672. *The Stereochemistry of Some Addition Compounds of Silicon Tetrahalides*

By I. R. Beattie and M. Webster

The 1 : 2 addition compounds formed by silicon tetrahalides with triphenylphosphine oxide are shown (on the basis of infrared-spectroscopic examination in the cæsium bromide region) to be of the form $[SiX_4(Ph_3PO)_2]$ (where X = F, Cl, or Br). For the fluoride adduct, a *trans*-assignment is possible but, for the bromide and chloride adducts, assignment is complicated by ligand vibrations. Because of intensity effects, Raman spectroscopy on $[SiCl_4(Ph_3PO)_2]$ does not clarify the situation. Conductometric and spectral measurements on the 1 : 4 adducts $SiBr_4,4Ph_3PO$, $SiBr_2(ClO_4)_2,4Ph_3PO$, and $Si(ClO_4)_4,4Ph_3PO$ suggest that these compounds all contain the ion $[Si(Ph_3PO)_4]^{4+}$. By contrast, the related compound $SiCl_4,4Me_3PO$ apparently contains the ion *cis*-$[SiCl_2(Me_3PO)_4]^{2+}$. The infrared spectra of addition compounds of pyridine and 1,10-phenanthroline with silicon tetrafluoride are reported and, for $SiF_4,2py$, a *trans*-assignment is made.

UNTIL recently, the only well-established cationic co-ordination compound of silicon(IV) was represented by the ion $[Si(acac)_3]^+$ (where Hacac = acetylacetone), originally discovered by Dilthey[1] in 1903 and subsequently resolved into its enantiomers by Dhar *et al.*[2] During the past decade a number of related examples has been found, frequently involving the ionisation of a silicon–iodine linkage. Thus, the conductivity of acetonitrile solutions of the 1 : 1 adduct formed between silyl iodide and trimethylamine suggests the ionic formulation[3] $[Me_3NSiH_3]^+I^-$, although the method of filling the conductivity cell has been criticised.[4] As formulated, this derivative is closely related to hydrochlorides of substituted silylamines[5] (*e.g.*, Me_2NSiCl_3,HCl) and is suitably referred to as based on quaternised nitrogen. However, the cation $[Si(acac)_3]^+$ has been referred to as a siliconium ion,[6,7] while more recently the ion 2,2′-bipyridyltriphenylsilicon(IV) has been similarly described[8] and likened to a supposed boronium ion.[9] These "onium" ions are inadequately named and are not as novel as they may at first sight appear. (The I.U.P.A.C. rules for nomenclature identify the terminology siliconium with cations of the type SiH_{4-n}^{n+} where n has the values 1—3 inclusive.[10]) Similarly, the compound named as 2,2′-bipyridyldiphenylboronium perchlorate[9] and containing the ion $[(2,2'\text{-bipyridyl})BPh_2]^+$

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[1] W. Dilthey, *Ber.*, 1903, **36**, 923.

[2] S. K. Dhar, V. Doron, and S. Kirschner, *J. Amer. Chem. Soc.*, 1958, **80**, 753.

[3] B. J. Aylett, H. J. Emeléus, and A. G. Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 187.

[4] E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, London, 1963.

[5] R. Cass and G. E. Coates, *J.*, 1952, 2347.

[6] D. W. A. Sharp, *J.*, 1958, 2558.

[7] M. M. Millard and G. Urry, American Chemical Society 144th Meeting, 1963, Division of Inorganic Chemistry, Paper No. 43.

[8] J. Y. Corey and R. West, *J. Amer. Chem. Soc.*, 1963, **85**, 4034.

[9] J. M. Davidson and C. M. French, *J.*, 1962, 3364; *Chem. and Ind.*, 1959, 750.

