THE NATURE OF THE INTERACTION OF NUCLEOPHILES SUCH AS HMPT, DMSO, DMF AND Ph3PO WITH TRIORGANOHALO-SILANES, -GERMANES, AND -STANNANES AND ORGANOPHOSPHORUS COMPOUNDS. MECHANISM OF NUCLEOPHILE INDUCED RACEMIZATION AND SUBSTITUTION AT METAL

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(Received July 10th, 1979)

Summary

The systematic conductivity studies of various triorganohalides of the main Group IV elements in the presence of nucleophiles known as racemization agents (HMPT, DMSO, DMF and Ph3PO) do not show the existence of ionic 1/1 adducts. Those observed with R_3SiBr and HMPT are a particular case due to lability of the Si—Br bond. The bromogermane and chlorostannane show very different behaviour. Molecular 1/1 and 1/2 adducts formed by interaction of nucleophilic reagents and Ph_3SnCl were obterved in polarographic studies. These observations confirm the existence of pentacoordinate or hexacoordinate species.

Introduction

The formation of ionic adducts between Me_3SiBr and HMPT was recently reported [1]. We now have undertaken a kinetic study of the racemization of triorganohalo-silanes, -germanes and -stannanes [2—4] catalysed by nucleophiles which indicates that two molecules of nucleophile are involved in attack at the metal atom. The racemization is second order in the nucleophile (Table 1) and the strongly negative activation entropy results suggest a highly organised transition state. These results are interpreted in terms of extension of coordination at silicon by the reversible formation of a pentacoordinated silicon intermediate in an initial step. This is followed by the attack of a second molecule of nucleophile in the rate-determining step, which involves either a symmetrical

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* No reprints available.

TABLE 1

COMPARISON BETWEEN RACEMIZATION AND HYDROLYSIS OF CHLOROSILANES

	rate low	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal mol^{-1} K^{-1})
Racemization			
i-PrPh-1-NpSiCl (HMPT/CCl$_4$)	$v = k_3[R_3SiCl][Nu]^2$	3.15	—55
EtPh-1-NpSiCl (HMPT/CCl$_4$)	$v = k_3[R_3SiCl][Nu]^2$	0.39	—57
Hydrolysis			
Ph$_3$SiCl (HMPT/anisole)	$v = k_3[R_3SiCl][Nu][H_2O]$	—3.4	—56
MePh-1-NpSiCl (DMSO/anisole)	$v = k_3[R_3SiCl][Nu][H_2O]$	1.6	—43

octahedral intermediate or a pentacoordinated siliconium ion. In both cases racemization will take place.

Hydrolysis catalysed by nucleophiles exhibits great similarities to the racemization [5], but the presence of a nucleophilic agent (such as HMPT, DMSO, DMF) changes the stereochemistry of this reaction and retention is observed instead of the inversion which normally occurs in the absence of a nucleophilic catalyst. The mechanism shown in Scheme 1 was therefore proposed.

SCHEME 1
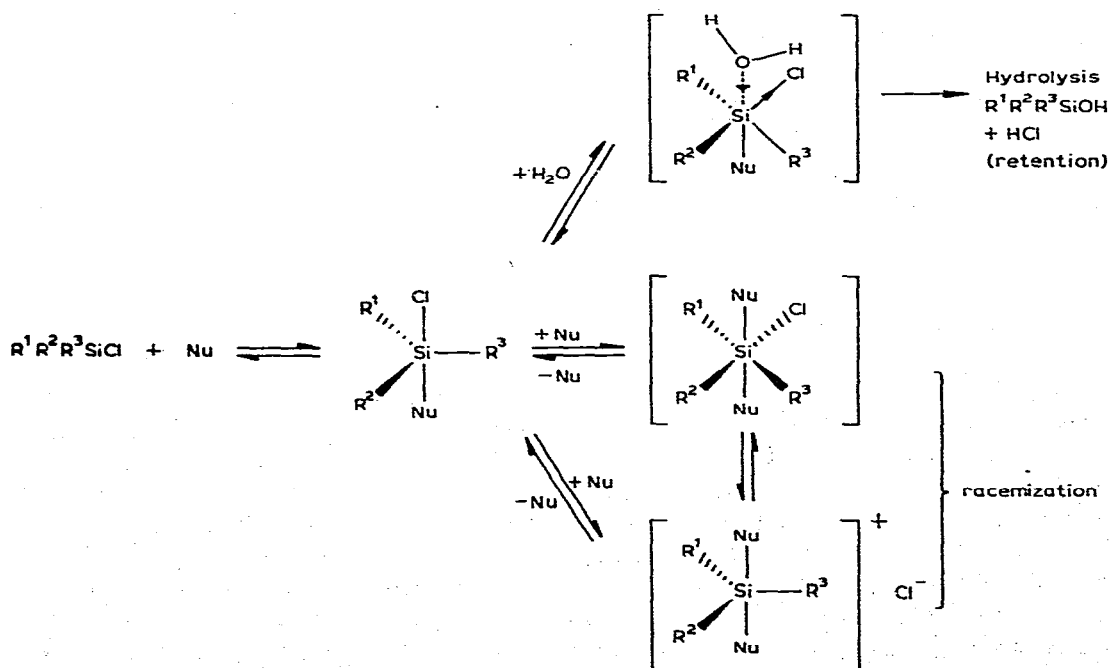
Chojnowski et al. [1] isolated the ionic 1/1 adducts [(Me$_2$N)$_3$POSiMe$_3$]$^+$X$^-$ from the interaction of HMPT with Me$_3$SiBr and Me$_3$SiI, (but not with Me$_3$SiCl).

