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Phosphine and phosphine oxide adducts of vanadium(IV) chloride: synthesis and structural studies

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Abstract

The reaction products of VCl_4 with PEt_3, PMe_3, PMe_2Ph, Et_3PO and $PhMe_2PO$ have been structurally characterized. Compound **1**, $[HPEt_3][VCl_4(PEt_3)_2]$, crystallizes in space group *C2/c* with $a=17.422(2)$, $b=12.671(1)$, $C=13.390(1)$ Å, $\beta=95.76(2)°$, $V=2941(2)$ Å^3 and $Z=4$. The $[VCl_4(PEt_3)_2]^-$ anion has a *trans* arrangement of the phosphines with mean V–Cl and V–P distances of 2.360(3) and 2.551(4) Å, respectively. Compound **2**, *mer*-$VCl_3(OPEt_3)_3$, crystallizes in an orthorhombic cell ($P2_12_12_1$) with $a=13.310(4)$, $b=17.754(6)$, $c=12.383(3)$ Å, $V=2926(2)$ Å^3 and $Z=4$; V–Cl distance (av.) = 2.396(7) and V–O (av.) = 2.00(2) Å. Compound **3**, *mer*-$VCl_3(PMe_2Ph)_2(OPMe_2Ph)$ which has been reported before in a different space group, crystallizes with an orthorhombic ($Pmn2_1$) unit cell: $a=13.590(4)$, $b=11.673(4)$, $c=8.964(4)$ Å, $V=1422(1)$ Å^3 and $Z=2$. A mirror plane bisects the molecule. The V–Cl, V–P and V–O distances are similar to those in **1** and **2**. Compound **4**, $V_2Cl_6(PMe_3)_4$, is a dinuclear compound which crystallizes with an orthorhombic unit cell ($Pna2_1$) with cell dimensions: $a=11.470(4)$, $b=18.433(4)$, $c=13.677(4)$ Å, $V=2892(2)$ Å^3 and $Z=4$, distance V–Cl_t (av.) = 2.30(1), V–Cl_b(av.) = 2.44(1) and V–P (av.) = 2.524(6) Å. The phosphines have the common 1,3,6,8 arrangement. The V V distance of 3.691(2) Å is non-bonding. The reaction chemistry of these compounds is compared with that of the Nb and Ta analogs, and EPR measurements made on compound **1** are discussed. EPR spectra recorded for solutions of **1** in CH_2Cl_2 were shown to be due to about 1% of the vanadium in the form of $VOCl_2(PEt_3)_2$.

Key words Crystal structures, Vanadium complexes; Halide complexes; Phosphine complexes

Introduction

The phosphine complexes of niobium(IV) chloride and tantalum(IV) chloride have been extensively studied by this research group [1, 2], but information on vanadium(IV) chloride phosphine adducts is still scarce. In 1965, Walton and co-workers reported reduction of VCl_4 by PPh_3 at room temperature [3], but the product was not structurally characterized. Samuel and co-workers assumed a *trans* arrangement of the phosphine ligands in the MCl_4 (M = V, Nb, Ta) adducts [4, 5], and this has been shown to be true by structure determinations for $NbCl_4(PEt_3)_2$ [1] and $TaCl_4(PEt_3)_2$ [2]. The previous literature reports disagreed on the oxidation state of vanadium and neither the stoichiometry nor the structures of the reaction products were determined.

In this paper we report four compounds obtained from reactions between VCl_4 and three different phosphines. The common feature of all reactions is reduction of vanadium from IV to III, but the products formed are quite different. Presumably the phosphine is the reducing agent and in two cases, the phosphine oxide occurs in the product. Dimerization occurs in the trimethylphosphine case, and an ionic species was isolated from the reaction between VCl_4 and PEt_3.

Experimental

All operations were carried out under an atmosphere of argon. All of the following compounds are very sensitive to air and/or moisture; they turn into greenish oils in open air in less than 1 h. Standard vacuum-line and Schlenk techniques were used. VCl_4 (90%) purchased from Alfa and phosphines purchased from Strem were used as received. VCl_4 was diluted by toluene to make a 0.5 M solution. The ^{31}P NMR spectra were recorded on a Varian XL-200 spectrometer operating at 81 MHz, and EPR spectra were recorded on a Bruker

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TABLE 1. Crystal data for $(HPEt_3)[VCl_4(PEt_3)_2]$ (**1**), $VCl_3(OPEt_3)_3$ (**2**), $VCl_3(PMe_2Ph)_2(OPMe_2Ph)$ (**3**) and $V_2Cl_6(PMe_3)_4$ (**4**)