[10] See, *e.g.*, "Handbook for Chemical Society Authors," *Chem. Soc. Special Publ.*, No. 14, 1960.

is closely related to the ions [11] $[(NH_3)_2BH_2]^+$ found [12] in the " diammoniate of diborane " and to the ion [13] [ethylenediamine $BH_2]^+$. Perhaps the simplest way of summarising this is to say that, although for an inorganic chemist it is tempting to think of *N*-methylpyridinium chloride as a co-ordination compound of carbon, it would be dangerous to think of the charge as being located on the carbon and to refer to the compound as a carbonium ion.[14]

We have recently shown [15] that the 1 : 4 adduct between silicon tetraiodide and pyridine contains an ion with four pyridine ligands and probably of the form *cis*-$[SiI_2py_4]^{2+}$ (where py = pyridine). The only other reasonably well-established 1 : 4 adducts of silicon tetrahalides are described in a Paper by Issleib and Reinhold,[16] where it is suggested that these compounds are based on eight-co-ordinate silicon. This assumption seemed to us rather unlikely, and examination of a model of an ion of the type $[Si(Ph_3PO)_4]^{4+}$ showed that considerable difficulty would be experienced in introducing two further groups (such as Br^-), let alone attempting to introduce four. We decided to investigate the compound $SiBr_4,4Ph_3PO$ (and related compounds) in the hope of finding adducts of the Si^{4+} ion.

Initial work confirmed the existence of the known compounds $SiCl_4,2Ph_3PO$ [16,17] and $SiBr_4,4Ph_3PO$,[16] but in addition (under similar experimental conditions) demonstrated the presence of the 1 : 2 adduct $SiBr_4,2Ph_3PO$. The infrared spectra of these compounds (540—270 cm.$^{-1}$) are given in Table 1. In a previous Paper [15] on 1 : 2 adducts formed between silicon tetrahalides and tertiary aromatic nitrogen donors, it was shown that the " Si–Cl stretching vibrations " lay in the region 482—382 cm.$^{-1}$, while for the corresponding bromides the region covered was 425—350 cm.$^{-1}$. The results for $SiX_4,2Ph_3PO$ (X = Cl or Br) suggest that strong bands at 420 and 369 cm.$^{-1}$ are to be assigned to silicon–chlorine and silicon–bromine stretching vibrations, respectively. The other absorptions which might be attributed to Si–Cl and Si–Br modes are at 359 and 342 cm.$^{-1}$ (chloride) and 337 and 300 cm.$^{-1}$ (bromide). However, they might equally well be attributed to

TABLE 1

The infrared spectra of some triphenylphosphine oxide complexes of silicon tetrahalides and related compounds (540—270 cm.$^{-1}$)

Compound	Method	Frequency (cm.$^{-1}$)						
$SiBr_4,4Ph_3PO$	Nujol mull	531s	~470w br *	377m	320vw br *			
$SiBr_4,4Ph_3PO$	C_6H_6 soln.	537s	486s †	~400w br ‡	300w br			
$SiBr_4,4Ph_3PO$	EtCN soln.		(See Figure)					
Propionitrile	Liquid	539m		376m				
$SiBr_4$	EtCN soln.	539 §	487	375 §				
Benzene	Liquid			400w				
Ph_3PO	Nujol mull	538s	496w	450w	303w	291w		
Ph_3PO	C_6H_6 soln.	537s	499w	~400w br ‡	294w br			
$Si(ClO_4)_4,4Ph_3PO$ ...	Nujol mull	530s	~488m br *	379m				
$SiBr_2(ClO_4)_2,4Ph_3PO$	Nujol mull	532s	477w	377m				
$SiBr_4,2Ph_3PO$	Nujol mull	530s	488w *	463w	442w	369s	337m	~300w br
$SiBr_4,2Ph_3PO$	C_6H_6 soln.	539s	487s †	~400w br ‡	301vw			
$SiBr_4,2Ph_3PO$	EtCN soln.	535 §	485 †	(400—350 cm.$^{-1}$ obscured by EtCN)				
$SiCl_4,2Ph_3PO$	Nujol mull	532vs	463w	443m	420vs	359m	342s	
$SiCl_4,2Ph_3PO$	C_6H_6 soln.	536s		~400w br ‡				
$SiCl_4,4Me_3PO$	Nujol mull	565s	526s	421m br ¶				
Me_3PO	Nujol mull			358				

* May contain impurity due to hydrolysis, since the bands increased if the sample was kept. † ν_3 of $SiBr_4$. ‡ Benzene absorption (the solvent also obscured ν_3 of $SiCl_4$). § EtCN absorption. ¶ Probably due to co-ordinated Me_3PO.