Conductimetric titrations of HMPT with these halides gave curves indicating quantitative formation of 1/1 ionic adducts which are strong electrolytes.

$$(Me_2N)_3PO + Me_3SiX \rightarrow [(Me_2N)_3POSiMe_3]^+X^-$$
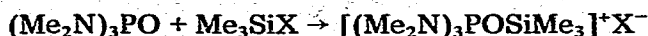
This behaviour is consistent with the formation of tris(dimethylamino)trimethyl-siloxyphosphonium halides. The results led the authors to propose another mechanism to explain the racemisation and hydrolysis data. In spite of the low conductivity observed with Me$_3$SiCl, they extended that mechanism to the chlorosilanes. The retention of configuration at silicon observed in hydrolysis catalysed by nucleophiles was explained in terms of two consecutive inversions, according to Scheme 2. Thus the HMPT-induced racemization of the halosilanes would involve nucleophilic attack of a second HMPT molecule at silicon in the phosphonium cation.

SCHEME 2
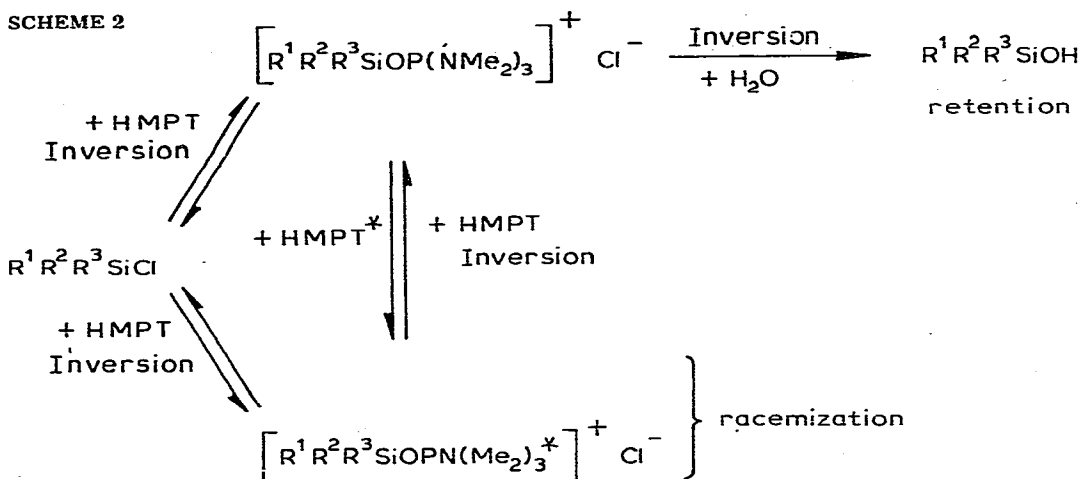
This proposal seems very unlikely for the following reasons:

(1) Although the high negative entropy of activation observed could be accounted for by ionic structures with ordered arrangement of the surrounding solvent molecules, Chojnowski's mechanism did not explain the low (or negative) value of the enthalpy of activation observed both in racemization and hydrolysis (cf. Table 1).

(2) Such a mechanism cannot account for the nucleophile-induced epimerization of chlorosilacyclobutanes, since with such a strained cycle retention of configuration is the only stereochemistry observed [6]. Thus two consecutive substitutions by HMPT could only give retention.

(3) The mechanism does not account for the racemization observed with other nucleophiles such as CH$_3$CN or RNO$_2$, which are too weakly nucleophilic to bring about the nucleophilic replacement of Si–X bonds, but are very efficient racemization agents.

(4) The low conductivity observed with chlorosilanes could be attributed to the HMPT-assisted hydrolysis of these compounds by traces of water present in the solvents [7] rather than to the formation of ionic adducts.

We have therefore re-examined aspects of the work of Chojnowski et al. in order

to see wether the mechanism they proposed was applicable to all halides or valid only in specific cases because of the lability of Si—Br and Si—I bonds towards nucleophiles. We have also extended the study to halostannanes which are known to be very easily racemisable in a process showing the kinetics by the same characteristics observed with the silicon compounds. We also studied halogermanes and chlorophosphorus compounds for which we previously demonstrated the possibility of nucleophile-activated hydrolysis and racemization.

Experimental

Following the procedure used by Chojnowski et al. [1] (who obtained a crystalline ionic product by adding Me_3SiBr to HMPT), we examined the behaviour of Ph_3SiCl, Ph_3SiBr, Ph_3GeBr, Et_3GeBr and Ph_3SnCl towards nucleophiles such as HMPT or Ph_3PO, which are known to be racemization catalysts. Although the chloro-germanes and -stannanes are more easily racemizable than the halosilanes, we did not obtain any crystallisable ionic adduct. However,
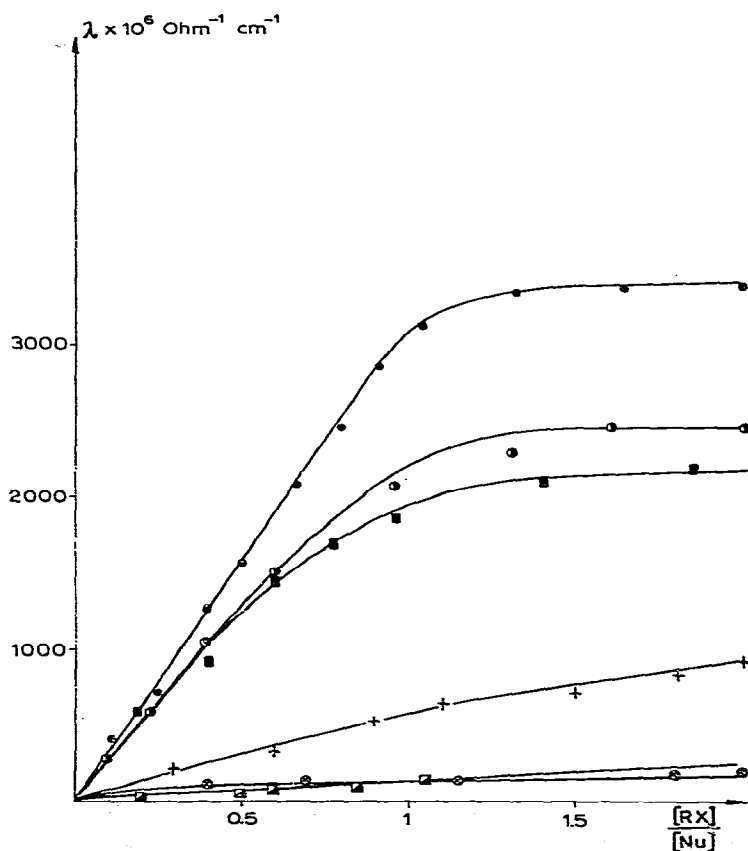

