An Investigation of Halide Abstraction by Arsenic(III): Reactions of $AsCl_3$ with MCl_2 (M = Mg or Zn) and $TiCl_4$ in Donor Solvents (MeCN or $POCl_3$). Formation and Crystal Structure of the Dimeric Titanium(IV) Compound $[Ti_2Cl_6(POCl_3)_2(PO_2Cl_2)_2]$ *

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Reactions of $TiCl_4$, $MgCl_2$, and $ZnCl_2$ with $AsCl_3$ in acetonitrile as solvent (L) have been studied. Rather than the expected halide abstraction by As^{III} to provide anionic chloroarsenic(III) and cationic chlorometal species, the simple adducts $TiCl_4L_2$, $MgCl_2L_2$, and $ZnCl_2L_2$ were isolated. Treatment of $TiCl_4$ and $AsCl_3$ with L = $POCl_3$ provides the yellow complex $[Ti_2Cl_6(POCl_3)_2(PO_2Cl_2)_2]$ (**1**) whose structure has been determined by *X*-ray crystallography. Crystals are monoclinic, space group $P2_1/n$, with $a = 8.612(8)$, $b = 15.339(13)$, $c = 10.232(11)$ Å, $\beta = 98.0(1)°$, and $Z = 2$. 1 899 Independent reflections were measured on a diffractometer of which 1 341 were used in the final refinement. The structure was refined to R' 0.075. The crystal contains discrete centrosymmetric dimeric molecules involving *O,O'*-dichlorophosphate bridging ligands. The titanium centres are octahedrally co-ordinated to three chlorine atoms and three oxygen atoms each in the *fac* arrangement. Two of these oxygens belong to separate bridging dichlorophosphate groups and the third is provided by a co-ordinated $POCl_3$ molecule. Possible reaction pathways leading to the formation of the eight-membered bimetallocycle (**1**) are discussed.

Recent observations in these laboratories indicate that Sb^{III} [1] and Sb^{V} [2,3] can effectively remove halide ion(s) from transition and non-transition metal halides to provide discrete cationic metal species, *e.g.* equations (1)—(3) (L = MeCN). In the

$$VCl_3 + SbCl_5 \longrightarrow [VCl_2L_4][SbCl_6] \qquad (1)$$

$$MgCl_2 + 2SbCl_3 \longrightarrow [MgL_6][Sb_2Cl_8] \qquad (2)$$

$$SnCl_4 + SbCl_5 \longrightarrow [SnCl_3L_3][SbCl_6] \qquad (3)$$

knowledge that As^{III} shows a similar Lewis acid trait as a powerful halide acceptor, *e.g.* $[AsCl_4]^-$, $[As_2Cl_8]^{2-}$, or $[As_2Cl_9]^{3-}$,[4] we have initiated a parallel study of various MCl_n–$AsCl_3$ systems as an alternative and perhaps more selective route to cationic chloro metal (M) species.

In this report we describe the reactions of several covalent metal chlorides with arsenic trichloride; in particular the reaction of $TiCl_4$ with $AsCl_3$ in $POCl_3$ as solvent and its surprising outcome.

Experimental

Manipulations of materials were carried out using a conventional N_2-filled 'dry-box' and, on occasions, an all-glass vacuum line system. Anhydrous metal chlorides were used as supplied commercially. MeCN and $POCl_3$ were purified following the recommended procedures,[5] stored over P_4O_{10}, and distilled under N_2 prior to use. Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer with samples as Nujol mulls placed between CsI plates. The ^{31}P n.m.r. spectra were obtained using a Bruker WH400 instrument (162 MHz) with samples as $CDCl_3$ solutions (internal capillary reference 85% H_3PO_4).