	1	**2**	**3**	**4**
Formula	$VCl_4P_3C_{18}H_{46}$	$VCl_3P_3O_3C_{18}H_{45}$	$VCl_3P_3OC_{24}H_{33}$	$V_2Cl_6P_4C_{12}H_{36}$
Formula weight	548.24	923.83	587.7	618.9
Space group	*C2/c* (No. 15)	$P2_12_12_1$ (No. 19)	$Pmn2_1$ (No. 31)	$Pna2_1$ (No. 33)
a (Å)	17.422(2)	13.310(4)	13.590(5)	11.470(3)
b (Å)	12.671(1)	17.754(6)	11.673(4)	18.433(4)
c (Å)	13.390(1)	12.383(3)	8.964(4)	13.677(4)
α (°)	90	90	90	90
β (°)	95.76(2)	90	90	90
γ (°)	90	90	90	90
V (Å^3)	2941(2)	2926(2)	1422(1)	2892(2)
Z	4	4	2	4
D_{calc} (g/cm^3)	1.236	1.039	1.373	1.422
Crystal size (mm)	0.32 × 0.28 × 0.28	0.07 × 0.52 × 0.58	0.25 × 0.20 × 0.18	0.35 × 0.48 × 0.42
μ(Mo Kα) (cm^{-1})	8.582	7.203	8.034	14.042
Data collection instrument	Nicolet P3	Nicolet P3	Enraf-Nonius CAD-4	Nicolet P3
Radiation monochromated in incident beam (Mo Kα, Å)	0.71073	0.71073	0.71073	0.71073
Orientation reflections no.; range (2θ)	25; 17–21	25, 18–24	25, 17–29	25, 25–35
Temperature (°C)	20	20	−60	20
Scan method	2θ–ω	2θ–ω	2θ–ω	2θ–ω
Data collection range, 2θ (°)	4–46	4–45	4–50	4–45
No. unique data: total	1898	2194	1473	1949
with $F_o^2 > 3\sigma(F_o^2)$	1272	1625	776	1250
No. parameters refined	109	253	162	216
Transmission factors max., min.	1.00, 0.96	0.97, 0.89	1.00, 0.80	0.90, 0.80
R[a]	0.068	0.052	0.052	0.052
R_w[b]	0.074	0.068	0.072	0.064
Quality-of-fit indicator[c]	1.767	1.476	1.626	1.807
Largest shift/e.s.d., final cycle	0.004	0.01	0.03	0.08
Largest peak (e/Å^3)	0.226	0.322	0.535	0.476

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obsd} - N_{param})]^{1/2}$

ESP 300 spectrometer. The intensity standard for EPR calibration was a 0.1 M Cu–EDTA aqueous solution. Magnetic susceptibility was measured on a Series 300 Lewis coil force magnetometer

Preparation of $[HPEt_3][VCl_4(PEt_3)_2]$ *(1)*

A 1:1 mixture of toluene and hexanes (20 ml) was layered on the top of the VCl_4 solution (2 ml, 0.5 M) in a Schlenk tube, and a PEt_3 solution (0.29 ml, 2 mmol) was slowly added to the top. A large quantity (*c.* 300 mg) of orange block-shaped crystals of X-ray quality formed over a period of one week.

The ^{31}P NMR of this compound showed a doublet at 96.63 ppm with a splitting of 530 Hz, corresponding to H–P direct coupling. The room temperature magnetic susceptibility measurement gave $\mu_{eff} = 2.69$ BM. The EPR spectra recorded for a solution of this compound in dichloromethane at both room and low temperature were essentially the same as those reported before for the reaction solution of VCl_4 and PEt_3 in toluene [4, 5].

Preparation of $VCl_3(OPEt_3)_3$ *(2)*

PEt_3 (0.29 ml, 2 mmol) was added directly to 2 ml of 0.5 M VCl_4 in toluene under stirring. The solution turned mauve-pink and some white precipitate formed (probably oxidized phosphine). After filtration, the solution was layered with toluene and hexane. This procedure yielded crystals of both **1** and **2**. $VCl_3(OPEt_3)_3$ formed as purple needles (*c.* 200 mg). **1** and **2** were separated by picking out the different colored crystals.

Preparation of $VCl_3(PMe_2Ph)_2(OPMe_2Ph)$ *(3)*

A method similar to the preparation of **1** was used with the only change being that PMe_2Ph was used in place of PEt_3. After two weeks, some purple–brown crystals (*c.* 400 mg) formed on the side of the tube.

Preparation of $V_2Cl_6(PMe_3)_4$ *(4)*

A procedure similar to that for **1** was carried out by using PMe_3. Upon refrigeration at 0 °C for about two weeks, large quantities (*c.* 200 mg) of black block crystals appeared along with a yellow precipitate. The identity of this precipitate is unknown. The crystals of **4** were picked out from the precipitate.

X-ray crystallography

The structures of single crystals of the above compounds have been determined by following general procedures described elsewhere [6]. The data pertinent to the structure determinations are summarized in Table 1. Some details for individual compounds are given below. See also 'Supplementary material'.

Compound 1

An orange crystal of dimensions 0.32×0.28×0.28 mm was wedged in a Lindemann capillary with mineral oil and mother liquor. Indexing based on 25 reflections with $17 < 2\theta < 21°$ yielded a *C*-centered monoclinic cell. The *C*-centering and *2/m* Laue group were confirmed by axial photos. The systematic absences suggested two possible space groups, *Cc* (No. 9) and *C2/c* (No. 15). *C2/c* was chosen and led to successful structural refinement. The diffraction data were gathered on a Nicolet P3 diffractometer by using a 2θ–ω scan method. Total loss of intensity was 7.7%.