Fig. 1. Conductimetric titration of 0.11 M nucleophile solution in methylene chloride with halides: ● HMPT/Me_3SiBr, ◐ HMPT/Ph_3SiBr, ■ HMPT/$OPCl_3$, + Ph_3PO/Me_3SiBr, ◎ Ph_3PO/Ph_3SiBr, ⊟ HMPT/Ph_3SnCl.

1/1 adducts of HMPT with Ph_3SiBr or Ph_3SiCl were isolated as white crystals which separated on addition of HMPT to a solution of halide in hexane. Their identities were confirmed by proton NMR spectroscopy. The adducts are stable at ambient temperature. The conductivities of these adducts at 0.1 M concentration in CH_2Cl_2 are very different; we found 2000×10^{-6} Ohm^{-1} cm^{-1} for the Ph_3SiBr/HMPT adduct and only 100×10^{-6} Ohm^{-1} cm^{-1} for the Ph_3SiCl/HMPT adduct.

We also carried out conductimetric titrations of HMPT, Ph_3PO, DMSO and DMF solutions in methylene chloride against triorganohalo-silanes, -germanes and -stannanes, and also chlorophosphorus and chlorothiophosphorus compounds. Three types of behaviour were observed: (1) Formation of an ionic 1/1 adduct demonstrated by the breaks in conductimetric titration curves, as shown in Fig. 1. This was observed for Me_3SiBr/HMPT, Ph_3SiBr/HMPT, and $OPCl_3$/HMPT.

(2) An increase in conductivity (see Fig. 1) but without reaching a value characteristic of the 1/1 adduct while greater than that due to halide hydrolysis. This was observed for Me_3SiBr/Ph_3OP ($\lambda_1 = 600 \times 10^{-6}$ Ohm^{-1} cm^{-1}); Ph_3SiBr/
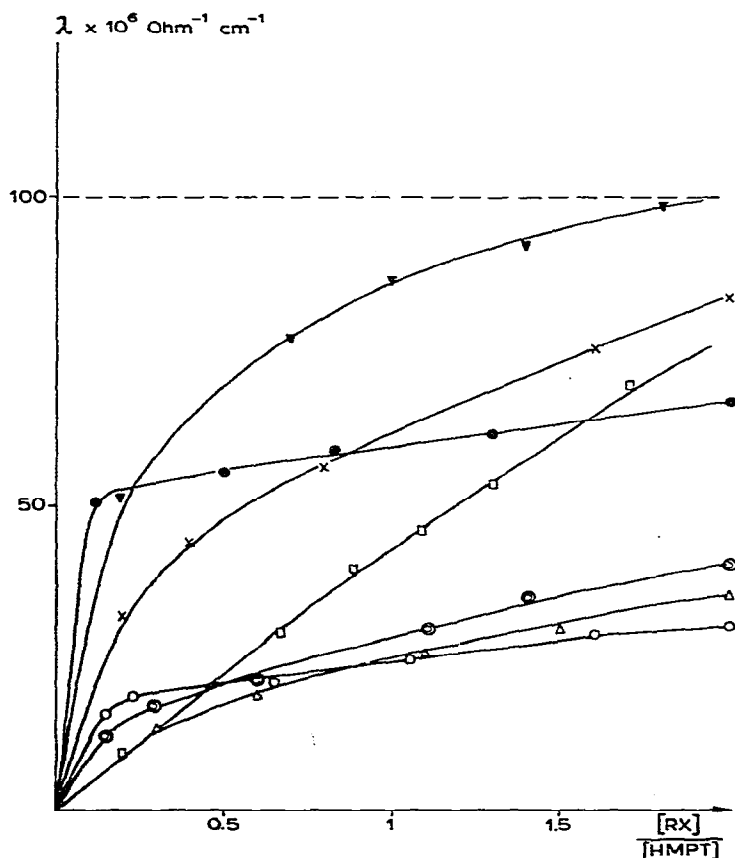

Fig. 2. Conductimetric titration of 0.11 M of HMPT solution in methylene chloride with halides: ▼ Me_3SiCl, × Ph_3GeBr, □ Bu_3SnCl, ● Ph_3SiCl, ◉ Et_3GeCl, △ Ph_3GeCl, ○ Et_3GeBr. ----- conductivity limit of HCl corresponding to hydrolysis of halides by residual water.