Preparation of Complexes.—(*a*) $TiCl_4(MeCN)_2$, $MgCl_2(MeCN)_2$, *and* $ZnCl_2(MeCN)_2$. Dropwise addition of $AsCl_3$ (1 mol) in MeCN solution to the particular covalent metal halide MCl_4 (M = Ti) or MCl_2 (M = Mg and Zn) (1 mol) dissolved in MeCN (50 cm^3) at 0 °C and maintained under an inert atmosphere of nitrogen provided clear solutions. These solutions were warmed (50 °C) and stirred mechanically for 12 h. Removal of solvent followed by general work-up procedures provided the appropriate bis-adducts: $TiCl_4(MeCN)_2$ (Found: C, 17.6; H, 2.2; Cl, 52.1; N, 10.2. Calc. for $C_4H_6Cl_4N_2Ti$: C, 17.7; H, 2.2; Cl, 52.2; N, 10.3%), $MgCl_2(MeCN)_2$ (Found: C, 27.0; H, 3.2; Cl, 39.9; N, 15.8. Calc. for $C_4H_6Cl_2MgN_2$: C, 27.1; H, 3.4; Cl, 40.0; N, 15.8%), and $ZnCl_2(MeCN)_2$ (Found: C, 22.0; H, 2.7; Cl, 32.5; N, 12.7. Calc. for $C_4H_6Cl_2N_2Zn$: C, 22.0; H, 2.8; Cl, 32.5; N, 12.8%).

(*b*) $[Ti_2Cl_6(POCl_3)_2(PO_2Cl_2)_2]$ (**1**). A solution of $TiCl_4$ (2.3 cm^3, 20.9 mmol) in $POCl_3$ (50 cm^3) was added slowly to a chilled (0 °C) and stirred solution of $AsCl_3$ (1.8 cm^3, 21.5 mmol) in $POCl_3$ (100 cm^3) maintained under a nitrogen atmosphere. The resulting clear yellow solution was stirred at room temperature for 6 h. Slow removal of solvent *in vacuo* led to the deposition of a bright yellow solid. The *product* was collected, washed with hexane (3 × 25 cm^3), and dried *in vacuo* at room temperature for 2 h, m.p. 98—100 °C (yield: 3.7 g, 42%) (Found: Cl, 64.2; Ti, 10.8. Calc. for $Cl_{16}O_6P_4Ti_2$: Cl, 64.2; Ti, 10.9%). Recrystallisation from $POCl_3$–C_6H_6 (1:1) provided yellow needle crystals suitable for *X*-ray diffraction studies.

(*c*) (**1**) *from controlled hydrolysis of* $[TiCl_4(POCl_3)_2]$. The compound $[TiCl_4(POCl_3)_2]$ (2.78 g, 5.6 mmol) was dissolved in freshly-distilled Et_2O (100 cm^3) and then added dropwise to a stirred solution of Et_2O (50 cm^3)–H_2O (0.1 cm^3, 5.6 mmol) at room temperature maintained under an inert atmosphere of nitrogen. The initial clear yellow solution became cloudy during

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* Di-μ-dichlorophosphato-*O,O'*-bis[trichloro(trichlorophosphine oxide)titanium(IV)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Ti(1)	−754(5)	1 359(2)	1 375(4)
Cl(1)	−3 092(8)	1 833(4)	466(7)
Cl(2)	408(9)	2 646(3)	1 584(7)
Cl(3)	−1 196(9)	1 287(4)	3 465(6)
P(10)	2 995(9)	698(4)	2 870(6)
Cl(11)	4 193(10)	1 759(5)	3 044(9)
Cl(12)	4 326(10)	−149(5)	2 141(8)
Cl(13)	2 828(11)	344(7)	4 652(7)
O(14)	1 518(17)	771(9)	1 998(14)
P(20)	−1 023(8)	−848(3)	1 226(5)
Cl(21)	−3 012(9)	−1 496(4)	818(8)
Cl(22)	−224(10)	−1 146(4)	3 098(6)
O(23)	−1 434(18)	86(8)	1 121(15)
O(24)	−142(18)	1 201(8)	−430(12)