The initial positions of the vanadium atom and those atoms directly connected to it were located by using the direct methods option in SHELXS-86. The other atoms of the molecule were located from difference Fourier maps. The vanadium atom resides on an inversion center, and the phosphorus atom of the phosphonium cation resides on a two-fold axis, which requires one ethyl group on the latter to be disordered with half occupancy on each side of the two-fold axis. The carbon atoms of the phosphonium ion were refined isotropically while the other atoms were refined anisotropically.

Compound 2

A purple plate crystal of size 0.07×0.52×0.58 mm was mounted in a Lindemann capillary under the protection of mineral oil. An orthorhombic cell was derived from indexing of 25 reflections in the 2θ interval of 18–24 °. The space group $P2_12_12_1$ (No. 19) was uniquely determined from the systematic absences. The *mmm* Laue class was confirmed by axial photos. The data were collected on a Nicolet P3 diffractometer, and the overall intensity change was −5.8%.

The Patterson method was applied to obtain the position of the vanadium atom and the other non-hydrogen atoms were found in difference Fourier maps. All atoms were refined anisotropically and the final residual peaks ($\leqslant 0.322$ e/Å^3) are not chemically meaningful.

Compound 3

A purple, block crystal (0.25×0.20×0.18 mm) was mounted on a quartz fiber with silicone grease, and quickly put on an Enraf-Nonius CAD-4 diffractometer under the protection of an N_2 stream (−60 °C). Indexing of 25 reflections in the range $17 < 2\theta < 29°$ indicated an orthorhombic cell, which was confirmed by axial photos. The systematic absences allowed two possible space groups, namely $Pnm2_1$ (No. 31) and *Pnmm* (No. 59). Since there can only be two molecules in one unit cell and the molecules can have at most one mirror plane, the former space group was chosen and the cell was transformed to the standard setting of $Pmn2_1$. The data collecting method was 2θ–ω scan, and a decay (−3.6%) correction was applied. The structure model was derived from a three-dimensional Patterson map. A mirror plane passing through the vanadium atom and three chloride atoms made only half of the molecule unique.

Compound 4

A black, diamond-shaped crystal (0.35×0.48×0.42 mm) was sealed in a Lindemann capillary with mineral oil, and mounted on a Nicolet P3 diffractometer. 25 reflections were centered with $25 < 2\theta < 35°$. The indexing of these reflections led to an orthorhombic cell. $P2_1cn$ (No. 33) and *Pmcn* (No. 62) were the two space groups that were consistent with the systematic absences. The structure was successfully refined in space group $Pna2_1$ (standard setting of $P2_1cn$). The methyl groups on the equatorial phosphines are staggered and therefore there is no mirror symmetry in this molecule, as would have been required by space group No. 62. The intensity decay in the data collection was 6.4%. The Patterson method was chosen to determine the positions of vanadium atoms and those atoms directly connected to them. The refinement was carried out by the same procedure used for **1**.

Results and discussion

Reaction chemistry

The reduction of VCl_4 and $TiBr_4$ by triphenylphosphine at room temperature has been previously reported [3, 7] In the VCl_4 case, no pure reduced products were isolated. Our results have confirmed that reactions between VCl_4 and various types of phosphines all led to the reduction of V(IV) to V(III). On the contrary, oxidation states were conserved in the similar reactions for $NbCl_4$ and $TaCl_4$ [1, 2].

For compound **1**, $[HPEt_3][VCl_4(PEt_3)_2]$, the oxidation state of vanadium was not determined for certain by the structure alone because the hydrogen atom on the phosphonium ion cannot be detected crystallographically. The ^{31}P NMR spectrum revealed a doublet for the cation part which is due to H–P direct coupling. The H–P splitting of 530 Hz is typical of proton–phosphorus direct coupling [8, 9]. A magnetic susceptibility measurement at room temperature gave $\mu_{eff}=2.69$ BM, consistent with a compound having two unpaired electrons. All the results taken together confirm that the vanadium in this compound is in oxidation state III.

In compounds **2** and **3**, phosphine oxides are present in the structures. They might have arisen by oxidation of phosphine during the storage and/or transfer, but they could also have come from the oxidation of phosphine by a vanadyl impurity in VCl_4. It has been reported that $VOCl_3$ reacting with an excess of PMe_2Ph also results in the formation of $VCl_3(PMe_2Ph)_2(OPMe_2Ph)$ (3) [10]. The reaction of VCl_4 with PMe_3 yielded the dinuclear edge-sharing compound **4** while the reactions of VCl_4 with other phosphines gave mononuclear products. This may be due in part to the smaller steric requirement of PMe_3

EPR spectra of 1

The EPR spectra of compound **1** in CH_2Cl_2 (the crystal did not redissolve in toluene), gave signals identical to those reported for '$VCl_4 \cdot 2PEt_3$' at both low and room temperature [4, 5]. However, compound **1** is a V(III) species, a d^2 system, which should be EPR silent due to the large zero-field splitting [11]. A quantitation done at low temperature revealed that only about 1% of the total vanadium contributed to the signal. A computer simulation of the EPR spectrum at low temperature further proved that the signal came from an $S=1/2$ system instead of an $S=1$ system. A detailed search of the literature showed that the spectra could be assigned to an adduct of $VOCl_2$ with PEt_3 [12]. $VOCl_2$ could either have come from an impurity originally present in the purchased VCl_4 (Alfa, 90%) or it could have come from the hydrolysis of VCl_4 [13] in the course of the preparation or subsequent handling.

