Some Metal Halide–Phosphorus Halide–Alkyl Halide Complexes. Part I. Reactions with Boron, Aluminium, Silicon, Germanium, and Tin Halides

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The reaction systems metal chloride–phosphorus trichloride–tert-butyl chloride (metal = Al, B, Si, Ge, or Sn) and metal chloride–methyldichlorophosphine–tert-butyl chloride (metal = B, Ge, or Sn) have been investigated. Solid products were obtained in each case with the exception of silicon and germanium. These solids have been characterised by vibrational spectroscopy as ionic complexes of alkylchlorophosphonium cations with the univalent anionic species $AlCl_4^-$, BCl_4^-, and $SnCl_5^-$.

ALTHOUGH the complexes of aluminium trichloride with phosphorus trichloride and alkyl chlorides have been much used as starting materials for the synthesis of organophosphorus compounds,[1-8] little work to determine the structure of these complexes has been attempted. From conductivity[1] and thermographic[9] measurements, the ionic structure $[RPCl_3^+][AlCl_4^-]$ (R = alkyl) has been proposed but no vibrational or crystallographic data has been presented. Since it seemed likely that other metal chlorides might form complexes, we have investigated the MCl_x–PCl_3–RCl system with boron trichloride, silicon, germanium, and tin tetrachlorides as well as aluminium trichloride; tert-butyl chloride was used as the alkylating agent because of its known reactivity[1] with aluminium trichloride and phosphorus trichloride. In this paper, we present i.r., and where possible, Raman spectra of the reaction products of these systems. In addition, we report

TABLE 1

Preparations and Analyses

System	Rate of formation of solid *	Analyses			Notes	Suggested structure †
		% P	% Metal	% Cl		
$AlCl_3 + PCl_3 + Bu^tCl$	Very fast	8·55	7·5	68·7	$C_4H_9PAlCl_7$ requires P, 8·55; Al, 7·45; Cl, 68·3%	$[Bu^tPCl_3][AlCl_4]$
$BCl_3 + PCl_3 + Bu^tCl$	Very slow	8·8		71·0	$C_4H_9PBCl_7$ requires P, 8·9; Cl, 71·5%	$[Bu^tPCl_3][BCl_4]$
$SiCl_4 + PCl_3 + Bu^tCl$	No solid product obtained					
$GeCl_4 + PCl_3 + Bu^tCl$	No solid product obtained					
$SnCl_4 + PCl_3 + Bu^tCl$	Very slow	6·3	24·6	57·5	$C_4H_9PSnCl_8$ requires P, 6·3; Sn, 24·2; Cl, 57·85%	$[Bu^tPCl_3][SnCl_5]$
$BCl_3 + MePCl_2 + Bu^tCl$	Fast	13·3		75·8	CH_3PBCl_5 requires P, 13·25; Cl, 75·7%	See text
$GeCl_4 + MePCl_2 + Bu^tCl$	No solid product obtained					
$SnCl_4 + MePCl_2 + Bu^tCl$	Moderate	6·3	25·2	52·8	$C_5H_{12}PSnCl_7$ requires P, 6·6; Sn, 25·25; Cl, 52·8%	$[Bu^tMePCl_2][SnCl_5]$

* Rate of formation varied from very fast (10 s) to very slow (poor yield after 1—2 weeks). † Based on vibrational spectra discussed later.

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[1] A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 1952, 3437.

[2] J. P. Clay, *J. Org. Chem.*, 1951, **16**, 892.

[3] F. W. Hoffmann, T. C. Simmons, and L. J. Glunz, *J. Amer. Chem. Soc.*, 1957, **79**, 3570.

[4] S. Z. Ivin and K. V. Karavanov, *Zhur. obshchei Khim.*, 1958, **28**, 2958.

[5] I. P. Komkov, S. Z. Ivin, and K. V. Karavanov, *Zhur. obshchei Khim.*, 1958, **28**, 2960.

[6] K. V. Karavanov and S. Z. Ivin, *Zhur. obshchei Khim.*, 1963, **35**, 78.

[7] I. P. Komkov, K. V. Karavanov, and S. Z. Ivin, *Zhur. obshchei Khim.*, 1958, **28**, 2963.

[8] S. Z. Ivin, L. E. Dinitrieva, and K. V. Karavanov, *Zhur. obshchei Khim.*, 1966, **36**, 350.