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[11] C. E. Nordman and C. R. Peters, *J. Amer. Chem. Soc.*, 1959, **81**, 3551; see also N. E. Miller and E. L. Muetterties, *ibid.*, 1964, **86**, 1033.

[12] See, *e.g.*, D. R. Schultz and R. W. Parry, *J. Amer. Chem. Soc.*, 1958, **80**, 4.

[13] J. Goubeau and H. Schneider, *Chem. Ber.*, 1961, **94**, 816.

[14] See also R. N. Collinger, R. S. Nyholm, and M. Tobe, *Nature*, 1964, **201**, 1322.

[15] I. R. Beattie, T. Gilson, M. Webster, and (in part) G. P. McQuillan, *J.*, 1964, 238.

[16] K. Issleib and H. Reinhold, *Z. anorg. Chem.*, 1962, **314**, 113.

[17] M. J. Frazer, W. Gerrard, and R. Twaits, *J. Inorg. Nuclear Chem.*, 1963, **25**, 637.

ligand vibrations, for example in terms of $\geqslant$P=O deformations. Thus, in this case, assignment of configuration is impossible from the present infrared results.

We hoped that Raman spectroscopy on the solid might resolve this difficulty. For *cis*-L_2SiCl_4, we expected a group of three vibrational modes around 450 $cm.^{-1}$, active in both the infrared and the Raman effect (although, as recently noted,[18] intensity effects may be misleading in the Raman spectra). For *trans*-L_2SiCl_4 there may be one main infrared-active absorption around 450 $cm.^{-1}$ (associated with the Si–Cl antisymmetric stretching [19,20] of perturbed planar $SiCl_4$). In the Raman effect (because the silicon does not move during the symmetric " breathing " frequency of the assumed D_{4h} adduct) the main (a_{1g}) Raman-active vibration for the MCl_4 residue would lie at about 320 $cm.^{-1}$. We found one strong band at 316 $cm.^{-1}$ in $SiCl_4$,$2Ph_3PO$, together with a weaker band at 268 $cm.^{-1}$. Although it is tempting to assign a *trans*-configuration on the basis of this result, this is not justified. For *cis*-L_2SiCl_4, it is likely that the most intense Raman band will be the " linear " Cl–Si–Cl stretching mode (uncoupled in the *G*-matrix) previously [19] calculated to occur in the region of 260 $cm.^{-1}$. The configuration thus remains in doubt.

We also attempted to determine the stereochemical arrangement of SiF_4,$2Ph_3PO$, although assignments with the fluoride adducts are a little more difficult, as the amount of published work on the spectra of adducts of silicon tetrafluoride is small,[21] and the " silicon–fluorine " stretching vibrations frequently occur in the same region as those of the ligand. The SiF_6^{2-} ion in K_2SiF_6 shows infrared absorptions at 723 and 480 $cm.^{-1}$ (Nujol mull).[22,23] Similarly, in the adduct SiF_4,$2Ph_3PO$ (Table 2), absorptions at 795 $cm.^{-1}$ and at 449 and 415 $cm.^{-1}$ are probably associated Swithi–F modes. In agreement with this suggestion, SiF_4^- (1,10-phenanthroline) showed absorptions at 813 and 759 $cm.^{-1}$ and at 457 and 399 $cm.^{-1}$, whilst the pyridine adduct SiF_4,2py gave bands at 803 $cm.^{-1}$ and at 490 and 463 $cm.^{-1}$, which were again presumably Si–F vibrations. Ligand vibrations (found by comparison with analogous adducts of silicon tetrahalides) have been omitted from the above discussion. From the *number* of Si–F stretching vibrations, it appears that the triphenylphosphine oxide and the pyridine adducts of silicon tetrafluoride are *trans*. The 1,10-phenanthroline adduct is chelated, as expected (although it shows two, rather than the expected three, Si–F stretching vibrations). It may be noted that, with the *trans*-adducts, there appear to be more deformation vibrations than would have been expected for D_{4h} symmetry of the SiF_4 residue.

