Studies of Some Thermally Unstable Complexes of Group V Trihalides with Trimethylamine and [$^2H_9$]Trimethylamine by Infrared, Raman, and Matrix-isolation Raman Spectroscopy, Normal Co-ordinate Analysis, and Structural Methods

By **D. H. Boal** and **G. A. Ozin,*** Lash Miller Chemistry Laboratory and Erindale College, University of Toronto, Toronto 181, Ontario, Canada

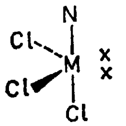
Low-temperature i.r. and Raman spectroscopy, ligand deuteriation, and matrix-isolation Raman techniques are used to determine the shapes of the thermally unstable complexes PCl_3,NMe_3 and PBr_3,NMe_3. Comparison of the observed and calculated vibrational spectra for the phosphine complexes with the similar data for $AsCl_3,NMe_3$ (whose crystal structure is known) suggest that they are all isostructural and form pseudotrigonal bipyramidal molecular complexes having a stereochemically active lone pair of electrons in the equatorial plane, which can be considered to be replacing an equatorial chlorine atom in the isoelectronic Group IV complexes MX_4,NMe_3.

Of particular interest is the effect of the lone pair of electrons on same Group V trihalides in determining the stereochemistry of their complexes with trimethylamine. Many mono- and bis-trimethylamine complexes are known, for example, MCl_4,NMe_3 (where M = Si, Ge, Sn, and Ti);[1] $SiCl_3X,NMe_3$ (where X = H, F, Br, or I);[2] and $MCl_3,2NMe_3$ (where M = Al, Ga, or In),[3] and have been shown to have a trigonal bipyramidal shape around the central metal atom, with the NMe_3 group always lying in the *axial* position.

Vibrational data have not yet been reported for complexes of the type MX_3,NMe_3 although it is known that PCl_3, PBr_3, and $AsCl_3$ form unstable 1 : 1 adducts with NMe_3.[4,5]

One can consider the Group V problem in the light of our knowledge of the isoelectronic Group IV species $SiCl_4,NMe_3$ and $GeCl_4,NMe_3$ which are known to have C_{3v} trigonal bipyramidal stereochemistries.[1] The replacement of a chlorine atom in $SiCl_4,NMe_3$ or $GeCl_4,NMe_3$ by a lone pair of electrons to yield PCl_3,NMe_3 or $AsCl_3,NMe_3$ might not be expected to alter the basic stereochemistry. Thus the axial NMe_3 is expected to persist in the Group V complexes, with the lone pair of electrons in either an axial or equatorial site.

The *X*-ray structures for $AsCl_3,NMe_3$[6] and $SbCl_3,PhNH_2$[7] have recently been reported and show the complexes to have pseudotrigonal bipyramidal co-ordination about the As and Sb, with the ligand lying axially as shown in structure (1). There is no known example of pseudotrigonal bipyramidal species (*e.g.*, ClF_3,SF_4,ICl_2^-, *etc.*) in which the stereochemically active lone pair(s) of electrons lies anywhere but in the equatorial plane.



(I)

Our vibrational study for the PCl_3–NMe_3 system can be divided into four parts: (*a*) the low-temperature spectra of (i) the pure 1 : 1 complex, (ii) the 1 : 1 complex in a CO_2 matrix, and (iii) the 1 : 1 complex in a NMe_3 matrix; (*b*) isotope substitution data for the completely deuteriated complex $PCl_3,N(CD_3)_3$; (*c*) comparison of these data with the analogous systems PBr_3,NMe_3 and $AsCl_3,NMe_3$; and (*d*) normal co-ordinate analysis of PCl_3,NMe_3, PBr_3,NMe_3, and $AsCl_3,NMe_3$ and their perdeuterio-analogues.

In considering the trigonal bipyramidal structure of the Group V complexes from a general point of view, the

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[1] I. R. Beattie and T. R. Gilson, *J. Chem. Soc.* (*A*), 1965, 6595.

[2] I. R. Beattie, D. H. Boal, and G. A. Ozin, to be published.

[3] I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1968, 1093.

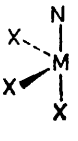
[4] R. R. Holmes, *J. Phys. Chem.*, 1960, **64**, 1295.