Molecular structures

The atomic positional and isotropic equivalent thermal parameters are listed in Table 2. Important interatomic distances and angles are presented in Tables 3–6. ORTEP drawings of these molecules are shown in Figs. 1–4.

The compound $[HPEt_3][VCl_4(PEt_3)_2]$ has the phosphorus atom in the phosphonium cation on a two-fold axis and the vanadium atom on an inversion center. An ethyl group of the $HPEt_3^+$ ion is disordered, with half occupancy on both sides of the two-fold axis. The $[VCl_4(PEt_3)_2]^-$ anion refined very well, to give a mean V–Cl distance of 2.360(3) Å, close to the mean M–Cl distance in $NbCl_4(PEt_3)_2$ [1] (2.366(9) Å) and in

TABLE 2 Positional parameters and their e.s.d.s for $[HPEt_3][VCl_4(PEt_3)_2]$ (**1**), $VCl_3(OPEt_3)_3$ (**2**), $VCl_3(PMe_2Ph)_2(OPMe_2Ph)$ (**3**) and $V_2Cl_6(PMe_3)_4$ (**4**)

Atom	*x*	*y*	*z*	B^a (Å^2)
1				
V	0.250	0.250	0.000	5.19(5)
Cl(1)	0.3241(2)	0.1756(2)	0.1396(2)	7.06(7)
Cl(2)	0.1474(2)	0.1340(2)	0.0234(2)	7.37(7)
P	0.3090(2)	0.1151(2)	−0.1114(2)	6.38(7)
C(1)	0.2947(7)	0.1377(9)	−0.2484(7)	9.0(3)
C(2)	0.3387(9)	0.235(1)	−0.2774(8)	11.1(4)
C(3)	0.2662(8)	−0.0210(8)	−0.1130(8)	9.1(4)
C(4)	0.2853(9)	−0.075(1)	−0.0100(9)	10.6(4)
C(5)	0.4162(7)	0.102(1)	−0.0803(8)	9.5(4)
C(6)	0.4526(8)	0.016(1)	−0.139(1)	13.5(5)
P(2)	0.500	0.3714(6)	0.250	17.0(3)
C(11)	0.465(1)	0.288(1)	0.346(1)	15.3(6)*
C(12)	0.427(1)	0.332(1)	0.416(1)	16.0(6)*
C(13)	0.451(2)	0.486(3)	0.245(3)	16(1)*
C(14)	0.517(2)	0.560(3)	0.306(2)	14(1)*
2				
V	0.9791(1)	0.92487(8)	0.1402(1)	4.13(3)
Cl(1)	1.0924(2)	0.9908(2)	0.2590(2)	7.06(7)
Cl(2)	0.8646(2)	0.8570(2)	0.0276(2)	6.21(6)
Cl(3)	0.8893(2)	1.0396(1)	0.1121(2)	6.29(6)
O(1)	0.8943(5)	0.8977(3)	0.2669(4)	5.0(1)
O(2)	1.0642(5)	0.9471(4)	0.0132(5)	6.7(2)
O(3)	1.0632(5)	0.8307(4)	0.1636(6)	6.7(2)
P(1)	0.8091(2)	0.9201(2)	0.3342(2)	6.10(6)
P(2)	1.1579(2)	0.9654(2)	−0.0457(3)	7.35(8)
P(3)	1.0703(3)	0.7508(2)	0.1921(3)	9.16(9)
C(11)	0.764(1)	0.8400(7)	0.411(1)	9.1(3)
C(12)	0.833(1)	0.9915(7)	0.426(1)	9.2(4)
C(13)	0.707(1)	0.951(1)	0.244(1)	11.7(5)
C(21)	1.265(1)	0.936(2)	0.012(2)	24(1)
C(22)	1.171(2)	1.057(1)	−0.072(2)	28.7(8)
C(23)	1.161(2)	0.922(2)	−0.175(1)	25(1)
C(31)	1.009(1)	0.6879(7)	0.086(1)	12.4(5)
C(32)	1.206(1)	0.728(1)	0.202(1)	24.5(6)
C(33)	1.010(2)	0.7347(9)	0.322(1)	17.3(5)
C(112)	0.723(2)	0.7741(8)	0.336(1)	13.6(5)
C(122)	0.918(1)	0.9716(9)	0.504(1)	10.4(4)
C(132)	0.610(1)	0.962(2)	0.303(1)	17.3(7)
C(212)	1.307(2)	0.935(2)	0.079(2)	22(1)
C(222)	1.122(2)	1.1157(9)	−0.029(2)	16.5(6)
C(232)	1.085(1)	0.8827(9)	−0.217(1)	11.6(5)
C(312)	1.058(1)	0.7023(9)	−0.024(1)	12.3(5)
C(322)	0.236(2)	0.274(3)	0.766(1)	31(1)
C(332)	1.064(2)	0.785(1)	0.418(1)	20.6(8)
3				
V(1)	0.000	0.1655(2)	0.000	2.62(5)
Cl(1)	0.000	0.0445(4)	−0.2077(6)	4.1(1)
Cl(2)	0.000	0.3314(4)	−0.1506(5)	3.25(9)
Cl(3)	0.000	0.0121(5)	0.1687(7)	5.7(1)
P(1)	0.1865(2)	0.1615(3)	−0.0169(5)	3.20(6)
P(2)	0.000	0.3065(4)	0.3340(6)	3.1(1)
O(1)	0.000	0.270(1)	0.171(2)	3.7(3)
C(11)	0.239(1)	0.017(1)	0.008(2)	5.1(3)
C(12)	0.233(1)	0.207(1)	−0.199(2)	4.9(4)
C(13)	0.2528(9)	0.250(1)	0.116(1)	3.0(3)