Ph_3PO ($\lambda_1 = 130 \times 10^{-6}$ Ohm^{-1} cm^{-1}) and $Ph_3SnCl/HMPT$ ($\lambda_1 = 130 \times 10^{-6}$ Ohm^{-1} cm^{-1}).

(3) In general case (including the case of Me_3SiBr/DMF, $\lambda = 10 \times 10^{-6}$ Ohm^{-1} cm^{-1}) the conductivities observed are less than those which can be attributed to hydrolysis of the halide. This is the commonly observed behaviour, and applies to the case of Me_3SiBr/DMF, $\lambda = 10 \times 10^{-6}$ Ohm^{-1} cm^{-1}.

The methylene chloride used always contained water. The water content rose rapidly with time even when rigorous precautions were taken to prevent moisture uptake during storage and solvent transfer operations. The water concentration in methylene chloride solutions varied between 1 mM and 12 mM. All the halogeno compounds undergo hydrolysis, catalysed by nucleophilic present in the solution, to HCl [5] or HBr. We therefore measured the conductivities of HCl or HBr solution of concentrations equivalent to that of water found in the solutions. It will be seen that the low conductivities obtained in the titration curves are generally lower than those obtained with HCl or HBr, the limits of the latter are indicated in Figs. 2—6.
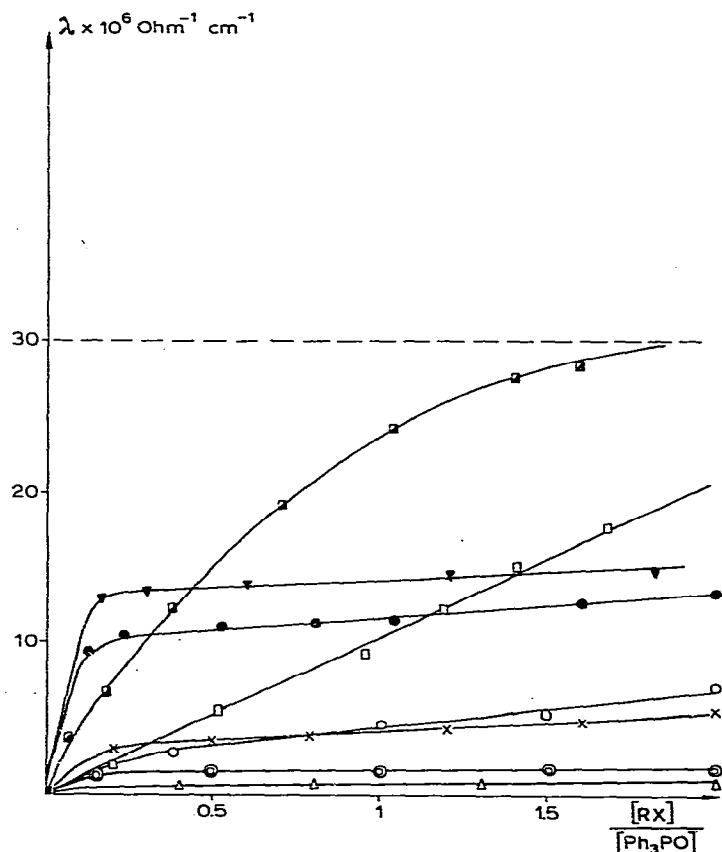

Fig. 3. Conductimetric titration of 0.13 M of Ph_3PO solution in methylene chloride with halides: ■ Ph_3SnCl, □ Bu_3SnCl, ▼ Me_3SiCl, ● Ph_3SiCl, ○ Et_3GeBr, x Ph_3GeBr, ⊙ Et_3GeCl, △ Ph_3GeCl.
------ Conductivity limit of HCl corresponding to hydrolysis of halides by residual water.
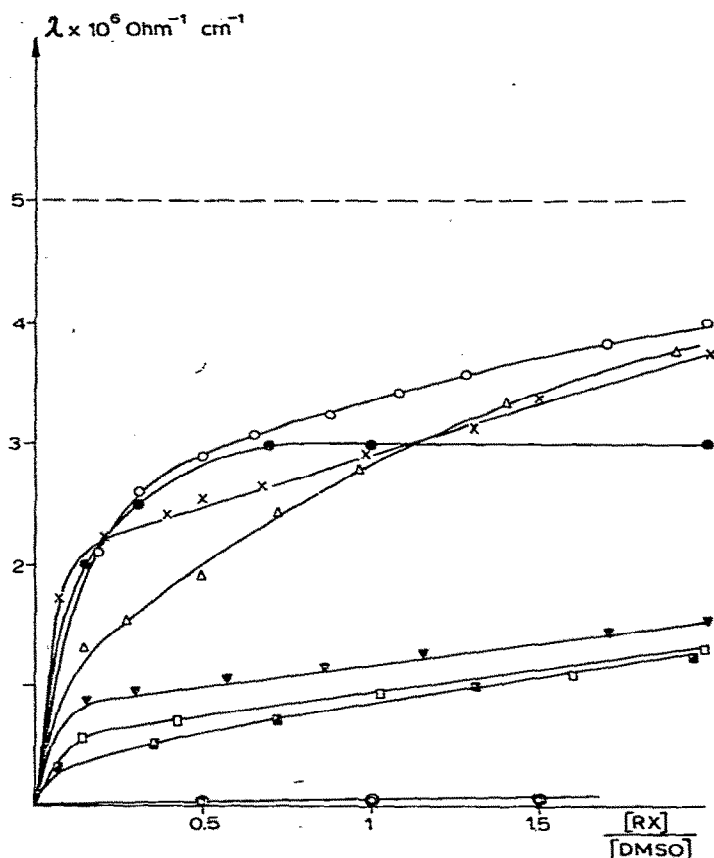
Fig. 4. Conductimetric titration of 0.14 M of DMSO solution in methylene chloride with halides: ■ Ph$_3$SnCl, ▢ Bu$_3$SnCl, ▼ Me$_3$SiCl, ● Ph$_3$SiCl, ○ Et$_3$GeBr, x Ph$_3$GeBr, ◇ Et$_3$GeCl, △ Ph$_3$GeCl.
- - - - - - Conducitivity limit of HCl corresponding to hydrolysis of halides by residual water.