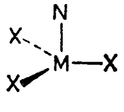
[5] R. R. Holmes and E. F. Bertant, *J. Amer. Chem. Soc.*, 1958, **80**, 2980; 1960, **82**, 5285.

[6] M. Webster and S. Keats, *J. Chem. Soc.* (*A*), 1971, 836; *J. Amer. Chem. Soc.*, 1958, **80**, 2980.

[7] R. Hulme and J. C. Scruton, *J. Chem. Soc.* (*A*), 1968, 2448.

atoms could arrange themselves around the central atom in four possible configurations (A)—(D). In the examination of the vibrational spectra which are expected for these models, the modes which involve mainly


(A)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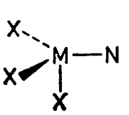
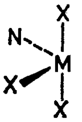

(C)


(D)

the trimethylamine group will vary little for the four models. Normal modes that will vary substantially from (A) to (D) will be the metal–halogen stretching modes.

It has been extensively proven that main-group metal–halogen stretching modes appear at *low* frequency when the central metal atom is light (*e.g.*, Al, Si, P, or S) and does not move appreciably during the mode.[8] Modes of this type are usually totally symmetrical and are expected to occur at *ca.* 300—380 and 200—250 cm^{-1} for light metal-atom chlorides and bromides respectively. Thus, if models (B) and (D) are the correct structures they should exhibit one intense, low-frequency Raman line at 300—380 and 200—250 cm^{-1} corresponding to the PCl and PBr totally symmetrical stretching modes for PCl_3,NMe_3 and PBr_3,NMe_3 respectively.

However, the metal–halogen symmetric stretching modes in models (A) and (C) involve motion of the metal atom (which will make a contribution to the *G* matrix and raise the frequency) and are expected at *high* frequency, that is *ca.* 420—510 cm^{-1} for PCl_3,NMe_3 and 300—400 cm^{-1} for PBr_3,NMe_3.

One should thus be able to deduce the stereochemistry of PCl_3,NMe_3 and PBr_3,NMe_3 on the basis of the *frequencies* and *intensities* of the metal–halogen stretching modes. These skeletal modes can easily be distinguished from ones involving the NMe_3 ligand modes as the latter experience 30—70 cm^{-1} shifts on deuteriation of the ligand whereas the metal–halogen stretching modes generally show only small shifts (2—5 cm^{-1}). Additional information can be obtained by replacing one halogen by another as in PCl_3,NMe_3 and PBr_3,NMe_3.

$AsCl_3,N(CH_3)_3$ *and* $AsCl_3,N(CD_3)_3$.—The former compound is considered in the light of its known *X*-ray structure.[6] The spectra for the complex and its perdeuterio-analogue are in Table 1, together with the computed frequencies for C_s symmetry. Arsenic–chlorine totally symmetric stretching modes (A') are observed at 384 and 363 cm^{-1}. A more explicit assignment to axial and equatorial motions is not possible owing to the highly mixed character (determined from the calculated potential energy contributions) of these modes. The strong i.r. band observed at 354—356 cm^{-1} (which is very weak in the Raman) is assigned to the A'' (equatorial) arsenic–chlorine stretching mode.

TABLE 1

Vibrational spectrum [a] of $AsCl_3,NMe_3$ [b]

$AsCl_3,NMe_3$		$AsCl_3,N(CD_3)_3$		Calculated for $AsCl_3,NMe_3$	Approximate description of mode
I.r.	Raman	Raman	I.r.		
466s	463mw			411	A'' δNMe_3
430vw	427vvw			420	A' δNMe_3
		400s	397w,sh		A' $\delta N(CD_3)_3$
387s	*384s*	*385ms*	*388s*	390	A' $\nu AsCl$
	363s	*362m*	*365w,sh*	349	A' $\nu AsCl$ [c]
356s		*354w,sh*	*354vs*	376	A'' $\nu AsCl_{equ} + \delta N(CD_3)_3$
255s,br	262vvw		250s,br		
220w,br	232mw	226w,sh	220w,br	216	A'
		208ms		212	A'
190w	199ms		190m		
	184mw	184s		175	A'
	170w				
160w			160w,br	171	A''
	155mw	154ms		157	A'
		144w,sh			
102w	102mw	100m	102mw	108	A''
	56s			73	A'
	42s				

Arsenic–chlorine stretching modes are in italics. [b] Frequencies are reported in units of cm^{-1}. [c] Very mixed modes.