[9] G. Lindner and P. O. Granbom, *Acta Chem. Scand.*, 1966, **20**, 432.

results for the systems MCl_x–$MePCl_2$–Bu^tCl, (M = B, Ge, and Sn).

RESULTS AND DISCUSSION

In agreement with the conclusions of the conductivity measurements of Kinnear and Perren,[1] the vibrational spectra of the compounds treated here can readily be interpreted in terms of univalent ionic species with the exception of the methyldichlorophosphine–boron trichloride adduct. In order to simplify interpretation, the spectra attributable to the cations are considered initially and then each anion is considered individually.

Cation Spectra.—The expected tert-butyltrichlorophosphonium cation $Bu^tPCl_3^+$ should be a distorted tetrahedron of symmetry C_{3v} with $\Gamma_{vib} = 3A_1(\text{i.r.,R}) + 3E(\text{i.r.,R})$. The similar species $MePCl_3^+$ has [10,11] a well-characterised spectrum with [10] $3A_1$ at 795, 491, and 247 and $3E$ at 629, 271, and 153 cm^{-1}. Several lines persisted in the spectra when the metal chloride was changed such that we assign the values listed in Table 2 to the cation by comparison with the known values for $MePCl_3^+$. The internal C–C and C–H vibrations of the tert-butyl group have been omitted.

The tert-butylmethyldichlorophosphonium cation $Bu^tMePCl_2^+$ has expected symmetry C_s with $\Gamma_{vib} = 6A'(\text{i.r.,R}) + 3A''(\text{i.r.,R})$ such that two P–C ($2A'$) and two P–Cl ($A' + A''$) stretching modes and five deformation modes ($3A' + 2A''$) are expected. The vibrational spectrum and tentative assignments for the cation of $[Bu^tMePCl_2][SnCl_5]$ are listed in Table 3 since the fundamentals of $SnCl_5^-$ are well-known [12,13] and are readily subtracted. Furthermore, the positions of the stretching modes are comparable to the reported spectrum [11] of $Me_2PCl_2^+$ (symmetry C_{2v}). The 631 cm^{-1} band is only observed in the i.r. and is of somewhat variable intensity. However, since only four stretching modes are expected, this band is probably an overtone or combination band in resonance with the 614 cm^{-1} band.

Anion Spectra.—(*i*) $AlCl_4^-$ *and* BCl_4^-. The vibrational spectra of these species have been reported several times; for $AlCl_4^-$, see ref. 14 and BCl_4^-, see ref. 15. The i.r. absorptions of $[Bu^tPCl_3][AlCl_4]$ and $[Bu^tPCl_3][BCl_4]$ attributable to these anions are shown in Table 4. The observed spectra are in good agreement with the literature values. Both species exhibit breakdown in the T_d selection rules with the appearance of ν_1 in the i.r. Bands not due to fundamentals have been tentatively assigned to various combination modes.

(*ii*) $SnCl_5^-$. The vibrational spectra of $[Bu^tPCl_3]$-$[SnCl_5]$ and $[Bu^tMePCl_2][SnCl_5]$ assignable to $SnCl_5^-$ are given in Table 5. The $SnCl_5^-$ anion is considered to be a trigonal bipyramid of symmetry D_{3h}; $\Gamma_{vib} = 2A_1'(\text{R}) + 2A_2''(\text{i.r.}) + 3E'(\text{i.r.,R}) + E''(\text{R})$. The observed spectra agree favourably with reported spectra.[12,13] However, the assignments of the deformation modes ν_4, ν_6, and ν_8 have been tentatively altered from the assignments of Creighton and Green [12] in view of the observed coincidences. Bands assigned to $SnCl_4$ probably result from decomposition of the samples whilst the spectra were being obtained. Both these complexes exhibit decomposition when heated to 40 °C.

TABLE 2

Vibrational assignments † of $Bu^tPCl_3^+$

$[Bu^tPCl_3]$-$[AlCl_4]$ i.r.	$[Bu^tPCl_3]$-$[BCl_4]$ i.r.	$[Bu^tPCl_3][SnCl_5]$ i.r.	$[Bu^tPCl_3][SnCl_5]$ Raman	Assignments
783vw	783vw	781vw		A_1 νP–C
482ssh	481m	483mw	485m	νP–Cl
229ms	229m	230w	234w	δPCl_3
642vs	640vs	641s	645vw	E νP–Cl
209mw	210mw	211w	213w	δBu^t–P–Cl
154wsh	159wbr	*	*	δCl–P–Cl

* This region obscured by strong anion vibrations. † Anion vibrations omitted in this Table.