Table 2. Molecular dimensions; distances in Å, angles in degrees

Ti(1)–Cl(1)	2.219(8)	P(10)–Cl(12)	1.948(10)
Ti(1)–Cl(2)	2.211(7)	P(10)–Cl(13)	1.927(9)
Ti(1)–Cl(3)	2.227(7)	P(10)–O(14)	1.453(15)
Ti(1)–O(14)	2.168(15)	P(20)–Cl(21)	1.974(9)
Ti(1)–O(23)	2.045(12)	P(20)–Cl(22)	1.996(8)
Ti(1)–O(24)	2.004(13)	P(20)–O(23)	1.475(13)
P(10)–Cl(11)	1.922(10)	P(20)–O(24)*	1.475(13)
Cl(1)–Ti(1)–Cl(2)	96.9(3)	Cl(11)–P(10)–Cl(12)	105.3(5)
Cl(1)–Ti(1)–Cl(3)	98.7(3)	Cl(11)–P(10)–Cl(13)	105.1(5)
Cl(2)–Ti(1)–Cl(3)	95.0(3)	Cl(12)–P(10)–Cl(13)	107.5(5)
Cl(1)–Ti(1)–O(14)	171.3(5)	Cl(11)–P(10)–O(14)	113.9(7)
Cl(2)–Ti(1)–O(14)	88.0(4)	Cl(12)–P(10)–O(14)	109.1(7)
Cl(3)–Ti(1)–O(14)	88.0(5)	Cl(13)–P(10)–O(14)	115.4(7)
Cl(1)–Ti(1)–O(23)	91.9(5)	Ti(1)–O(14)–P(10)	152.9(9)
Cl(2)–Ti(1)–O(23)	169.5(5)	Cl(21)–P(20)–Cl(22)	105.1(4)
Cl(3)–Ti(1)–O(23)	89.5(5)	Cl(21)–P(20)–O(23)	106.3(7)
O(14)–Ti(1)–O(23)	82.6(5)	Cl(22)–P(20)–O(23)	109.9(7)
Cl(1)–Ti(1)–O(24)	89.6(5)	Cl(21)–P(20)–O(24)*	109.5(6)
Cl(2)–Ti(1)–O(24)	91.3(4)	Cl(22)–P(20)–O(24)*	105.9(6)
Cl(3)–Ti(1)–O(24)	168.8(4)	O(23)–P(20)–O(24)*	119.3(9)
O(14)–Ti(1)–O(24)	83.0(5)	Ti(1)–O(23)–P(20)	148.9(10)
O(23)–Ti(1)–O(24)	82.8(5)	Ti(1)–O(24)–P(20)*	146.8(10)

* Symmetry element $-x$, $-y$, $-z$.

stirring (6 h) and a fine white solid slowly deposited; this was subsequently collected and identified as TiO_2. The resulting solution was filtered and slow removal of solvent provided a small crop of yellow crystals which were collected, washed with n-hexane (3 × 25 cm^3), and dried *in vacuo* at room temperature for several hours (yield: 0.22 g, 8.4%). Identification of this product as (**1**) followed from m.p. 98—101 °C, chloride analysis (found: 64.0, calc. 64.2%) and i.r. spectrum comparisons with those of an authentic sample.

Crystal Structure Determination of $[Ti_2Cl_6(POCl_3)_2(PO_2Cl_2)_2]$ (**1**).—*Crystal data.* $Cl_{16}O_6P_4Ti_2$, $M = 882.9$, monoclinic, $a = 8.612(8)$, $b = 15.339(13)$, $c = 10.232(11)$ Å, $\beta = 98.0(1)°$, $U = 1\,338.5$ Å^3, $F(000) = 848$, $D_m = 2.18$ g cm^{-3}, $D_c = 2.20$ g cm^{-3}, $Z = 2$, Mo-K_α radiation ($\lambda = 0.7107$ Å), μ(Mo-K_α) = 22.4 cm^{-1}, space group $P2_1/n$.

A crystal of approximate size 0.3 × 0.3 × 0.3 mm was set up to rotate about the a axis on a Stoe-Stadi2 diffractometer and data were collected *via* a variable width ω scan. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of $(1.5 + \sin\mu/\tan\theta)$. 1 899 Independent reflections with $2\theta < 50°$ were measured in this manner of which 1 341 with $I > 2\sigma(I)$ were used in the calculations. The data were not corrected for absorption. The structure was solved by statistical methods and refined *via* anisotropic thermal parameters to R 0.072 ($R' = 0.075$). In the refinement, the weighting scheme used was $w = 1/[\sigma^2(F) + 0.003F^2]$. Calculations were carried out using SHELX 76[6] and some of our own programs on the Amdahl V7 at the University of Reading. Positional parameters are given in Table 1 and molecular dimensions in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

Direct treatment (equimolar) of $AsCl_3$ and $TiCl_4$ in $POCl_3$ solutions under our laboratory precautions for strict anhydrous conditions provided the yellow crystalline solid (**1**). The product is extremely sensitive to air and moisture (hydrolysis) but can be stored safely under an atmosphere of nitrogen. There is reasonable solubility in chloroform and benzene. The i.r. spectrum shows bands at 375, 405 $\nu(TiCl_{terminal})$; 525 $\nu_{sym}(PCl_2)$; 590, 615, 628 $\nu_{asym}(PCl_3) + \nu_{asym}(PCl_2) + \delta(PO_2)$; 1 082 $\nu_{sym}(PO_2)$; 1 202 $\nu_{asym}(PO_2)$; and 1 245 cm^{-1} ν(P=O).[7–9] Two signals are observed in the ^{31}P n.m.r. spectrum consistent with two separate phosphorus environments δ 5.1 ($POCl_3$) and 7.5 p.p.m. (PO_2Cl_2).