We have studied in some detail the case of organotin compounds since they are the most racemisable [4—10] and most easily extend their coordination.
The measurement of the half wave potential by polarography allows the study of such complexes. The half wave potential changes with the concentration of a complexing agent Nu, according to the equation.

$$E_{1/2} = \frac{0.058}{n}\ (pK_f + m\ \log[Nu])$$

where Nu = HMPT, Ph$_3$PO, DMSO (= Nucleophile)
The slope of the appropriate plot gives the number of ligands (m) and the intercept on the y-axis gives the constant formation K_f. The results obtained are indicated in Table 2. In the case of DMF the displacement of the polarographic wave is too small to permit a precise measure, but we conclude that the same behaviour takes place to some extent.
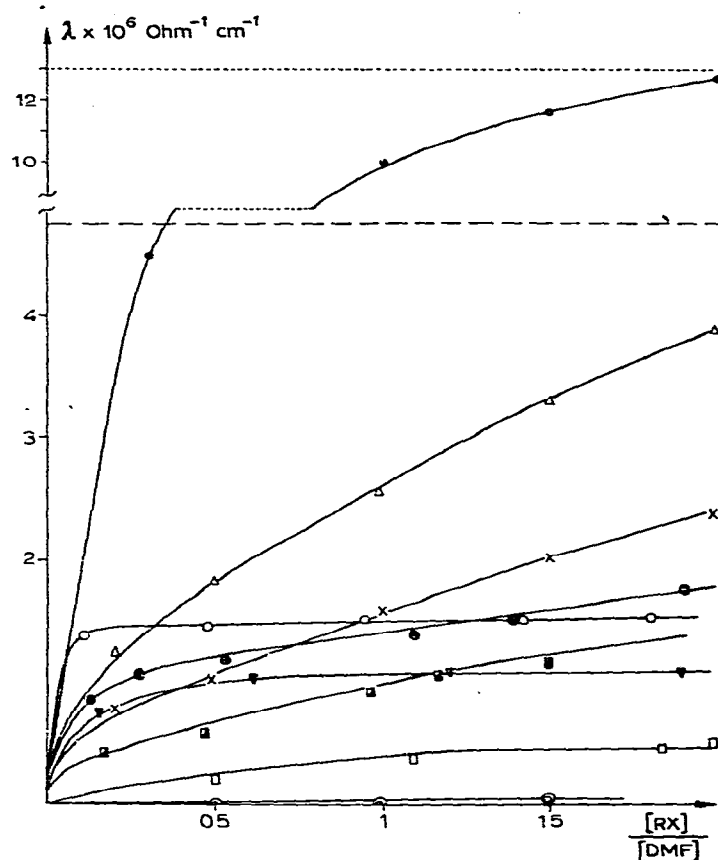
Fig. 5. Conductimetric titration of 0.13 M of DMF solution in methylene chloride with halides: ■ Ph₃SnCl, □ Bu₃SnCl, ▼ Me₃SiCl, · Me₃SiBr, ● Ph₃SiCl, ○ Et₃GeBr, x Ph₃GeBr, ⊙ Et₃GeCl, △ Ph₃GeCl.
- - - - - Conductivity limit of HCl corresponding to hydrolysis of halides by residual water.
—·—·—·— Conductivity limit of HBr corresponding to hydrolysis of halides by residual water.

TABLE 2

RESULTS OF CONSTANT FORMATION AND NUMBER OF LIGANDS FROM POLAROGRAPHIC
MEASUREMENTS

(The last three lines correspond to determinations of compounds obtained from other physical methods,
IR, NMR and calorimetry)

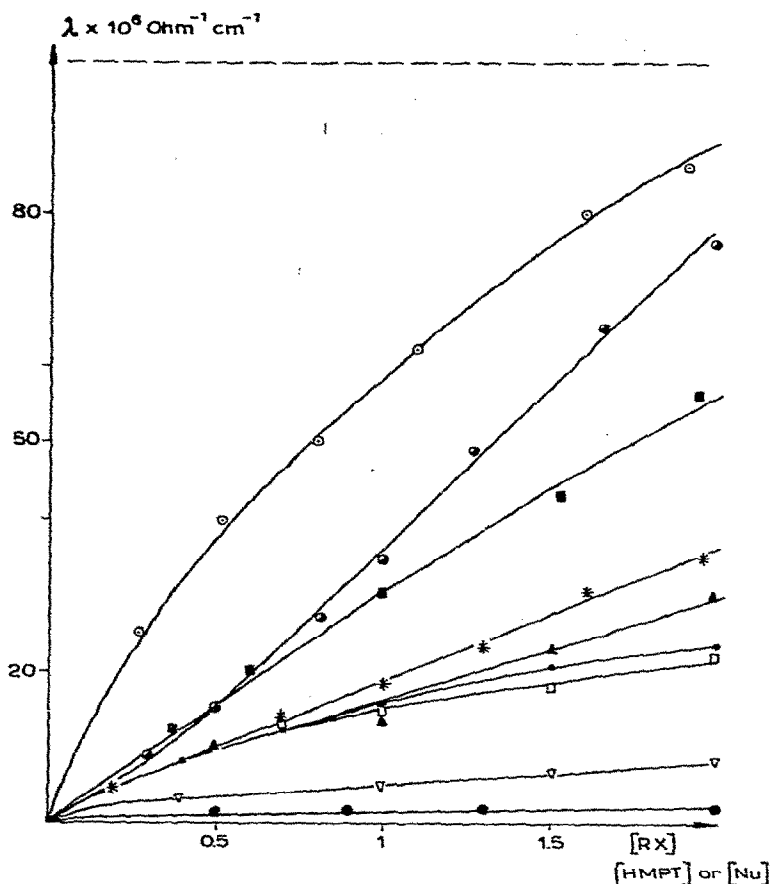| R_3SnCl	Complexing nucleophile	Solvent	Number of ligands	K_f (M^{-1})	Reference
Bu₃SnCl	DMSO	DME	1	20	
Bu₃SnCl	HMPT	DME	1	315	
Ph₃SnCl	Ph₃PO	DME	1	355	
Ph₃SnCl	DMSO	DME	2	4000 [a]	
Ph₃SnCl	HMPT	DME	2	150000 [a]	
Ph₃SnCl	DMSO	MeCN	1	50	
Me₃SnCl	HMPT	Isooctane	1	380	8
Me₃SnCl	DMSO	Isooctane	1	9	8
Me₃SnCl	Ph₃PO	Toluene	1	100	9