TABLE 3

Vibrational assignments † of $Bu^tMePCl_2^+$

$[Bu^tMePCl_2]$ i.r.	$[SnCl_5]$ Raman	Assignments
803ms		A' νP–C(Me)
781ms		A' νP–C(Bu^t)
631s		Overtone or combination?
614vs	611vw	A'' νP–Cl
508s	507m	A' νP–Cl
248vw	250sh	
229vw		Deformation modes
212w	211w	

† Anion vibrations omitted in this Table.

TABLE 4

I.r. spectra * of $AlCl_4^-$ and BCl_4^-

$[Bu^tPCl_3][AlCl_4]$	$[Bu^tPCl_3][BCl_4]$	Assignments
844wbr	1130, 1075vwbr	$\nu_1 + \nu_3$
	923, 894vw	$\nu_2 + \nu_3$
491vs	723s (B^{10}), 696vs (B^{11})	ν_3
527ms	667s	$\nu_1 + \nu_4$
	490sh	$\nu_3 - \nu_2$?
349m	396mw	ν_1
	308mw	$\nu_3 - \nu_1$?
183s, 175s	275w	ν_4
	196vwsh	ν_2?
568w	350mw	
307w	260w	Other bands
74ms	78w	
64s	66w	
	46w	

* Cation vibrations omitted.

$MePCl_2,BCl_3$ *Adduct.*—The spectrum of this compound contains the vibrations expected for the adduct

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[10] I. R. Beattie, K. Livingston, and T. Gilson, *J. Chem. Soc.* (*A*), 1968, 1.

[11] R. Baumgartner, W. Sawodny, and J. Goubeau, *Z. anorg. Chem.*, 1964, **333**, 171.

[12] J. A. Creighton and J. H. S. Green, *J. Chem. Soc.* (*A*), 1968, 808.

[13] I. R. Beattie, T. Gilson, K. Livingston, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1967, 712.

[14] I. R. Beattie and M. Webster, *J. Chem. Soc.*, 1963, 38; J. Reddijk and W. L. Groeneveld, *Rec. Trav. chim.*, 1968, **87**, 513; K. Balasubrahmangam and L. Nanis, *J. Chem. Phys.*, 1965, **42**, 676; D. E. H. Jones and J. L. Wood, *Spectrochim. Acta*, 1967, **23A**, 2695.

[15] W. Kynaston, B. E. Larcombe, and H. S. Turner, *J. Chem. Soc.*, 1960, 1172; W. Garrard, E. F. Mooney, and H. A. Willis, *ibid*, 1961, 4255; L. Atkinson and P. Day, *J. Chem. Soc.* (*A*), 1969, 2423.

$MePCl_2,BCl_3$ but the fundamentals of the anion BCl_4^- are also clearly recognisible. For this anion to be present, ionic structures such as $[(MePCl_2)_2BCl_2][BCl_4]$ and $[MePCl][BCl_4]$ may be postulated. The former structure is not unlike the pyridine–BCl_3 adduct which is thought[16] to be $[(C_5H_5N)_2BCl_2][BCl_4]$. Cations such as PCl_2^+ have been postulated[17] but not identified, and we here tentatively assign the observed spectrum in terms of the equilibrium $MePCl_2,BCl_3 \rightleftharpoons [MePCl]$-$[BCl_4]$, (see Table 6). This complex was observed to sublime even at room temperature but a vapour-phase i.r. spectrum only indicated the presence of boron trichloride and methyldichlorophosphine. The instability of this compound and the associated difficulty in manipulation indicate that the structure may only be resolved by crystallography.

TABLE 5

Vibrational spectra † of $SnCl_5^-$

$[Bu^tPCl_3][SnCl_5]$		$[Bu^tMePCl_2][SnCl_5]$		
i.r.	Raman	i.r.	Raman	Assignments
404brsh	405w	404w	403wbr	ν_3, $SnCl_4$ *
368sh	368sh		364m	ν_1, $SnCl_4$ *
350vs	353m	360s	358sh	ν_5, E'
340sh	338vs	336wsh	333vs	ν_1, A_1'
314vs	312vw	321s		ν_3, A_2''
	269w		265mw	ν_2, A_1'
169vs	171w		170sh	ν_8, E''?
160vs		163m	161m	ν_4, A_2''?
150vs	152m	154brsh	147wsh	ν_6, E'?
	124vw	127vw	129wbr	ν_4, $SnCl_4$ *
	104w		97wbr	ν_2, $SnCl_4$ *
66vw		69w	70sh	ν_7, E'
			65w	
52vw		56w		Lattice modes, *etc.*
44vw		50w		

* Decomposition of sample. † Cation vibrations omitted.

