Journal of Organometallic Chemistry, 161 (1978) C31—C35

Preliminary communication

THE NATURE OF THE INTERACTION BETWEEN HEXAMETHYLPHOSPHORTRIAMIDE AND TRIMETHYLHALOSILANES; CATIONS CONTAINING TETRACOVALENT SILICON AS POSSIBLE INTERMEDIATES IN NUCLEOPHILE-INDUCED SUBSTITUTION OF SILICON HALIDES

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(Received August 7th, 1978)

Summary

Stable ionic 1/1 adducts, thought to be of the type $[(Me_2N)_3POSiMe_3]^+ X^-$, have been isolated from the interaction of HMPT with the halides Me_3SiX (X = Br or I). Conductometric studies show that the equilibrium for formation of these adducts in CH_2Cl_2 lies well over to the products for X = Br or I, but for X = Cl the equilibrium lies close to the reactants. The known kinetic characteristics of reaction involving HMPT-catalysed racemisations or substitutions of silicon halides can be interpreted in terms of the formation of such phosphonium intermediates.

Hexamethylphosphortriamide (HMPT) is a very effective catalyst for racemization of optically active triorganohalosilanes [1—4]. The reaction in several solvents is second order in the phosphoroamide and has very low activation energy and large negative entropy of activation. Of the various mechanisms considered, all involved formation of an intermediate containing silicon with expanded valency. HMPT was also found to assist halosilane hydrolysis [5] and halogen exchange at silicon [6]. Some of these processes are highly stereoselective and lead to the products with retention of configuration at silicon. Mechanisms involving nucleophilic attack of the other reagent on the silicon coordinated to HMPT with the formation of a six-coordinated silicon transition state or intermediate were proposed.

On the other hand the reaction of trimethyliodosilane as well as of trimethylbromosilane with esters of phosphorus was shown to proceed through phosphonium salt intermediate [7,8]. In our recent studies [8] we noticed that the formation of this salt constituted the first reversible step, which was fast on the ^{31}P NMR time scale even at −80°C. It thus seemed likely that the catalytic activity of HMPT in some substitutions at silicon involved analogous behaviour, and that in order to test this idea the HMPT adducts with trimethylbromosilane and trimethyliodosilane were isolated and characterized and conductometric studies were made on HMPT/trimethylhalosilanes solutions.

The conductivities of methylene chloride solutions of the trimethylhalosilanes measured were very low, comparable with the conductivity of the solvent itself. However a ternary system involving HMPT and trimethyliodosilane or trimethylbromosilane showed a considerable conductivity (the molar conductivity at 0.1 mol dm^{-3} of both components was about 30 ohm^{-1} cm^2 mol^{-1}). The results of conductometric titration of HMPT with the halides are shown in Fig. 1. The curves for trimethylsilyl bromide and iodide indicate quantitative formation of 1/1 adducts which are strong electrolytes.

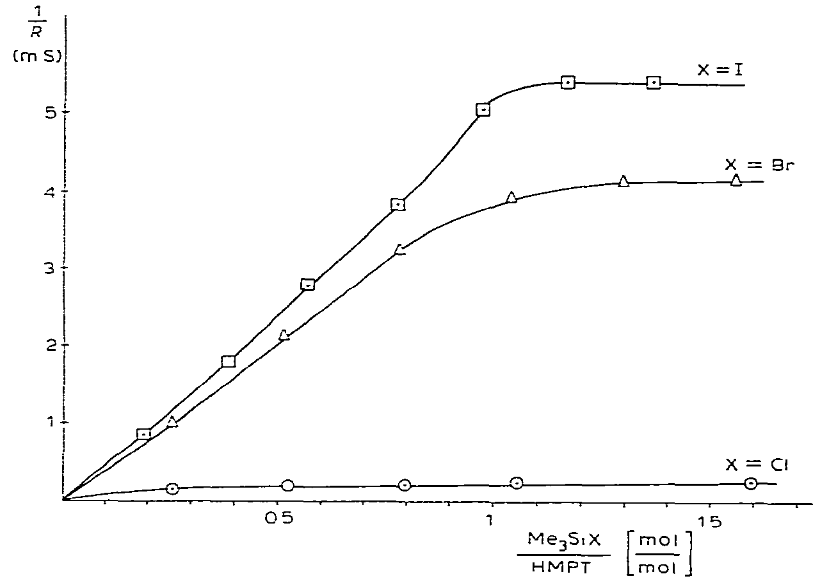
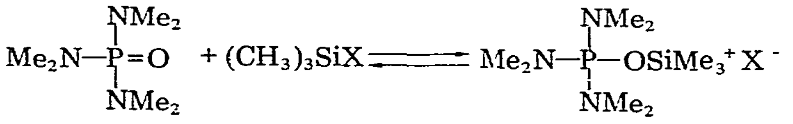


Fig. 1. The conductometric titration of 0.12 mol dm^{-3} HMPT solution in methylene chloride with trimethylhalosilanes: ○, $(CH_3)_3SiCl$; △, $(CH_3)_3SiBr$; □, $(CH_3)_3SiI$.