TABLE 2

The infrared spectra of silicon tetrafluoride adducts (Nujol mulls) in the 850—290 $cm.^{-1}$ region

Compound	Frequencies ($cm.^{-1}$)											
SiF_4,$2Ph_3PO$ ...	795s*	760w	755m	723s	693s	570m	561sh	539s	449s*	436sh	415s*	348w
SiF_4,1,10-phenanthroline ...	855m	813s*	759s*	754w	745m	726m	603w	457s*	428w	399m*		
SiF_4,$2C_5H_5N$ ...	803vs*	763s	686s	657m	490vs*	~463sh br*						

* Bands probably due largely to Si–F vibrations.

The infrared spectrum of the 1 : 4 adduct $SiBr_4$,$4Ph_3PO$ is surprisingly simple in the 500—270 $cm.^{-1}$ region, where there is only one band of reasonable intensity. This band, at 377 $cm.^{-1}$, lies at the lower end of the previously found "silicon–bromine stretching

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[18] I. R. Beattie and L. Rule, *J.*, 1965, 2995.

[19] I. R. Beattie, M. Webster, and G. W. Chantry, *J.*, 1964, 6172.

[20] See K. Nakamoto, " Infrared Spectra of Inorganic and Co-ordination Compounds," Wiley, London, 1963. (There is a misprint on p. 114, Table II-29 where ν_2 and ν_4 are transposed.)

[21] See, *e.g.*, V. Gutmann, P. Heilmeyer, and K. Utvary, *Monatsh.*, 1961, **92**, 322; V. Gutmann and K. Utvary, *ibid.*, 1959, **90**, 706. (Note that silica shows a broad absorption around 1100 $cm.^{-1}$) E. Schnell, *ibid.*, 1962, **93**, 1136.

[22] Cf. R. D. Peacock and D. W. A. Sharp, *J.*, 1959, 2762.

[23] I. R. Beattie, G. P. McQuillan, L. Rule, and M. Webster, *J.*, 1963, 1514.

region." The most likely species chemically are $[SiBr_2(Ph_3PO)_4]^{2+}$ and $[Si(Ph_3PO)_4]^{4+}$. The improbable adduct $[SiBr_4(Ph_3PO)_4]$, by analogy with previous work,[24] would be likely to contain approximately tetrahedrally disposed $SiBr_4$. As ν_3 of silicon tetrabromide is at 487 cm.$^{-1}$, we may expect a 1 : 4 adduct to have fundamental silicon–bromine stretching vibrations well below 350 cm.$^{-1}$. In contrast, for $[SiBr_2(Ph_3PO)_4]^{2+}$ we may expect silicon–bromine stretching vibrations above 400 cm.$^{-1}$, by comparison [15] with $[SiI_2py_4]^{2+}$. The most likely explanation, purely from infrared results, is that the adduct is $[Si(Ph_3PO)_4]Br_4$; confirmation of this is afforded by a study of the adduct formed between silicon tetrachloride and trimethylphosphine oxide. When silicon tetrachloride is added to a solution of trimethylphosphine oxide in ether, a 1 : 4 adduct results, which shows strong infrared absorptions at 565 and 526 cm.$^{-1}$, whereas trimethylphosphine oxide adducts of tin tetrachloride and tin tetrabromide showed no absorption in the range 670—430 cm.$^{-1}$. It is evident that the adduct is ionic and exhibits at least two silicon–chlorine stretching vibrations, both appreciably higher than those found for adducts such as $SiCl_4,2py$, where the highest frequency is at 482 cm.$^{-1}$. A formulation that is in agreement with the chemistry of silicon and with the infrared results is *cis*-$[SiCl_2(Me_3PO)_4]^{2+}$. Clearly, by analogy with *cis*-$[SiCl_2(Me_3PO)_4]^{2+}$, the adduct *trans*-$[SiBr_2(Ph_3PO)_4]^{2+}$ would be expected to show an infrared-active Si–Br stretching mode above 400 cm.$^{-1}$. Additional evidence supporting the complete ionisation of the bromine in $SiBr_4,4Ph_3PO$ is afforded by a comparison of the spectra of $SiBr_4,4Ph_3PO$, $SiBr_2(ClO_4)_2,4Ph_3PO$, and $Si(ClO_4)_4,4Ph_3PO$. These spectra are virtually identical in the 400 cm.$^{-1}$ region, apart from small intensity changes in the band at about 380 cm.$^{-1}$. Similarly, there is no apparent splitting of the ClO_4^- band at *ca.* 660 cm.$^{-1}$ (ν_4 of this ion, as ν_3 is obscured by ligand vibrations).