TABLE 6

Vibrational spectrum of $MePCl_2,BCl_3$ adduct

I.r.	Raman	Assignments
	(*a*) $[BCl_4^-]$	
1078wbr		$\nu_1 + \nu_3$
723s	724wbr	ν_3
692sh	694wbr	
666brsh		$\nu_1 + \nu_4$
395s	397s	ν_1
274s	275ms	ν_4
201ms	200m	ν_2
	(*b*) $[MePCl^+]$ *	
769sh	772w	νP–C
576br	580wsh	νP–Cl
219s	219vw	δMe–P–Cl
1462m		Asym. C–H def. Methyl group deformations
1393mw	1396w	Sym. C–H def.
905m		
889m	906w	CH_3 def.
881m		
	(*c*) $MePCl_2,BCl_3$ †	
787brsh		B^{10} νB–Cl asym.
755sh		B^{11}
590sh	590mw	νP–B ‡
512sbr	514m	νP–Cl
484brsh		
306vs	304w	νB–Cl sym.
240vw		δB–Cl
	235vw	
173s	172s	δP–Cl
162sh	162s	
	(*d*) Other bands	
980wbr		
940m		
866w		
111w	110w	
101w	100w	
	79mw	
68sh		
55ms		

* Considered as bent triatomic. † C_s Symmetry. ‡ P–B Probably a somewhat mixed mode.

The general applicability of this type of reaction to systems other than aluminium trichloride is evident. Later, several other metal chloride–phosphorus trichloride–alkyl chloride systems will be described.

The formation of the unstable species $SnCl_5^-$ in preference to the usually encountered stable anion $SnCl_6^{2-}$ suggests that this type of reaction may be a suitable synthesis for low-charged chloro-anions. The failure to observe any reaction products with silicon and germanium tetrachlorides is not unexpected in view of the known instability[18] of the anions $SiCl_5^-$ and $GeCl_5^-$, the former only being found in solution.

EXPERIMENTAL

Purification of Reagents.—Aluminium trichloride was purified by initial sublimation from a mixture of aluminium trichloride (95%) and sodium chloride (5%) and then repeated sublimation of the trichloride alone.

Boron trichloride, phosphorus trichloride, methyldichlorophosphine, silicon, germanium, and tin tetrachlorides and tert-butyl chloride were purified by fractional distillation either *in vacuo* or in a current of dry nitrogen. Methylene chloride was dried over phosphorus pentoxide and distilled in a current of dry nitrogen, the first and last quarters being rejected.

Preparation of Samples.—Since all the compounds investigated are water sensitive, vacuum-line and glove-box techniques were employed for all sample preparations and manipulations.

In all cases (except aluminium trichloride), slight excesses of phosphine and tert-butyl chloride with respect to the metal chloride, were used to minimise the chance of polymeric anions being formed. With aluminium trichloride, a ten-fold excess of phosphorus trichloride was found necessary to suppress this effect. The analytical results for the complexes prepared are listed in Table 1.

The reaction system BCl_3–$MePCl_2$–Bu^tCl yielded a

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[16] N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1960, 1130.

[17] N. N. Greenwood, P. G. Perkins, and K. Wade, *J. Chem. Soc.*, 1957, 4345.

[18] I. R. Beattie and K. M. Livingston, *J. Chem. Soc.* (*A*), 1969. 859.

product CH_3PBCl_5; an identical product was prepared in absence of the last reagent.

All complexes were prepared as white powders. The aluminium trichloride complex was recrystallised as colourless needles from methylene chloride. Efforts to recrystallise the other complexes using a variety of solvents failed.

Spectroscopy.—Raman spectra were obtained using a Spex 1401 Spectrometer with helium–neon laser excitation. Sample presentation was in sealed capillary tubes. Some samples exhibited strong fluorescence effects prohibiting the observation of Raman spectra.

The Grubb–Parsons Spectromaster (400—1000 cm^{-1}) and the R.I.I.C. FS720 Interferometer (30—400 cm^{-1}) were utilised to obtain i.r. spectra over the desired region of the spectrum. Sample presentation was as Nujol mulls between either potassium bromide or Polythene plates.

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