These results are best interpreted in terms of the formation of tris(dimethylamino)trimethylsiloxyphosphonium halides according to eq. 1. The curve for the titration of HMPT with trimethylchlorosilane is different; the increase of the conductivity with the amount of the silane is much smaller, but it is still observed, even when a large excess of the silane is present. Presumably the position of eq. 1 lies to the right in the case of iodo and bromo derivatives but is shifted to the side of reactants in the case of chloride. It should be empha-



$$Me_2N\!-\!\underset{NMe_2}{\overset{NMe_2}{P}}\!=\!O + (CH_3)_3SiX \rightleftharpoons Me_2N\!-\!\underset{NMe_2}{\overset{NMe_2}{P}}\!-\!OSiMe_3^+X^- \qquad (1)$$

(X = Cl, Br, I)

sized that the formation of the phosphonium salt from HMPT and trimethylhalosilanes is not surprising since a similar salt was obtained earlier from trimethylphosphine oxide and trimethyliodosilane [9].

Adducts of HMPT with trimethylsilyl bromide and iodide were isolated as white crystals precipitated by addition of trimethylsilyl halides to the solution of HMPT in n-heptane. Their identities were confirmed by elemental analysis and ^1H NMR spectroscopy (Table 1). The complex of Me_3SiI with triphenylphosphine oxide was also isolated for comparison. The compounds are stable at ambient temperatures, but are extremely sensitive to moisture.

TABLE 1

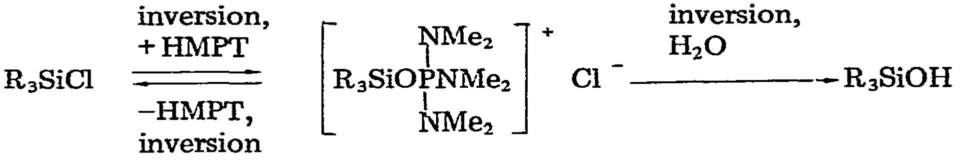
PROPERTIES OF ADDUCTS OF TRIMETHYLHALOSILANES WITH SOME COMPOUNDS CONTAINING PHOSPHORYL GROUPS

Adduct	Elemental analysis[a] (%)			M.p.[b] (°C)	^1H NMR[c] (ppm)	^{31}P NMR[c]	
	Si	N	X			δ (ppm)	Δδ (ppm)[d]
$HMPT \cdot Me_3SiBr$	8.60	13.0	24.6	40	$0.4(s;18H;Si(C\underline{H}_3)_3)$;	26.2 (m)	3
	(8.43)	(12.7)	(24.1)		$2.8(d;36H;P[N(C\underline{H}_3)_2]_3)$		
$HMPT \cdot Me_3SiI$	7.40	11.2	33.5	85	$0.4(s;18H;Si(C\underline{H}_3)_3)$;	26.2 (m)	3
	(7.33)	(11.1)	(33.34)		$2.8(d;36H;P[N(C\underline{H}_3)_2]_3)$		
$Ph_3PO \cdot Me_3SiI$						51 (m)	15
$MeEtPhPO \cdot Me_3SiI$						74 (m)	36

[a] Calculated values are given in brackets.
[b] With partial decomposition.
[c] In methylene chloride.
[d] The change of chemical shift on salt formation.

The ^{31}P NMR signals for both HMPT complexes show almost the same chemical shift, but are only about 3 ppm downfield from the HMPT signal. The solution containing excess of HMPT over the silane shows only one signal whose chemical shift adopts an average value of the value for HMPT and the value for the phosphonium halide, what confirms that reaction 1 could constitute a fast equilibrium step in substitution at silicon. The small difference between the ^{31}P NMR chemical shift of HMPT and that of the phosphonium cation is presumably due to an increased electron back donation from nitrogens to phosphorus, which partly disperses positive charge from phosphorus to its ligands and consequently increases the shielding of the phosphorus nucleus. A large effect of the interaction of the phosphoryl group with trimethyliodosilane on the ^{31}P NMR chemical shift is demonstrated in the case of the triphenylphosphine oxide/iodosilane complex ($\Delta\delta$ +15 ppm). A still larger effect is observed for phosphine oxide with alkyl groups at phosphorus (see Table 1). The interaction of trimethyliodosilane with phosphates causes an additional shift of ca. +10 ppm [8].