The observed and calculated frequencies for $AsCl_3,NMe_3$ are found to be more compatible with models (A) or (C) than with (B) or (D). Experimentally, of course, (A) is the correct structure.

$PCl_3,N(CH_3)_3$ *and* $PCl_3,N(CD_3)_3$.—Holmes[4,5] has reported that PCl_3 and NMe_3 form a single 1 : 1 addition complex at low temperatures. Evidence was not cited for any complexes of higher stoicheiometries in this system.

The low-temperature (−196 °C) spectra for the pure 1 : 1 complex and its perdeuterio-analogue are in Table 2. Unlike $AsCl_3,NMe_3$ which exists as a volatile solid at room temperature, PCl_3,NMe_3 is completely dissociated into its constituent species. Once again, low-frequency stretching modes are *not* observed, leaving the choice between models (A) and (C). The stretching modes observed in the Raman spectrum of PCl_3,NMe_3 are, as expected, of higher frequency (496 and 471 cm^{-1}) than the $AsCl_3,NMe_3$ complex. As with the arsenic compound,

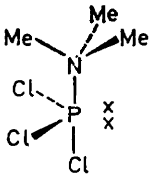
TABLE 2

Vibrational spectrum [a] of PCl_3,NMe_3 [b]

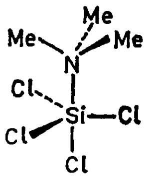
PCl_3,NMe_3		$PCl_3,N(CD_3)_3$	Calculated	Approximate
Infra-red (−196 °C)	Raman (−196 °C)	Raman (−196 °C)	for PCl_3,NMe_3	description of mode
500w,sh	*500vs*	*498vs*	493	A' νPCl [c]
480s		*483ms*	511	A'' νPCl
	476ms	*474ms*	482	A' νPCl [c]
	453ms		454	A' δNMe_3
431ms	429w		419	A' } δNMe_3
	421w,sh		410	A''
		388ms		A' } $\delta N(CD_3)_3$
		340w		A'
	293vw			$\rho_r NMe_3$
277ms	270w,sh			
	263w	253w	269	A'
	243m,sh	246w,sh		
236m	236vs	228vs	235	A
		214mw	222	A'
	197w,sh	192mw		
	189s		183	A'
		168ms	177	A'
	159m	156m,br		
	141m	140m	121	A''
	117mw	116m		
	67w		87	A'
	53vs		78	A'
	46s			
	35s			

[a] Phosphorus–chlorine stretching modes are in italics. [b] All frequencies are in units of cm^{-1}. [c] Highly coupled.

the small separation of the high-frequency P–Cl stretching modes (25 cm^{-1}), together with the satisfactory agreement between the observed and calculated spectra (Table 2) lend strong support to model (A) as being correct.



(G)



(E) (ref. 8)

Matrix Raman Studies of PCl_3,NMe_3.—It is possible to apply the matrix isolation technique to the complex PCl_3,NMe_3. This was performed (Table 3) with carbon dioxide and with trimethylamine as matrix gases. The (100 : 1) spectrum in CO_2 shows little change from the 1 : 1 complex, indicating that the complex is unimolecular rather than polymeric. It is interesting to compare the shapes of the known isoelectronic species shown as (E)—(H).[8,9] Our data thus imply that on replacing a chlorine atom in the *silicon* complexes (E) and (F) by a chemically active lone pair of electrons in the isoelectronic *phosphorus* complex (G) and (H) respectively, the basic molecular framework remains unchanged.

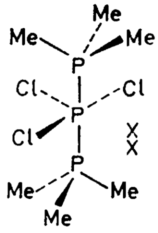
TABLE 3

Raman spectra of matrix-isolated PCl_3,NMe_3 [a]

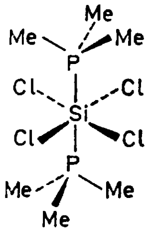
$PCl_3 : NMe_3 : CO_2$ (1 : 1 : 100)	$PCl_3 : NMe_3$ (1 : 100)	Approximate [b] description of mode
505s		νPCl (1 : 1)
	486s	νPCl (1 : 2)
480m,sh		νPCl (1 : 1)
439m	435m	δNMe_3 (1 : 1) and (1 : 2)
426m		
	412w,sh	δNMe_3 (1 : 2)
	402m	νPCl (1 : 2)
	373ms	νPCl (1 : 2)

[a] In this Table, only the P–Cl and N–Me stretches and deformations are shown. All frequencies are in cm^{-1}. [b] In these assignments (1 : 1) refers to PCl_3,NMe_3 and (1 : 2) refers to $PCl_3,2NMe_3$.

