: Cl = 49·7; B = 3·8	Similar to Me_4NBCl_4
Me_4NBF_3Cl	calc.: Cl = 20·0; B = 6·1 C = 27·1; H = 7·1; N = 7·9 found: Cl = 17·5; B = 6·1 C = 25·5; H = 6·9; N = 7·6	A white solid, extremely sensitive to moisture
PCl_4BF_3Cl	calc.: Cl = 64·2; B = 3·9 F = 20·7; P = 11·2 found: Cl = 64·7; B = 3·8 F = 19·9; P = 11·3	A white solid, stable to dry air
$NOBF_3Cl$	calc.: Cl = 26·6; B = 8·1 found: Cl = 25·7; B = 7·9	A light yellow solid, with a high dissociation pressure at room temperature
$NO(BEt_3Cl)$	calc.: Cl = 21·7; B = 6.6 found: Cl = 21·0; B = 6·5	M.P. = – 36 to –38° C, forming a deep red liquid
PH_4BF_3Cl	calc.: Cl = 25·6; B = 7·8 found: Cl = 22·1; B = 7·7	A slightly yellowish solid, with a high dissociation pressure at room temperature
PH_4BCl_4	calc.: Cl = 75·9; B = 5·8 found: Cl = 73·9; B = 5·8	A fine white powder, behaviour similar to PH_4I
$POCl_3 \cdot BF_3$	calc.: Cl = 48·1; B = 4·9 F = 25·8; P = 14·1 found: Cl = 46·2; B = 5·0 F = 25·2; P = 14·1	A white solid, extremely hygroscopic; M.P. = – 3° C with dissociation into BF_3 and $POCl_3$

All the compounds listed in the table, together with others, have been prepared using anhydrous liquid hydrogen chloride as an ionizing solvent. Details of the experimental techniques employed will be given elsewhere[2]). It should be emphasized, however, that all the compounds listed above are extremely sensitive to moisture, and that all manipulations must be carried out in a dry-box. Of these compounds only Me_4NBCl_4, prepared by another method, has been described before[3]). The successful preparation of $NOBF_3Cl$ and of $POCl_3 \cdot BF_3$ provide striking examples of the usefulness of liquid HCl as a media in preparative inorganic chemistry. NOCl and BF_3 are reported to yield the compound $NOF \cdot 2BF_3$ by an unspecified direct interaction[4]), and previous attempts