Structure of $[Ti_2Cl_6(POCl_3)_2(PO_2Cl_2)_2]$ (**1**).—The structure consists of individual centrosymmetric dimers of $[Ti_2Cl_6(POCl_3)_2(PO_2Cl_2)_2]$ as shown in the Figure. Each titanium atom has a distorted octahedral environment, being bonded to three chlorine atoms and three oxygen atoms each in the *fac* formation. Two of the oxygens belong to two separate bridging PO_2Cl_2 groups and the third comes from a monodentate $POCl_3$ ligand. The dimensions of the dimer are much as expected. The Ti–Cl distances, 2.211(7), 2.219(8), 2.227(7) Å compare favourably with other terminal Ti–Cl bonds of six-co-ordinate Ti^{IV} dimeric molecules, *e.g.* $[\{TiCl_4(CH_3NO_2)\}_2]$[10] 2.203(3), 2.206(4), 2.202(3) Å, $[\{TiCl_4(POCl_3)\}_2]$[11] 2.24(1), 2.23(1), 2.20(1) Å, and co-ordination of $POCl_3$ to titanium appears to have a minimal effect on the dimensions of the ligand, *e.g.* $POCl_3$,[12] P–O 1.45, P–Cl(av) 1.99 Å, O–P–Cl(av) 114.9, Cl–P–Cl(av) 103.5°; (**1**) P–O 1.453(15), P–Cl(av) 1.932 Å, O–P–Cl(av) 112.8, Cl–P–Cl(av) 105.9°. The Ti–O(14) bond to the monodentate ligand is slightly longer at 2.168(15) Å than those to the bridging ligands [Ti–O(23) 2.045(12), Ti–O(24) 2.004(13) Å]. The reason for this is not clear but it could be the result of steric effects; it is noticeable that the Ti–O–P angle is larger for the monodentate ligand [152.9(9)°] than the similar angles for the bridging ligands [148.9(10), 146.8(10)°]. This enlargement could also be caused by steric effects for which the net result would be a displacement of the three chlorine atoms as a group away from the metal co-ordination sphere. Thus Cl(2) ··· Cl(11) and Cl(3) ··· Cl(13) distances are reasonable at 3.65 and 3.80 Å respectively. The Cl–Ti–Cl angles are all greater than 90° and the O–Ti–O angles are less than 90° presumably a reflection of the appreciable atomic size difference between oxygen and chlorine. There are no intermolecular contacts less than the sum of van der Waals radii.

There are precedents for this type of structure, *viz.* $[Mn(PO_2Cl_2)_2(MeCO_2Et)_2]$ (**2**),[13] $[Mg(PO_2Cl_2)_2(POCl_3)_2]$ (**3**),[14] and $[\{SnCl_3(POCl_3)(PO_2Cl_2)\}_2]$ (**4**).[15] As a general point the P–O bond lengths of the bridging PO_2Cl_2 units are symmetrical, *e.g.* (**1**) 1.475(13), 1.475 (13); (**2**) 1.46, 1.47, 1.45, 1.47; (**3**) 1.441, 1.440, 1.440, 1.43 Å; and (**4**) 1.485(12), 1.498(12) Å, but there appears to be quite a large variation possible for the bridging P–O–metal angles, *e.g.* (**1**) 148.9(10), 146.8(10); (**2**) 150.7, 141.3, 143.0, 173.3; (**3**) 162.0, 144.2; and (**4**) 139.9, 141.2°.