TABLE 3

Raman spectra (200—650 cm.$^{-1}$) (solid-state spectra, only intense bands recorded)

Compound	Raman shifts from Hg 4358 Å line (cm.$^{-1}$)			
Ph_3PO	256m			624m
$SiCl_4,2Ph_3PO$	231m	268m	316s	621s
$SiBr_4,4Ph_3PO$				623s

An ion of the type SiL_4^{4+} may form, with bromide ions, a crystal in which the $4Br^-$ packed around the tetrahedral SiL_4^{4+} in the tetrahedron faces, effectively giving molecular SiL_4Br_4. The identification of a relatively high-frequency Si–Br stretching vibration would (if the four bromines were equivalent) stamp the compound as eight-co-ordinate [see $TiCl_4$ (*o*-phenylenebisdimethylarsine)$_2$][24]. With $SiBr_4,4Ph_3PO$ the infrared results are relatively unambiguous, although some doubt must remain in view of the band at about 380 cm.$^{-1}$ showing slight intensity changes as noted above. Similarly, although in $SiCl_4,2Ph_3PO$ the Si–Cl stretching vibration in the Raman effect is of roughly the same intensity as the ligand vibration at about 620 cm.$^{-1}$, for $SiBr_4,4Ph_3PO$ there is no band comparable in intensity to the 620 cm.$^{-1}$ band in the range 200—350 cm.$^{-1}$.

In solution in benzene, the adducts $SiCl_4,2Ph_3PO$, $SiBr_4,2Ph_3PO$, and $SiBr_4,4Ph_3PO$ are effectively fully dissociated into their constituents (see Table 1). However, in solution in propionitrile in the concentration range 0·6—0·01M, the compound $SiBr_4,4Ph_3PO$ has a Λ_c value of about 90 ohm^{-1} cm.^{2} mole^{-1}. The value begins to increase rapidly below 0·01M but, bearing in mind the effect of a few p.p.m. of water at these concentrations, we merely note that the compound is a relatively good conductor. Similarly the Figure shows the effect on the infrared spectrum of adding triphenylphosphine oxide to silicon tetrabromide in 2 : 1 and 4 : 1 mole ratios in ethyl cyanide. It is evident that a 1 : 4 adduct of quite high stability is formed. Solution of $SiBr_4,2Ph_3PO$ in propionitrile leads to release of silicon tetrabromide owing to the reaction