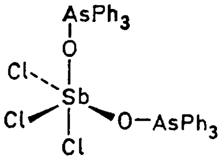
Drastic spectral changes are observed when trimethylamine (a reactive matrix) was used both as ligand and matrix diluent. The presence of new bands and the shifting to lower frequencies of all the P–Cl stretches in the trimethylamine matrix indicates that a new compound has been formed, most likely by the co-ordination of a second trimethylamine ligand. Although it is difficult to determine the stereochemistry of the new complex on the basis of these data alone, a useful comparison can be made with $SbCl_3$. Antimony trichloride is known to react with $PhNH_2$ to form a 1 : 1 adduct whose structure[7] is known to be the same as configuration (A). The only known *X*-ray structure of a 1 : 2 adduct of $SbCl_3$ [10] is with triphenylarsine oxide which has the *cis*-pseudo-octahedral stereochemistry shown as (I). Our spectra suggest that a similar reaction has occurred with PCl_3 to yield $PCl_3,2NMe_3$ since there are only *high*-frequency P–Cl stretching modes present [indicating a *cis*-arrangement of the PCl_3 residue as shown in (J)] as well as a shift to *lower* frequencies, compatible with increased negative charge being placed on the phosphorus by an additional trimethylamine ligand.



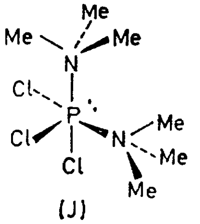
(H) (ref. 9)



(F) (ref. 8)



(I)



(J)

PBr_3,NMe_3.—The spectra, as with the PCl_3 complex, show only *high*-frequency bands in the P–Br stretching region. The 361 and 341 cm^{-1} peaks (strong in the Raman) are assigned as the A' P–Br stretching modes, while the 391 cm^{-1} absorption (strong in the i.r.), is assigned as the A'' P–Br asymmetric stretching mode.

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[8] I. R. Beattie and G. A. Ozin, *J. Chem. Soc.* (*A*), 1969, 370.

[9] D. Frieson, M.Sc. Thesis, University of Toronto, 1972.

[10] I. Lindquist, 'Inorganic Adduct Molecules of Oxo-compounds,' Springer-Verlag, Berlin, 1963, p. 71.

The frequencies of these bands also serves to distinguish phosphorus–halogen stretching modes from ligand deformational modes in the compounds PCl_3,NMe_3 and PBr_3,NMe_3. The small separation (20 cm^{-1}) between the A' stretching modes, and the greater intensity of the higher-frequency mode indicates that PBr_3,NMe_3 is isostructural with the previous 1 : 1 compounds.

Normal Co-ordinate Analysis.—In the absence of structural parameters for the unstable phosphorus complexes we tested the suitability of the transference force field approximation by computing initially the vibrational spectrum of $AsCl_3,NMe_3$ whose symmetry is known to be C_s [model (A)]. Arsenic–chlorine force constants for the approximately pyramidal $AsCl_3$ residue in the complex were transfered from free $AsCl_3$. Trimethylamine force constants were the same as those used previously.[1,3] The metal–ligand bond stretching force constant was set at 1·25 mdyne Å^{-1} which is in the range calculated from single-crystal Raman polarisation data for main-group trimethylamine complexes.[11] The weakening of the arsenic–chlorine bonds in $AsCl_3,NMe_3$ through co-ordination to NMe_3, relative to those in free $AsCl_3$, could be satisfactorily accounted for by reducing the k_{AsCl} bond stretching force constants by 10%. The reasonably close agreement between the observed and calculated spectra for $AsCl_3,NMe_3$ (Table 1) lend support to the approximations made in the force field, the basis of which is used in the similar computations of the phosphorus complexes (see text and Tables 2, 4, 5, and 6). The internal and symmetry co-ordinates used in the calculations are shown in Figure 2 and Table 7.