Initially the formation of (**1**) was rationalised as shown in

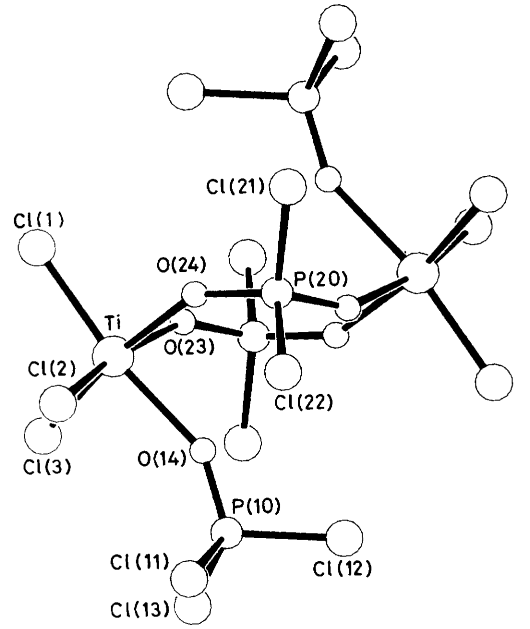
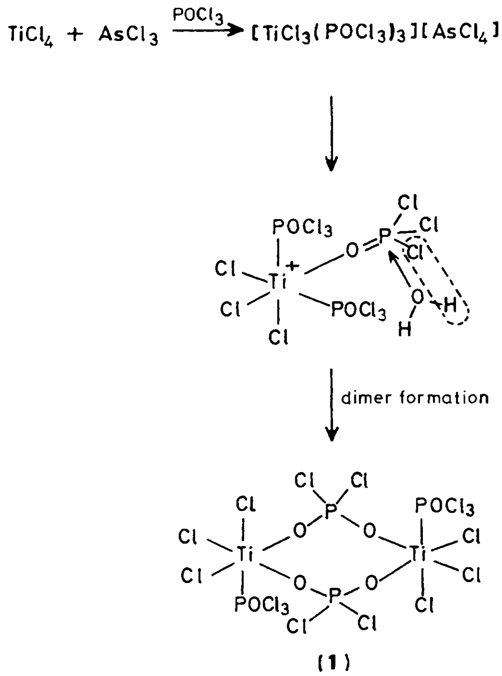


Figure. The molecular structure of $[Ti_2Cl_6(POCl_3)_2(PO_2Cl_2)_2]$



(1)

Scheme.

the Scheme. In the first step halide abstraction by As^{III} provides the chlorotitanium(IV) cation $[TiCl_3(POCl_3)_3][AsCl_4]$, *cf.* the recently reported *fac*-$[TiCl_3(MeCN)_3][SbCl_6]$.[2] Subsequently nucleophilic attack by water at a phosphorus centre of a co-ordinated $POCl_3$ ligand leads to elimination of HCl and the 'free' oxygen of the bound $[PO_2Cl_2]^-$ anion with its incipient charge delocalisation can then bind to a separate titanium cation *via* an *O,O'* bidentate bridge to give (**1**). Alternatively we can have direct co-ordination of a pre-formed $[PO_2Cl_2]^-$ anion: studies by Grunze[16] confirm the ready hydrolysis $POCl_3 + H_2O \longrightarrow H^+[PO_2Cl_2]^- + HCl$. Exchange of co-ordinated ⟷ bulk solvent ($POCl_3$) is assumed throughout.

Two points are crucial to this scheme: (*a*) the involvement of water molecules since they provide the source of the 'second' oxygen of the bridging PO_2Cl_2 unit and (*b*) the *initial* formation of a cationic chlorotitanium(IV) species possessing high oxophilicity. With regard to the latter it should be noted that (**1**) crystallised from the original reaction mixture and although we made several attempts to identify an $[AsCl_4]^-$ anion in the remaining mother-liquor these were unsuccessful. Moreover the supporting reaction systems studied [equations (4) and (5)]

$$TiCl_4\text{–}AsCl_3\text{–}MeCN \longrightarrow TiCl_4(MeCN)_2 \qquad (4)$$

$$MCl_2\text{–}2AsCl_3\text{–}MeCN \longrightarrow MCl_2(MeCN)_2 \qquad (5)$$

(M = Mg or Zn) gave neutral bis-acetonitrile adducts even in the case of the strongly electropositive Mg^{II} chloride. In view of this conclusive evidence against halide abstraction by As^{III} in such systems, an alternative approach was considered, namely the hydrolysis of *neutral* $[TiCl_4(POCl_3)_x]$ ($x = 1$ or 2) adducts involving nucleophilic attack by water at a phosphorus centre and at a metal centre.