(continued)

TABLE 2 (*continued*)

Atom	x	y	z	B^{a} (Å^2)
C(14)	0.321(1)	0.204(1)	0.213(2)	3.7(3)
C(15)	0.369(1)	0.272(1)	0.321(2)	6.2(4)
C(16)	0.352(1)	0.391(1)	0.319(2)	5.9(4)
C(17)	0.280(1)	0.440(1)	0.219(2)	6.3(4)
C(18)	0.233(1)	0.365(1)	0.116(2)	5.0(3)
C(22)	0.105(1)	0.258(1)	0.437(2)	4.3(3)
C(23)	0.000	0.459(1)	0.343(2)	2.8(3)
C(24)	0.000	0.518(2)	0.481(3)	4.0(4)
C(25)	0.000	0.638(2)	0.479(3)	5.1(5)
C(26)	0.000	0.696(2)	0.344(3)	4.2(5)
C(27)	0.000	0.638(2)	0.206(2)	4.4(5)
C(28)	0.000	0.518(2)	0.205(2)	3.7(4)
4				
V(1)	0.2152(1)	0.07405(9)	0.000	3.22(4)
V(2)	0.4262(1)	−0.07718(9)	0.0002(4)	3.25(4)
Cl(1)	0.3484(3)	0.1672(2)	0.0001(9)	6.13(8)
Cl(2)	0.0495(3)	0.0036(2)	−0.0007(9)	6.29(8)
Cl(3)	0.5047(4)	−0.1372(2)	−0.1278(3)	6.1(1)
Cl(4)	0.5113(3)	−0.1388(2)	0.1287(3)	4.71(8)
Cl(5)	0.3202(3)	−0.0012(2)	0.1175(2)	3.98(7)
Cl(6)	0.3197(3)	0.0005(2)	−0.1160(3)	4.31(8)
P(1)	0.1201(4)	0.1388(2)	0.1430(3)	5.2(1)
P(2)	0.1221(5)	0.1407(3)	−0.1399(4)	6.2(1)
P(3)	0.2666(3)	−0.1706(2)	0.0018(8)	4.29(7)
P(4)	0.5978(3)	0.0092(2)	0.0031(7)	4.71(7)
C(11)	0.206(2)	0.214(1)	0.202(2)	14.3(8)
C(12)	−0.021(2)	0.178(1)	0.132(2)	14.5(6)
C(13)	0.105(2)	0.080(1)	0.245(1)	11.0(6)
C(21)	0.119(3)	0.238(1)	−0.127(2)	14.3(9)
C(22)	0.176(3)	0.122(2)	−0.254(1)	23.6(9)
C(23)	−0.047(2)	0.137(2)	−0.143(2)	12.1(8)
C(31)	0.170(1)	−0.1622(9)	−0.114(1)	7.7(4)
C(32)	0.325(1)	−0.2637(6)	−0.005(2)	6.8(4)
C(33)	0.161(1)	−0.1762(8)	0.102(1)	5.6(4)
C(41)	0.616(1)	0.0652(8)	−0.115(1)	6.1(4)
C(42)	0.737(1)	−0.0420(7)	−0.010(2)	6.6(4)
C(43)	0.601(1)	0.077(1)	0.102(1)	7.7(5)

Starred items were refined isotropically Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$

$TaCl_4(PEt_3)_2$ [2] (2.36(2) Å). The V–P distance is 2.551(4) Å, which is 0.113 Å shorter than Nb–P in $NbCl_4(PEt_3)_2$ and 0.085 Å shorter than Ta–P in $TaCl_4(PEt_3)_2$. The angles between all *cis* pairs of atoms are very close to 90°, and the anion $[VCl_4(PEt_3)_2]^-$ can be regarded as an elongated octahedron, with the VCl_4P_2 core having essentially D_{4h} symmetry.