$$2SiBr_4,2Ph_3PO \longrightarrow SiBr_4,4Ph_3PO + SiBr_4$$

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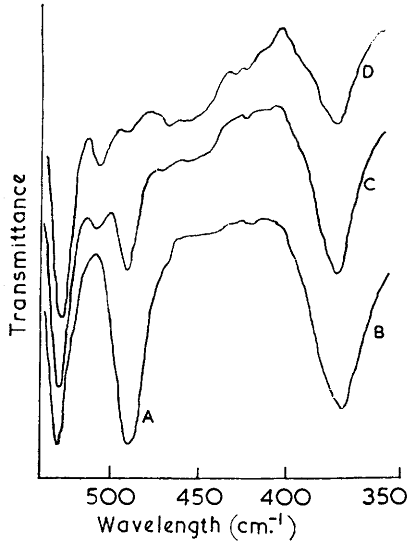
[24] R. J. H. Clark, J. Lewis, and R. S. Nyholm, *J.*, 1962, 2461.

From a stereochemical point of view the results on SiF_4,2py are interesting. Steric factors can account for the sequence *trans*-[SiF_4py_2], *cis*-[$SiCl_4py_2$], *cis*-[$SiBr_4py_2$]. It is not clear how the assignment [25] *cis*-SnF_4py_2 can be rationalised in the light of a *trans*-assignment for the corresponding silicon adduct.

It is also noteworthy that the ionic *cis*-[$SiCl_2(Me_3PO)_4$]Cl_2 is very readily made, whereas recrystallisation of *trans*-[$SiCl_4(Ph_3PO)_2$] from the strongly ionising solvent acetonitrile leaves this compound unchanged as the covalent six-co-ordinate adduct. It is possible that Cl^- is too powerful a donor to yield [$Si(R_3PO)_4$]Cl_4, but that, for triphenylphosphine oxide, the ion [$SiCl_2(Ph_3PO)_4$]$^{2+}$ would be strongly sterically hindered compared with [$SiCl_2(Me_3PO)_4$]$^{2+}$.



The infrared spectrum of silicon tetrabromide in propionitrile and the effect of adding triphenylphosphine oxide: (A) ν_3 of $SiBr_4$ at 486 cm.$^{-1}$, (B) $SiBr_4$ in propionitrile, (C) $SiBr_4$ in propionitrile plus 2 moles of Ph_3PO per mole of $SiBr_4$, (D) $SiBr_4$ in propionitrile plus 4 moles of Ph_3PO per mole of $SiBr_4$. (Propionitrile shows absorptions at 540 and 376 cm.$^{-1}$)

EXPERIMENTAL

Purification of Solvents and Reagents.—Pyridine, 1,10-phenanthroline, silicon tetrachloride, and silicon tetrabromide were purified as described previously.[23, 26] Triphenylphosphine oxide was prepared from triphenylphosphine and dried by vacuum sublimation, m p. 159—161° (lit.,[27] 159°). Trimethylphosphine oxide was dried by vacuum sublimation, m. p. 140—142° (lit.,[28] 140—141°). Silicon tetrafluoride was prepared according to the method of Hoffman and Gutowsky.[29] Benzene, toluene, acetonitrile, and propionitrile were dried by refluxing them over calcium hydride, vacuum distilled on to more calcium hydride, and finally distilled into ampoules in an all-glass vacuum system. Diethyl ether was dried by refluxing over calcium hydride. Silver perchlorate (AnalaR) was dried at 120° under high vacuum and finally sealed off.

Analyses.—Halogen was determined, after hydrolysis, by titration with silver nitrate and a silver indicator electrode. Triphenylphosphine oxide was estimated by ultraviolet measurements on the 266 mμ band, after hydrolysis in 95% aqueous ethanol. The spectra agreed with previous work,[30] and with that of samples of the original triphenylphosphine oxide used during the initial calibration. Bromide, perchlorate, and hydrogen ions had no effect on the determination at the concentrations encountered. Perchlorate was estimated by using nitron reagent and weighing the precipitate of nitron perchlorate.