TABLE 4

Vibrational spectrum [a] of PBr_3,NMe_3 [b]

I.r. −196 °C)	Raman (−196 °C)	Calculated	Approximate description of mode
	451mw,br	423	A' δNMe_3
433m	423w,br	416	$A' + A''$ δNMe_3
390s	*391m*	399	A'' νPBr
	361s	406	A' νPBr
	341m	385	A' νPBr
290s			
214w			
208w		194	A''
	193m	194	A'
		167	A'
	155s		
		141	A'
	132m		
		119	A'
	101w	95	A''
		67	A''
		50	A'

[a] Phosphorus–bromine stretching modes are in italics. [b] All frequencies in cm^{-1}.

TABLE 5

Bond lengths used in vibrational analyses

Bond	Distance/Å	Bond	Distance/Å
P–Cl	2·043	P–N	2·010
P–Br	2·200	As–N	2·289
As–Cl	2·160	N–Me	1·470

TABLE 6

Force constants used in vibrational analyses of MX_3,NMe_3

Force constant [a]	PCl_3	PBr_3	$AsCl_3$
f_R	1·84	1·32	2·05
f_r	1·84	1·32	1·85
f_d	1·25	1·25	1·25
f_l	3·12	3·12	3·12
$f_{Rl} = f_{RR} = f_{Rr}$	0·20	0·15	0·23
f_{rd}	0·10	0·07$_5$	0·11$_5$
f_a	1·33	0·98$_5$	1·07
f_{aa}	0·29	0·34	0·09
f_{ll}	0·06$_5$	0·06$_5$	0·06$_5$
f_δ	1·01	1·01	1·01
$f_{l\delta}$	0·06$_5$	0·06$_5$	0·06$_5$
f_γ	0·42$_5$	0·42$_5$	0·42$_5$

[a] In units of mdyne Å^{-1}, mdyne radian^{-1}, or mdyne-Å radian^{-2}.

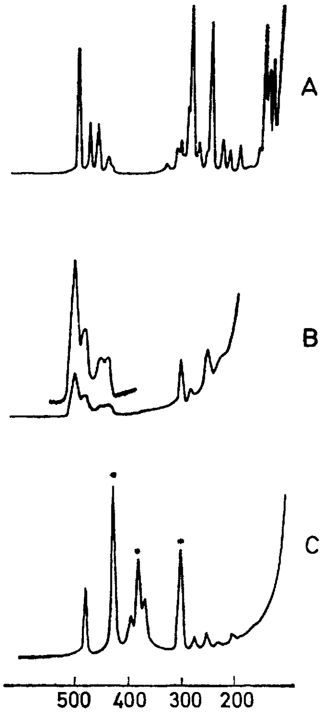

FIGURE 1 The low-temperature Raman spectra of A, pure PCl_3,NMe_3 (1 : 1); B, PCl_3,NMe_3 in CO_2 (1 : 100); and C, PCl_3,NMe_3 in NMe_3 (1 : 100)

TABLE 7

Symmetry co-ordinates (see Figure 2)

Type A'

$S_1 = (1/\sqrt{2})(\Delta R_1 + \Delta R_2)$
$S_2 = \Delta r$
$S_3 = \Delta d$
$S_4 = (1\sqrt{2})(\Delta l_1 + \Delta l_2)$
$S_5 = \Delta l_3$
$S_6 = (1/\sqrt{2})(\Delta\alpha_1 + \Delta\alpha_2)$
$S_7 = \Delta\alpha_3$
$S_8 = (1/\sqrt{2})(\Delta\beta_1 + \Delta\beta_2)$
$S_9 = (1/\sqrt{2})(\Delta\gamma_1 + \Delta\gamma_2)$
$S_{10} = \Delta\gamma_3$
$S_{11} = (1/\sqrt{2})(\Delta\delta_1 + \Delta\delta_2)$
$S_{12} = \Delta\delta_3$
$S_{13} = (1/\sqrt{2})(\Delta\tau_1 - \Delta\tau_2)$
$S_{14} = (1/\sqrt{2})(\Delta\tau_3 - \Delta\tau_4)$
$S_{15} = (1/\sqrt{2})(\Delta\tau_5 - \Delta\tau_6)$

Type A''