[a] K_f (M^{-2}).

Fig. 6. Conductimetric titration of 0.11 M nucleophile solution in methylene chloride with halides: ⊚ HMPT/Menthylchloro(phenyl)phosphonate; ◉ HMPT/2-chloro-2-oxo-1,2,3-dioxophosphorinane; ■ HMPT/2-chloro-2-oxo-1,3,2-dioxophospholane, * HMPT/O,O-diethylchlorothiophosphate; ◌ HMPT/O-ethylchloro(phenyl)thiophosphonate; △ HMPT/dichloro(phenyl)thiophosphonate; • N,N-dimethylacetamide/OPCl₃; ▽ DMF/mentyhlchloro(phenyl)phosphonate; ● DMF/O-ethylchloro(phenyl)thiophosphonate.

Discussion

The features of the results are as follows:

(1) The triorganohalo-germanes and -stannanes, which are even more easily racemisable than triorganohalosilanes, do not give ionic adducts with HMPT or with other nucleophiles. Thus the ease of racemization (especially in the case of the tin compounds) does not seem connected with the existence of ionic 1/1 adducts.

(2) In hexane, triphenylchlorosilane gives a crystalline adduct with HMPT as does Me₃SiBr, but this adduct is not ionic; the conductivity of a 0.1 M solution of this adduct in methylene dichloride is the same as that due to hydrolysis of the halides by the water in the solvent ($\lambda = 100 \pm 10 \times 10^{-6}$ Ohm^{-1} cm^{-1}). A similar result is observed in the case of the 1/1 Ph₃PO/Me₃SiCl adduct;

the formation of the latter has been demonstrated by ^{31}P NMR spectroscopy [9] but the conductivity of 1/1 mixtures in methylene dichloride is very low ($\lambda = 10 \pm 3 \times 10^{-6}$ Ohm^{-1} cm^{-1}). Thus the complexes between R$_3$SiX and nucleophiles do not necessarily have ionic structures.

(3) Nucleophiles such as DMF which are effective in the racemization of optically active compounds, do not give 1/1 ionic adducts even with Me$_3$SiBr ($\lambda = 10 \times 10^{-6}$ Ohm^{-1} cm^{-1}) or Ph$_3$SiBr ($\lambda = 2 \times 10^{-6}$ Ohm^{-1} cm^{-1}). In both cases the conductivities observed were lower than those corresponding to hydrolysis.

(4) The conductivity observed for most halide/nucleophile adducts is in the same range as that found for the HCl solution resulting from the nucleophile-activated hydrolysis of these halides by residual water (~4 mM) (The exception is in the case of R$_3$SiBr compounds).

From the above observations and in the light of formations given in the introduction, we conclude that the ionization process is a specific phenomenon due to the lability of the Si—Br bond and the affinity of silicon for oxygen. It is evident that not all racemization processes involve ionic 1/1 adducts.

The conductimetric behaviour of R$_3$MX is the same for M = Si, Ge, Sn or P; correspondingly we found the racemization process to be similar for all four elements. Despite the ease of their racemization, the tin compounds in methylene chloride have only a low conductivity, indicating that the process of racemization is more connected with the ability to increase the coordination number than to undergo ionization. This was confirmed by polarographic studies which show the existence in solution of 1/1 and 1/2 adducts between tin compounds and nucleophiles (Table 2). The tin compounds are known to give molecular pentavalent [11] or hexavalent complexes [12]. In DME solution, polarography shows the formation of the adducts: Ph$_3$SnCl/Ph$_3$PO, Ph$_3$SnCl/2 HMPT, and Ph$_3$SnCl/2 DMSO. However, the formation of a 1/1 Ph$_3$SnCl/HMPT complex in MeCN solution, rather than the 1/2 adducts observed in DME, can be interpreted in terms of coordination to tin of one mole of acetonitrile, suggesting the trimolecular complex HMPT/Ph$_3$SnCl/MeCN analogous to that proposed by Zeldin [9], viz: Ph$_3$PO/Me$_3$SiCl/MeCN, involves increase in the coordination number of the element.