$SiCl_4,2Ph_3PO$.—Triphenylphosphine oxide (0·8 g.) was dissolved in benzene (~8 ml.) and treated with silicon tetrachloride (~1 ml.) in benzene (~1 ml.) in an all-glass vacuum system,

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[25] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082.
[26] R. Hulme, G. J. Leigh, and I. R. Beattie, *J.*, 1960, 366.
[27] J. M. Phillips, J. S. Hunter, and L. E. Sutton, *J.*, 1945, 150.
[28] G. W. Fenton and C. K. Ingold, *J.*, 1929, 2342.
[29] C. J. Hoffman and H. S. Gutowsky, *Inorg. Synth.*, 1953, **4**, 145.
[30] H. H. Jaffé, *J. Chem. Phys.*, 1954, **22**, 1430.

Immediate precipitation of $SiCl_4,2Ph_3PO$ occurred. The preparation was also performed in a dry-box with toluene as a solvent. The adduct had m. p. 152—156° (sealed tube) [lit.,[17] 146—150° (decomp.),[16] 142°] (Found: Cl, 18·8; 19·25. Calc. for $C_{36}H_{30}Cl_4O_2P_2Si$: Cl, 19·5%). Crystals for Raman spectroscopy were obtained by recrystallisation from acetonitrile in an all-glass vacuum system.

$SiCl_4,4Me_3PO$.—Trimethylphosphine oxide in diethyl ether (saturated solution) was treated with silicon tetrachloride. The immediate *precipitate* of $SiCl_4,4Me_3PO$ was washed with ether (Found: Cl, 28·6, 25·2. $C_{12}H_{36}Cl_4O_4P_4Si$ requires Cl, 26·4%).

$SiBr_4,2Ph_3PO$.—A solution of triphenylphosphine oxide (1 g.) in benzene (~8 ml.) was treated with a solution of silicon tetrabromide (~1 ml.) in benzene (~1 ml.) in an all-glass vacuum system. An immediate precipitate of the *adduct* was formed (Found: Br, 36·0, 34·4. $C_{36}H_{30}Br_4O_2P_2Si$ requires Br, 35·55%).

$SiBr_4,4Ph_3PO$.—When silicon tetrabromide (~0·28 ml.) dissolved in toluene (1—2 ml.) was added to a solution of triphenylphosphine oxide (1 g.) in toluene (~20 ml.) (in the proportions given in ref. 16) in an all-glass vacuum system, an immediate precipitate was formed; when isolated, this was shown to be $SiBr_4,4Ph_3PO$ (Found: Br, 23·25, 23·4. Calc. for $C_{72}H_{60}Br_4O_4P_4Si$: Br, 21·9%).

$SiBr_2(ClO_4)_2,4Ph_3PO$.—When a solution of silver perchlorate (0·83 g.) in acetonitrile was added to a solution of silicon tetrabromide (0·248 ml.) in acetonitrile, a quantitative precipitate of silver bromide was obtained. A solution of triphenylphosphine oxide in acetonitrile was added to the resulting solution and the mixture was evaporated to dryness *in vacuo.* The resulting solid was dissolved in the minimum quantity of acetonitrile and treated with benzene to yield crystals of the *adduct* $SiBr_2(ClO_4)_2,4Ph_3PO$ (Found: Br, 10·35, 10·5; Ph_3PO, 73·9. $C_{72}H_{60}Br_2Cl_2O_{12}P_4Si$ requires Br, 10·65; Ph_3PO, 74·3%).

$Si(ClO_4)_4,4Ph_3PO$ (*see Figure*).—A solution of silicon tetrabromide (0·1 ml.) in propionitrile (25 ml.) was prepared and its infrared spectrum recorded. Solid triphenylphosphine oxide (0·40 g., corresponding to $SiBr_4,2Ph_3PO$) was added to the residual solution (23·5 ml.) and the infrared spectrum recorded again. A further addition of triphenylphosphine oxide (0·384 g.) brought the composition up to 1 : 4, and the infrared spectrum was recorded a third time. A solution of silver perchlorate in propionitrile was added slowly until no more precipitate of silver bromide was formed. The liquid was decanted from the solid and taken down nearly to dryness *in vacuo.* The resulting slurry was dissolved in the minimum quantity of propionitrile and treated with benzene. Small crystals of the *adduct* $Si(ClO_4)_4,4Ph_3PO$ were slowly deposited (Found: ClO_4, 22·1, 24·0; Ph_3PO, 64·0, 68·0; Br, 0. $C_{72}H_{60}Cl_4O_{20}P_4Si$, requires ClO_4, 25·8. Ph_3PO, 72·3%).