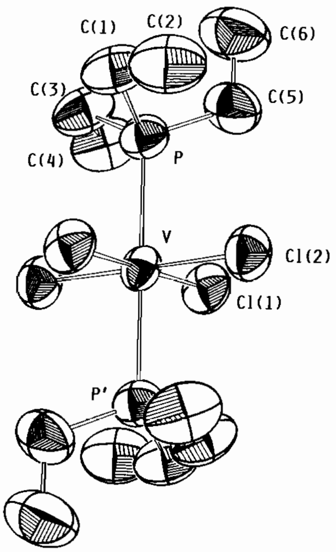

Fig 1. An ORTEP drawing of the $[VCl_4(PEt_3)_2]^-$ ion

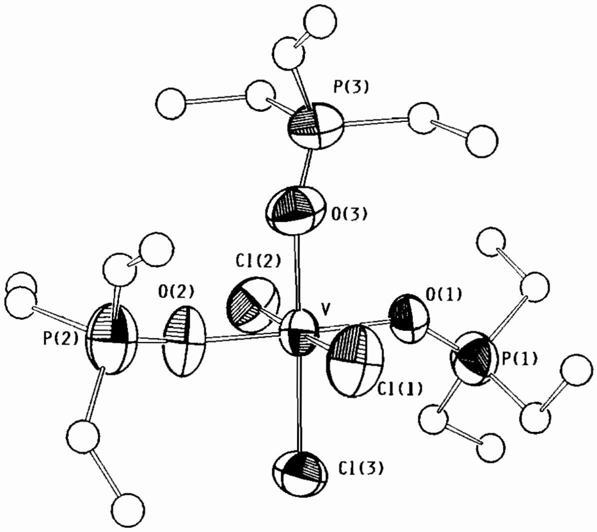

Fig. 2 An ORTEP drawing of compound **2**. Atoms are represented by 50% thermal ellipsoids, except for carbon atoms which are drawn as circles of arbitrary size.

TABLE 3. Selected bond distances (Å) and angles (°) for $[HPEt_3][VCl_4(PEt_3)_2]$

Bond distances					
V–Cl(1)	2.362(3)	V–P	2.551(4)	P–C(1)	1.84(1)
V–Cl(2)	2.357(4)	P–C(3)	1.87(1)	P–C(5)	1.89(2)
Bond angles					
Cl(1)–V–Cl(2)	90.4(1)	Cl(2)–V–P	90.8(1)	V–P–C(3)	116.3(5)
Cl(1)–V–P	88.6(1)	V–P–C(1)	117.3(5)	V–P–C(5)	112.2(5)

Numbers in parentheses are e.s.d.s in the least significant digits.

The molecule of *mer*-$VCl_3(OPEt_3)_3$ resides on a general position and there are four molecules in each unit cell. Its structure is similar to that of $VCl_3(THF)_3$ [14]. The V–Cl distances in this compound are longer than those in $VCl_3(THF)_3$ (V–Cl (av.) = 2.396(7) Å in $VCl_3(OPEt_3)_3$ compared to 2.32(1) Å in $VCl_3(THF)_3$), while the V–O distances are shorter than those in $VCl_3(THF)_3$ (V–O (av.) = 2.00(1) Å in $VCl_3(OPEt_3)_3$ and = 2.08(1) Å in $VCl_3(THF)_3$). This fact can be rationalized by comparing the steric demands of THF

TABLE 4 Selected bond distances (Å) and angles (°) for $VCl_3(OPEt_3)_3$

Bond distances					
V–Cl(1)	2.409(3)	V–O(1)	1.992(6)	O(1)–P(1)	1.463(6)
V–Cl(2)	2.392(3)	V–O(2)	1.978(6)	O(2)–P(2)	1.481(7)
V–Cl(3)	2.386(3)	V–O(3)	2.033(7)	O(3)–P(3)	1.464(7)
Bond angles					
Cl(1)–V–Cl(2)	178.0(1)	Cl(2)–V–O(1)	88.6(2)	O(1)–V–O(2)	177.5(3)
Cl(1)–V–Cl(3)	89.3(1)	Cl(2)–V–O(2)	90.1(2)	O(1)–V–O(3)	90.0(3)
Cl(1)–V–O(1)	89.5(2)	Cl(2)–V–O(3)	91.1(2)	O(2)–V–O(3)	87.8(3)
Cl(1)–V–O(2)	91.7(2)	Cl(3)–V–O(1)	92.2(2)	V–O(1)–P(1)	145.3(4)
Cl(1)–V–O(3)	88.2(2)	Cl(3)–V–O(2)	90.0(2)	V–O(2)–P(2)	156.6(4)
Cl(2)–V–Cl(3)	91.5(1)	Cl(3)–V–O(3)	176.6(2)	V–O(3)–P(3)	150.0(5)

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 5 Selected bond distances (Å) and angles (°) for $VCl_3(PMe_2Ph)_2(OPMe_2Ph)$

Bond distances					
V(1)–Cl(1)	2.336(5)	V(1)–O(1)	1.96(1)	P(2)–O(1)	1.52(1)
V(1)–Cl(2)	2.362(5)	P(1)–C(11)	1.84(1)	P(2)–C(22)	1.79(1)
V(1)–Cl(3)	2.343(6)	P(1)–C(12)	1.83(2)	P(2)–C(23)	1.78(2)
V(1)–P(1)	2.540(3)	P(1)–C(13)	1.82(1)		
Bond angles					
Cl(1)–V(1)–Cl(2)	92.3(2)	Cl(2)–V(1)–O(1)	86.4(4)	V(1)–P(1)–C(13)	116.4(4)
Cl(1)–V(1)–Cl(3)	93.0(2)	Cl(3)–V(1)–P(1)	91.4(1)	O(1)–P(2)–C(22)	114.1(5)
Cl(1)–V(1)–P(1)	86.65(9)	Cl(3)–V(1)–O(1)	88.3(4)	O(1)–P(2)–C(23)	109.0(8)
Cl(1)–V(1)–O(1)	178.6(4)	P(1)–V(1)–O(1)	93.3(1)	V(1)–O(1)–P(2)	157.7(8)
Cl(2)–V(1)–Cl(3)	174.7(2)	V(1)–P(1)–C(11)	113.4(5)		
Cl(2)–V(1)–P(1)	88.90(9)	V(1)–P(1)–C(12)	113.2(5)		