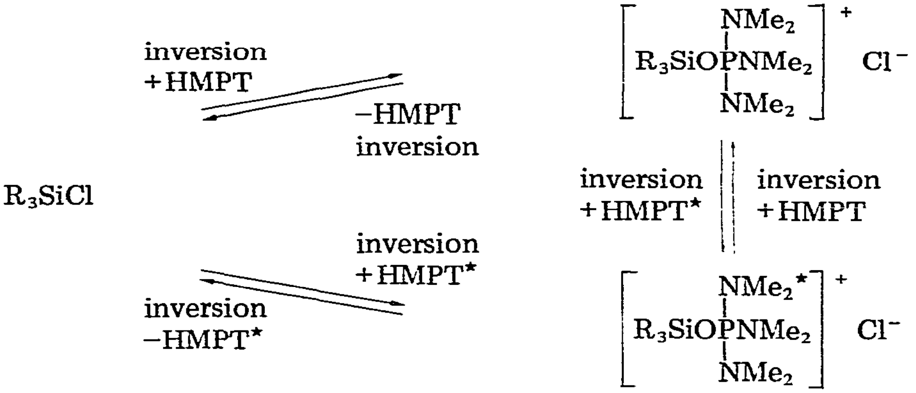
The above results indicate that the mechanism of HMPT induced substitution of halogen at silicon may involve the transient formation of a phosphonium cation. This cationic species contains a four-coordinated silicon atom. The retention of configuration at silicon observed in hydrolysis of triorganochlorosilane may be a result of two consecutive inversions according to eq. 2.



$$R_3SiCl \underset{-HMPT,\ \text{inversion}}{\overset{\text{inversion},\ +HMPT}{\rightleftharpoons}} \left[R_3SiO\overset{NMe_2}{\underset{NMe_2}{P}}NMe_2\right]^+ Cl^- \xrightarrow{\text{inversion},\ H_2O} R_3SiOH \qquad (2)$$

When the first step constitutes a fast equilibrium lying on the side of the halosilane, which is the case for trimethylchlorosilane in methylene chloride, and may be the case for some other triorganosilyl halides in some solvents, the rate of the reaction would be proportional to the concentration of both reagents, the silane and water, as well as to the concentration of HMPT. This would explain the third order of the reaction observed earlier [5].

The HMPT-induced racemisation of the halosilanes may involve a similar mechanism, involving nucleophilic attack of an other HMPT molecule on silicon in the phosphonium cation which results in exchange of an HMPT molecule in the intermediate with inversion of configuration at the silicon atom as in eq. 3.



$$\begin{tikzcd} & {\left[R_3SiO\overset{NMe_2}{\underset{NMe_2}{P}}NMe_2\right]^+ Cl^-} \arrow[dl, shift left, "\text{inversion}\ -HMPT"] \arrow[d, shift left, "\text{inversion}\ +HMPT"] \\ R_3SiCl \arrow[ur, shift left, "\text{inversion}\ +HMPT"] \arrow[dr, shift left, "\text{inversion}\ +HMPT^*"] & \\ & {\left[R_3SiO\overset{NMe_2^*}{\underset{NMe_2}{P}}NMe_2\right]^+ Cl^-} \arrow[ul, shift left, "\text{inversion}\ -HMPT^*"] \arrow[u, shift left, "\text{inversion}\ +HMPT^*"] \end{tikzcd} \qquad (3)$$

When the rate of reversal of the salt to the halosilane is faster than HMPT exchange the racemization would be of second order in HMPT, as observed [1—4]. At higher HMPT concentrations the rate of exchange may become comparable to or even faster than the rate of reversion R$_3$SiCl, and this would lead to a complex dependence of the rate on the HMPT concentration or finally to a system of first order in HMPT. Such kinetics have been observed [10].

It is worth mentioning that a decrease of temperature should shift eq. 1 to ionic form, and this would lead to low values for the activation energies of HMPT-induced hydrolysis and racemization of halosilanes [3,5]. Transition states in these processes would have almost ionic structures with a highly ordered arrangement of the surrounding solvent molecules, which would explain the high negative entropies of activation observed [3,5].

A mechanism of HMPT-induced halogen substitution involving the formation of a tetracovalent silicon cation intermediate is thus in agreement with most of the kinetic and stereochemical data. The catalytic action of some other nucleophiles such as DMF and DMSO may involve analogous mechanisms, especially since formation of adducts of halosilanes with nucleophilic species is rather common [11,12].

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