To probe the validity of this approach we carried out the controlled hydrolysis of *cis*-$[TiCl_4(POCl_3)_2]$,[17] equation (6),

$$2[TiCl_4(POCl_3)_2] + 2H_2O \longrightarrow (\mathbf{1}) + 4HCl \qquad (6)$$

and obtained the desired product (**1**), albeit in very small yield (8.4%), along with deposition of TiO_2. Other titanium intermediates are almost certainly produced but were not pursued.

Thus depending on the *exact* amount of H_2O introduced into the system either by accident or design the accompanying hydrolysis of Ti–Cl bonds provides limited formation of the metal oxide at the expense of (**1**). Several other examples can be cited in this context: partial hydrolysis of $TiCl_4(MeCN)_2$ in acetonitrile as solvent provides binuclear $Ti_2Cl_6O{\cdot}4MeCN$ (and $Ti_2Cl_6O{\cdot}6.5MeCN$) with an assumed $Cl_3Ti\text{–}O\text{–}TiCl_3$ framework.[18] The structure of this compound can be viewed as the condensation product of formal '$TiCl_3(OH)(MeCN)_2$'; partial hydrolysis of the chlorotitanium(IV) carboxylate derivatives $[TiCl_x(O_2CR)_{4-x}]$ (R = Me or Ph, $x = 3$; R = Me, $x = 2$) in L = ethyl acetate or tetrahydrofuran results in the formation of binuclear complexes $Ti_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2Cl_4{\cdot}2L$ which have both oxygen and carboxylate groups as bridging units. ^{17}O N.m.r. data confirm that the bridging oxygen atom comes from the water added.[19] Here again the bridging oxygen unit can be viewed as the condensation product of formal Ti–OH bonds 'locked' into suitable positions by the bridging carboxylate groups; the titanium hydroxychloride '$TiCl(OH)_3{\cdot}2H_2O$' obtained from the partial hydrolysis of $TiCl_4$ has a cubic structure based on $[Ti_8O_{12}(H_2O)_{24}]^{8+}$ containing edge μ-oxo (Ti–O–Ti) linkages and terminal $Ti\text{–}OH_2$ bonds.[20]

Historically (**2**) and (**3**) were obtained from direct reactions of the respective metal oxide and $POCl_3$ and were originally classifed as the bis-adducts $MO{\cdot}2POCl_3$;[21] their correct structural identification followed some fifty years later. Compound (**4**) was prepared in the first instance by Dehnicke[22] *via* reaction (7). (The successful *X*-ray structure determination

$$SnCl_4 + Cl_2O/O_2 \longrightarrow SnOCl_2 \xrightarrow{POCl_3} SnOCl_2{\cdot}2POCl_3 \qquad (7)$$

by Moras *et al.*[15] was carried out on a crystalline sample obtained following the same recipe.) In a subsequent report by Dehnicke[7] the titanium counterpart $TiOCl_2{\cdot}2POCl_3$ is described; by analogy with the Sn^{IV} system the present structure (**1**) provides the correct identity of this 'bis-adduct'. Although there is no direct mention of possible reaction pathways in the reports of (**2**)—(**4**) (refs. 13, 14, 15, and 23) Danielsen and Rasmussen[13] make the significant point for (**2**) that 'all recorded observations indicate that the presence of small amounts of water is necessary for the reaction to take place.'

In our view formation of the bimetallocyclic compounds (**1**)—(**4**) follows from hydrolysis of the P–Cl bonds of $POCl_3$ ligands, which may or may not be initially co-ordinated to the metal, in the presence of critically restricted amounts of water. In the case of (**1**) and, by implication (**4**), there is accompanying limited hydrolysis of metal–chlorine bonds. The adventitious presence of traces of water comes from 'wet' $POCl_3$. With a surfeit of water present it is suggested that (*i*) further hydrolysis of $POCl_3$ beyond the first ionization stage would lead to a diminution of $[PO_2Cl_2]^-$ anions which, consequently, would curtail bimetallocycle formation and (*ii*) extended hydrolysis of available metal–chlorine bonds especially in the present instance of (**1**) facilitates formation of the metal oxide [and other intermediate μ-oxo-titanium(IV) species?] as the dominant reaction.

Acknowledgements

We thank the S.E.R.C. for a studentship award (to P. P. K. C.) and for funds for the diffractometer and Mr. A. W. Johans for his assistance with the crystallographic investigations.

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Received 15*th March* 1988; *Paper* 8/01075G