Numbers in parentheses are e.s.d.s in the least significant digits

TABLE 6. Selected bond distances (Å) and angles (°) for $V_2Cl_6(PMe_3)_4$

Bond distances					
V(1)–Cl(1)	2.298(4)	V(1)–P(1)	2.537(4)	V(2)–Cl(5)	2.452(5)
V(1)–Cl(2)	2.302(3)	V(1)–P(2)	2.512(5)	V(2)–Cl(6)	2.463(5)
V(1)–Cl(5)	2.440(4)	V(2)–Cl(3)	2.258(7)	V(2)–P(3)	2.514(3)
V(1)–Cl(6)	2.406(4)	V(2)–Cl(4)	2.309(6)	V(2)–P(4)	2.531(3)
Bond angles					
Cl(1)–V(1)–Cl(2)	166.0(1)	Cl(5)–V(1)–P(2)	171.6(1)	Cl(4)–V(2)–P(3)	87.9(2)
Cl(1)–V(1)–Cl(5)	95.5(2)	Cl(6)–V(1)–P(1)	170.8(1)	Cl(4)–V(2)–P(4)	88.2(2)
Cl(1)–V(1)–Cl(6)	95.2(2)	Cl(6)–V(1)–P(2)	89.2(1)	Cl(5)–V(2)–Cl(6)	81.0(1)
Cl(1)–V(1)–P(1)	86.2(3)	P(1)–V(1)–P(2)	100.0(2)	Cl(5)–V(2)–P(3)	91.4(2)
Cl(1)–V(1)–P(2)	85.3(3)	Cl(3)–V(2)–Cl(4)	100.4(2)	Cl(5)–V(2)–P(4)	90.9(2)
Cl(2)–V(1)–Cl(5)	95.1(2)	Cl(3)–V(2)–Cl(5)	169.9(3)	Cl(6)–V(2)–P(3)	92.5(2)
Cl(2)–V(1)–Cl(6)	95.2(2)	Cl(3)–V(2)–Cl(6)	89.0(2)	Cl(6)–V(2)–P(4)	91.7(2)
Cl(2)–V(1)–P(1)	85.0(3)	Cl(3)–V(2)–P(3)	87.8(2)	P(3)–V(2)–P(4)	175.5(2)
Cl(2)–V(1)–P(2)	85.5(3)	Cl(3)–V(2)–P(4)	90.6(2)	V(1)–Cl(5)–V(2)	98.0(2)
Cl(5)–V(1)–Cl(6)	82.4(1)	Cl(4)–V(2)–Cl(5)	89.6(2)	V(1)–Cl(6)–V(2)	98.6(2)
Cl(5)–V(1)–P(1)	88.4(1)	Cl(4)–V(2)–Cl(6)	170.6(2)		

Numbers in parentheses are e.s.d.s in the least significant digits

and the phosphine oxide. The latter is less bulky when connecting to a metal center, so it can approach the vanadium atom more closely.

The structure of $VCl_3(PMe_2Ph)_2(OPMe_2Ph)$ has been reported in a different cell and in a different space group [10]. The important interatomic distances and angles found in the two studies are essentially identical The *a* axis of the previously used cell [10] (23.344(2) Å) is twice as long as the *b* axis in our cell (11.673(4) Å), and it was said that "some crystals suffered from disorder (with *hkl*, *h* odd reflections having very blurred spots in contrast to the other sharp spots)". Our crystal

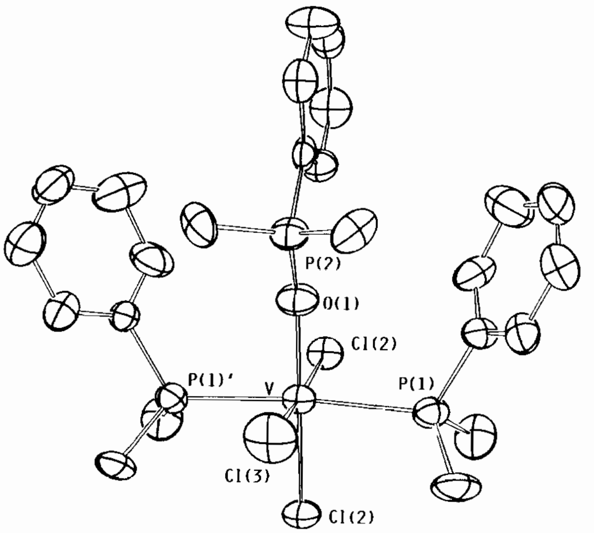

Fig 3. An ORTEP drawing of **3** All atoms are represented by 50% thermal ellipsoids.