Conductivity of $SiBr_4$ *and* $SiBr_4,4Ph_3PO$ *in Propionitrile.*—The experiment was performed at 25° in an all-glass vacuum system and with platinised platinum electrodes. The specific conductivity of the propionitrile was $0·86 \times 10^{-6}\ \Omega^{-1}$ cm.$^{-1}$. Silicon tetrabromide (0·0154 mole/l.) was added to the solvent, giving an equivalent conductance of 0·81 Ω^{-1} cm.^{2} mole^{-1}. Triphenylphosphine oxide in the mole ratio of $SiBr_4 : Ph_3PO$ of 1 : 4 was added to the solution, the equivalent conductance of which rose immediately to 85 Ω^{-1} cm.^{2} mole^{-1}.

$SiF_4,2C_5H_5N$.—Silicon tetrafluoride bubbled into a mixture of pyridine and benzene gave an immediate precipitate of SiF_4,2py. The precipitate was washed with benzene and pumped dry (Found: C, 46·0, H, 4·6. Calc. for $C_{10}H_{10}F_4N_2Si$: C, 45·8; H, 3·85%).

$SiF_4,2Ph_3PO$.—There was no immediate precipitate when silicon tetrafluoride was passed into a solution of triphenylphosphine oxide in benzene, but a white crystalline deposit of $SiF_4,2Ph_3PO$ slowly formed (Found: C, 66·9; H, 5·0. Calc. for $C_{36}H_{30}F_4O_2P_2Si$: C, 65·4; H, 4·55).

SiF_4, 1,10-$C_{12}H_8N_2$.—When silicon tetrafluoride was passed into a solution of 1,10-phenanthroline dissolved in benzene an immediate white precipitate of the 1 : 1 adduct was formed (Found: C, 49·5; H, 3·45. Calc. for $C_{12}H_8F_4N_2Si$: C, 50·7; H, 2·85%).

Infrared Spectra.—Infrared spectra were obtained with a Perkin-Elmer 221 Spectrometer equipped with grating, rock-salt, and cæsium bromide optics. During the course of this work a simple and efficient type of liquid cell was developed. A piece of thin-walled (0·020 in.) high-density Polythene tubing (0·5 in. o.d.) (British Resin Products Ltd.) about 3 in. long was flattened and one end was heat-sealed. The other end was pushed into a warm, tapered glass tube fitted with a ground joint. In use, the Polythene tube is fitted between two metal plates (the separation of which is adjustable) equipped with apertures to suit the sample beam. The cell is airtight and simple and inexpensive to construct, though it suffers from bowing of the windows (not a serious defect in its present applications).

Raman Spectra.—Raman spectra were obtained with a Carey 81 spectrophotometer and the mercury 4358 Å exciting line. Obtaining Raman spectra of solids presents a considerable number of problems, which have been partly overcome.[31-33] Because of the hygroscopic nature of our compounds it was necessary to modify these techniques, and successful spectra were obtained with a number of co-ordination compounds. A short Raman tube (7 mm. diam.) fitted with a ground-joint carrying a supporting rod was used in conjunction with the *solid-state* optics (cf. Ferraro [31]) and sample holder. Normally, a layer of compound *ca.* 2 mm. thick is placed in the tube and tamped down. The intensity of the Raman lines is strongly dependent on the position and crystallinity of the sample, and the former should certainly be optimised for each spectrum. In order to obtain the Raman spectrum of $SiCl_4,2Ph_3PO$, it was necessary to recrystallise the material from acetonitrile.

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