The very easy racemization and the low conductivity of 1/1 or 1/2 complexes are inconsistent with the ionic process. In this connection the case of the 1/2 complexes is interesting. The formation of such complexes is associated with a very low conductivity. If the racemization took place by the ionic process, we would expect an ionic structure for the 1/2 complex:

R$_3$SiX + Nu $\rightleftharpoons$ [R$_3$SiNu]$^+$X$^-$

[R$_3$SiNu]$^+$X$^-$ + Nu $\rightleftharpoons$ [NuR$_3$SiNu]$^+$X$^-$
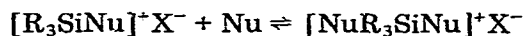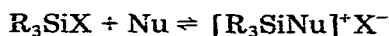
Thus we can conclude that the existence of 1/2 complexes with a very low conductivity excludes the ionic process.

All the observations are more consistent with the existence of an equilibrium relating to the extension of coordination, and possibly to some extent with ionisation of the 1/2 complexes.

The case of tin compounds shows that the ability to undergo racemization

is connected with the ability to increase the coordination number. Thus, since silicon, germanium, tin and phosphorus compounds show similar conductimetric and kinetic behaviour, we conclude that the mechanism involving coordination number extension applies to these also (Scheme 3).

SCHEME 3
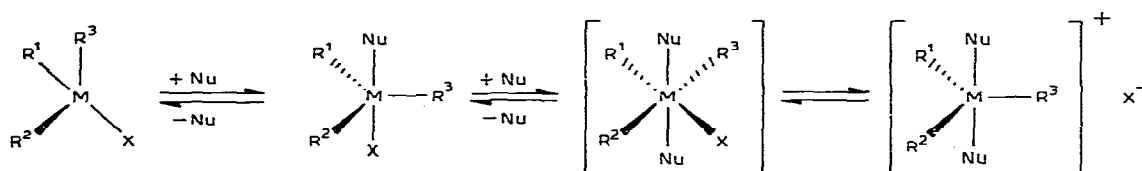
Finally we note that the importance of the close analogy between the behaviour of the phosphorus and silicon compounds. We have shown that halophosphorus compounds undergo nucleophile activated racemization and hydrolysis [13] in the same way as halosilanes. We have now demonstrated the close similarity between the conductivities of nucleophile-chlorophosphorus and -chlorosilicon compounds. This further confirms the similarity between the mechanisms for halogen-silicon and -phosphorus compounds [13].

Conclusion

The existence of ionic complexes is thus a particular case which can not be generalised. We conclude that for silicon, germanium, tin and phosphorus compounds racemization and nucleophilic substitution are both activated by nucleophiles and can be considered as a coordination extension process as shown in Scheme 1.

Experimental

Purification of solvents and reagents

DME and methylene chloride were distilled from AlLiH$_4$ under nitrogen. HMPT, DMSO and DMF were purified as described in ref. 4. Ph$_3$PO (Fluka A.G.) was used without further purification. All solutions were prepared under anhydrous conditions.

Products prepared by well known methods were triphenylchlorosilane, triphenylbromosilane [14], triphenylchlorogermane, triphenylbromogermane [15], n-tributylbromogermane [15], triethylbromogermane [16] triethylchlorogermane [17], 2-chloro-2-oxo-1,3,2-dioxophosphirane; 2-chloro-2-oxo-1,3,2-dioxophospholane [18]. The preparation of methylchloro(phenyl)phosphonate and O-ethylchloro(phenyl)thiophosphonate is described elsewhere [19]. In other cases commercial products were used, namely trimethylbromosilane (Fluka purum), trimethylchlorosilane (Fluka purum) (which was purified by distillation immediately before use), O,O-diethylchlorothiophosphate (Ega chimie), trichlorophosphine oxide (Merck) and the organotin compounds (Fluka A-6) (which were purified by recrystallization in the case of solids and by distillation in the case of liquids.

Adducts (1/1) of HMPT with triphenylbromosilane and triphenylchlorosilane

were obtained by adding 3×10^{-3} mol (520 μl) of HMPT to 3×10^{-3} mol of triphenylbromosilane (i.e. 1.017 g) or triphenylchlorosilane (i.e. 882 mg) in hexane. The white precipitates were filtered off and dried in a glove box, NMR spectroscopy shows a shift of peak corresponding to HMPT but the adducts are too unstable to give mass spectra.

Conductimetric titration

A Tacussel conductimeter and a conductance cell with constant of 1.07 cm^{-1} were used. The conductance cell was contained in a Schlenk tube. For titrations of solutions the halides were added by a calibrated syringe. Dilution corrections were made.