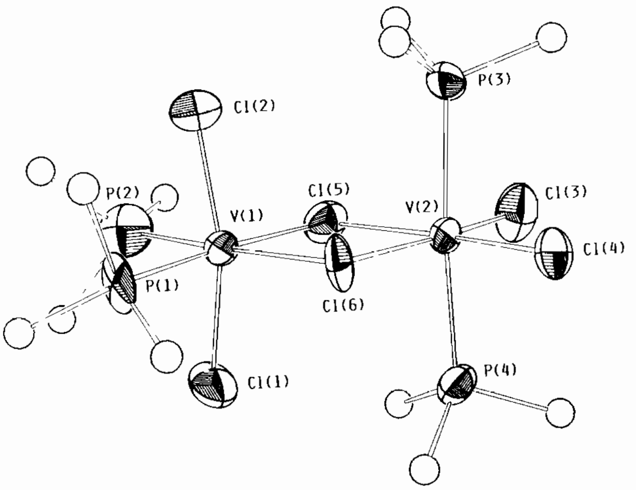

Fig 4. An ORTEP drawing of **4** Atoms are represented by 50% thermal ellipsoids except for carbon atoms which are drawn as circles with arbitrary radii

did not have this problem. A comparison of these two unit cells (Fig. 5) shows that the packing patterns in these two cases are the same. Presumably the only real difference is one of crystal quality.

The compound $V_2Cl_6(PMe_3)_4$ is the only dinuclear compound formed in the reactions we have examined between VCl_4 and phosphines. The uniqueness of PMe_3 is also evident in $Nb_2Cl_8(PMe_3)_4$ and $TaCl_4(PMe_3)_3$. The former is a dinuclear species [1], the latter a seven-coordinate compound [2]. $V_2Cl_6(PMe_3)_4$ is an edge-sharing bioctahedral compound, with two trimethylphosphines *trans* to each other on one vanadium center and two trimethylphosphines *cis* to each other on the other vanadium center. This is the most commonly observed structure for compounds of the type $M_2Cl_6(PR_3)_4$, whether with or without a metal–metal bond, and can be designated as 1,3,6,8 according to a systematic numbering scheme recently introduced [15]. The crystals of $V_2Cl_6(PMe_3)_4$ are isotypic with those of $Cr_2Cl_6(PMe_3)_4$ [16], and the $V_2Cl_6(PMe_3)_4$ has corresponding bond distances and bond angles close to those of $Cr_2Cl_6(PMe_3)_4$ As in typical edge-sharing compounds, vanadium to bridge Cl distances (av. 2.44(1) Å) are longer than vanadium to terminal Cl distances (av. 2.30(1) Å). The two vanadium atoms are 3.691(2) Å apart, indicating that there is no metal to metal bond in this molecule In the chromium analog the Cr···Cr distance is 3.587(5) Å.

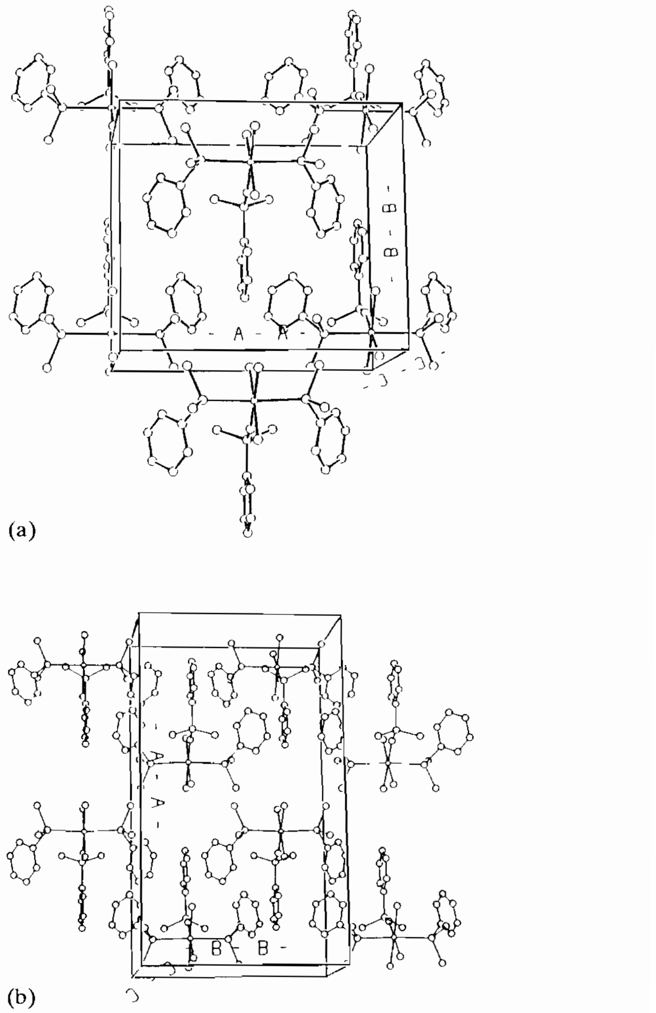

Fig 5 ORTEP packing diagrams of the unit cells of **3** (A) our cell, (B) the cell in ref. 10

Supplementary material

Full list of bond distances and angles, tables of anisotropic thermal parameters, and tables of observed and calculated structure factors (total of 32 pages) for all four compounds are available from author F.A.C.

Acknowledgement

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