$S_{16} = (1/\sqrt{2})(\Delta R_1 - \Delta R_2)$
$S_{17} = (1/\sqrt{2})(\Delta l_1 - \Delta l_2)$
$S_{18} = (1/\sqrt{2})(\Delta\alpha_1 - \Delta\alpha_2)$
$S_{19} = (1/\sqrt{2})(\Delta\beta_1 - \Delta\beta_2)$
$S_{20} = (1/\sqrt{2})(\Delta\tau_1 - \Delta\tau_2)$
$S_{21} = (1/\sqrt{2})(\Delta\delta_1 - \Delta\delta_2)$
$S_{22} = (1/\sqrt{2})(\Delta\tau_1 + \Delta\tau_2)$
$S_{23} = (1/\sqrt{2})(\Delta\tau_3 + \Delta\tau_4)$
$S_{24} = (1/\sqrt{2})(\Delta\tau_5 + \Delta\tau_6)$

The normal co-ordinate calculations for the phosphorus complexes provide evidence in support of the

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[11] G. A. Ozin and I. R. Beattie, *J. Chem. Soc.* (*A*), 1969, 2535, and references therein.

structural assignment to model (A) for which only ***high*** frequency metal–halogen stretching modes are calculated and observed (Tables 2 and 4).

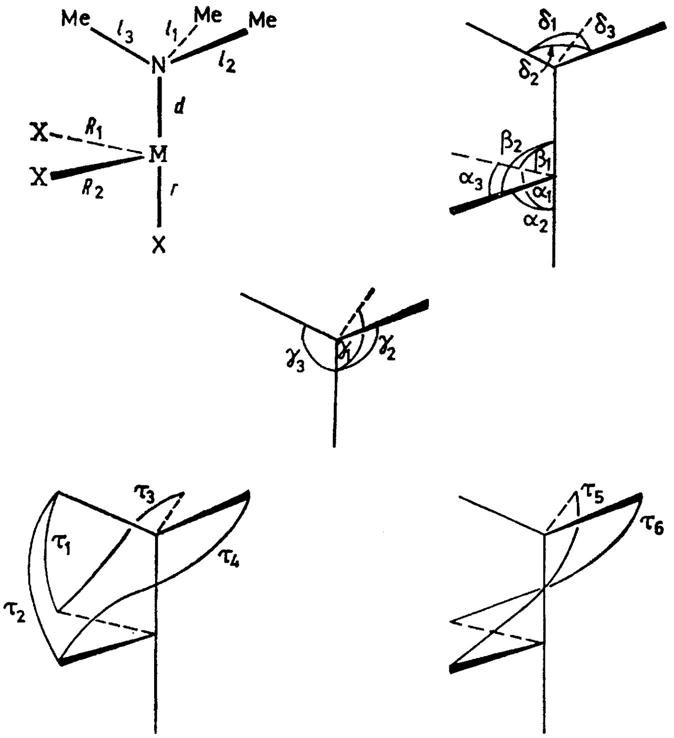

FIGURE 2 Internal co-ordinates in C_s symmetry

EXPERIMENTAL

All manipulations were carried out under vacuum, except for the preparation of mulls for the i.r. spectra of $AsCl_3,NMe_3$ (which were done in a glove box). The phosphorus and arsenic halides were outgassed and vacuum-distilled. Trimethylamine was purified by the standard procedure of treatment with silicon tetrachloride and pyridine. It was then outgassed at −78 °C and vacuum-distilled. The CO_2 used in the matrix work was research grade supplied by Matheson Co.

Holmes has used vapour pressure–composition studies to show the PCl_3, PBr_3, and $AsCl_3$ form 1 : 1 addition compounds with NMe_3 at low temperatures.[4,5] The method of preparation of the complexes for low-temperature spectral analysis in the present study was similar to that of Holmes work. Mixtures of the appropriate trihalide and trimethylamine (1 : 1) were prepared in the vapour phase. The gaseous mixture was then slowly deposited through a needle valve on the central cold plate of either a low-temperature i.r. or Raman cell. Each experiment was repeated at least twice to ensure reproducibility of the spectroscopic work.

In the case of $AsCl_3,NMe_3$ the compound was sufficiently stable to permit analysis by conventional argentometric and pH titration techniques (Found: Cl, 46·5%; As : NMe_3, 1 : 1·01. Calc. for $AsCl_3,NMe_3$, Cl, 46·9%). The Raman spectra were recorded on a Spex 1401 spectrometer with Carson argon and krypton ion laser excitation. I.r. spectra were recorded on a Beckmann Ir 11 instrument.

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