For HBr at a concentration equivalent to that of water found in the solvent the limits of conductivity were with HMPT 315×10^{-6} ohm^{-1} cm^{-1}; with DMSO 50×10^{-7} ohm^{-1} cm^{-1}; and with DMF 13×10^{-6} ohm^{-1} cm^{-1}.
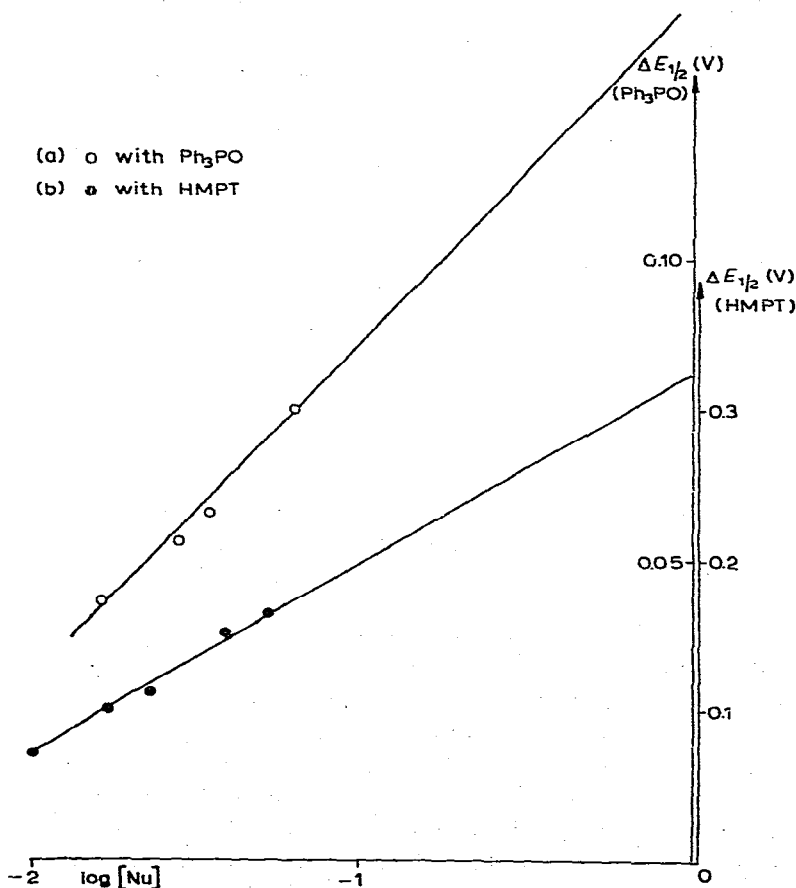
Fig. 7. Plots of $E_{1/2}$ vs. lg[Nu]. $\Delta E_{1/2} = E_{1/2}^1$ (with Nu) $- E_{1/2}^1$ (without Nu). The $E_{1/2}^1$ is the first wave potential of polarograms of Ph$_3$SnCl performed in 0.1 M TBAP/1,2-dimethoxyethane solution. (a) Ph$_3$SnCl: 3.4 10^{-3} M; Nu added = Ph$_3$PO = 2.0, 3.3, 4.8 and 6.6×10^{-2} M; slope 0.056 → ligand number $m = 0.96$. (b) Ph$_3$SnCl: 4.2×10^{-3} M; Nu added = HMPT = 1.4, 2.1, 2.8, 4.3 and 5.7×10^{-2} M; slope 0.126 → ligand number $m = 2.1$.

Polarographic measurements

Conventional three-electrode equipement was used. The reference electrode was n-Bu$_4$NI$_{Sat.}$, AgI/Ag system. A silver wire coated with silver iodide (obtained by electrolysis) placed in a tube closed by a sintered glass disk and filled with a saturated solutions of n-Bu$_4$NI. Platinum wire anode and dropping mercury cathode were used. Polarograms were recorded using a Tacussel PRT 10-05 L potentiostat and a Tacussel UAP 3 with mechanical control of the drop time. All experiments were performed at ambient temperatures under nitrogen. The polarograms were obtained using ≈4 mM of R$_3$SnCl in 20 ml of 0.1 M TBAP in 1,2-dimethoxyethane solution. The HMPT (or DMSO) was added from a calibrated syringe.

An example of the graphic determination of the number of ligands is given in Fig. 7. The slope gave the number of ligands $m = \dfrac{S}{0.058}$. The intercept on the y axis is $\dfrac{0.058}{n} pK_f$ (K_f is the formation constant fo the complex).

References

1 J. Chojnowski, M. Cypryk and J. Michalski, J. Organometal. Chem., 161 (1978) C31.
2 R. Corriu and M. Henner-Léard, J. Organometal. Chem., 64 (1974) 351; 74 (1974) 1.
3 F. Carré, R. Corriu and M. Léard, J. Organometal. Chem., 24 (1970) 101.
4 M. Gielen and H. Mohktar-Jamai, J. Organometal. Chem., 91 (1975) C33; 129 (1977) 325.
5 R.J.P. Corriu, G. Dabosi and M. Martineau, J. Organometal. Chem., 150 (1978) 27; 154 (1978) 33.
6 M.G. McKinnie, N.S. Bhacca, F.K. Cartledge and J. Fayssoux, J. Amer. Chem. Soc., 96 (1974) 2637.
7 A.B. Thomas and E.G. Rochow, J. Amer. Chem. Soc., 79 (1957) 1843.
8 T.F. Bolles and R.S. Drago, J. Amer. Chem. Soc., 88 (1966) 3921.
9 M. Zeldin, P. Mehta and W. Vernon, Inorg. Chem., 18 (1979) 463.
10 M. Gielen and Y. Tondeur, J. Organometal. Chem., 169 (1979) 265.
11 G.V. Koten and J.G. Noltes, J. Organometal. Chem., 118 (1976) 183.
12 P.G. Harrison and A. Mangia, J. Organometal. Chem., 120 (1976) 211.
13 R.J.P. Corriu, G.F. Lanneau and D. Leclerc, Chem. Commun., (1978) 104.
14 V. Bazant, V. Chavalowsky and J. Rathousky, Organosilicon compounds, Academic Press, New York, 1965.
15 M. Lesbres, P. Mazerolles and J. Satgé, The Organic compounds of germanium, Wiley-Interscience, London, 1971.
16 C. Eaborn and K.C. Pande, J. Chem. Soc., (1960) 3200.
17 H. Sakurai, K. Tominaga, T. Watanabe and M. Kumada, Tetrahedron Lett., (1966) 5493.
18 R.S. Edmundson, Chem. and Ind., (1962) 1828.
19 R.J.P. Corriu, G.F. Lanneau and D. Leclerc, in press.