Studies on [$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$]. Part 1. Synthesis, Structure and Reactivity of *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$], including the X-Ray Crystal Structure of *mer*-[$VCl_3(OPMe_2Ph)(Et_2PCH_2CH_2PEt_2)$]†

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The complex *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$] has been prepared and its octahedral structure established by X-ray crystallography with V–Cl$_{av}$ 2.346(7), V–P 2.547(2), V–O 1.966(5) Å and VOP 157.4(4)°. The phosphine ligands can be displaced by L–L = 2,2′-bipyridine, tetramethylethylenediamine or $Et_2PCH_2CH_2PEt_2$ to give [$VCl_3(OPMe_2Ph)(L–L)$]. The X-ray crystal structure of *mer*-[$VCl_3(OPMe_2Ph)(Et_2PCH_2CH_2PEt_2)$] has been determined with V–Cl$_{av}$ 2.340(11), V–P 2.538(2) Å (*trans* to Cl), 2.501(2) Å (*trans* to O), V–O 2.049(4) Å and VOP 134.6(2)°. Other reactions of *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$] have been investigated. Protonation with HCl gives [$PHMe_2Ph$][$VCl_4(OPMe_2Ph)$], reaction with $SiMe_3(S_2CNEt_2)$ gives [$V(S_2CNEt_2)_3$] and reduction with MgEtCl in the presence of an excess of $Me_2PCH_2CH_2PMe_2$ gives *trans*-[$VCl_2(Me_2PCH_2CH_2PMe_2)_2$].

Herein we report the synthesis of *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$] and its structural characterisation in the solid state by X-ray crystallography. The reactions of *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$] with 2,2′-bipyridine (bipy), tetramethylethylenediamine (tmen) or $Et_2PCH_2CH_2PEt_2$(depe) yield [$VCl_3(OPMe_2Ph)(L–L)$] and for *mer*-[$VCl_3(OPMe_2Ph)(depe)$] the solid-state structure has been determined by X-ray crystallography. Other reactions of *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$] include protonation to give [$PHMe_2Ph$][$VCl_4(OPMe_2Ph)$], and reduction by MgEtCl or reaction with $SiMe_3(S_2CNEt_2)$ which result in loss of the phosphine oxide. In contrast to the solid-state structures, solution studies (primarily conductivity measurements and EPR spectroscopy) demonstrate that in tetrahydrofuran (thf) the chloro-groups and phosphine ligands are rapidly displaced by the solvent. The preparation and structural characterisation of these compounds is an essential prerequisite to the detailed mechanistic study in the following paper.[1]

Results and Discussion

Preparation and Structure of trans,mer-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$].—The addition of PMe_2Ph to a toluene solution of $VOCl_3$ results in rapid precipitation of salmon-pink *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$]. Subsequent X-ray crystallographic analysis (see below) demonstrated that this material was a simple mononuclear fourteen-electron species. Details of the elemental analysis and characterisation of this and other new compounds reported in this paper are given in Table 1. The use of PMe_2Ph seems particularly advantageous in giving a tractable material in this system. With phosphines such as PMe_3 or $PMePh_2$ only intractable oils are produced in the reactions with $VOCl_3$.

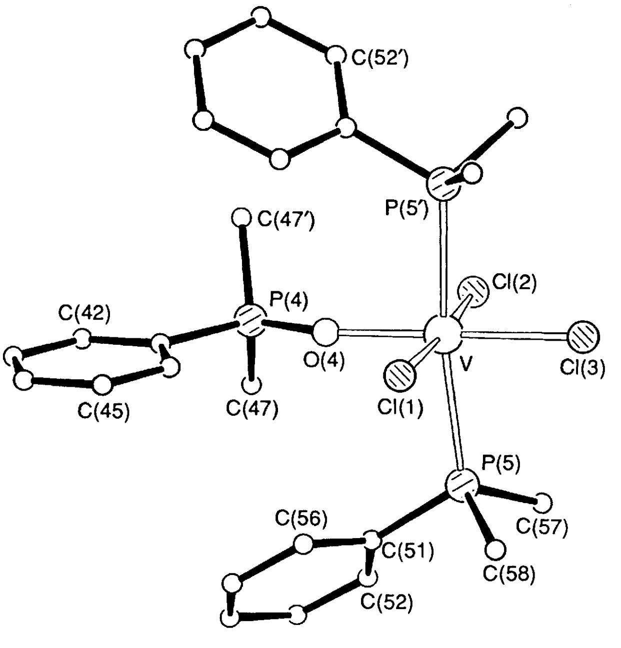

Fig. 1 A view of *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$]. Primed atoms are related by the mirror plane through the centre of the molecule

In the crystal, molecules of [$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$] are discrete monomers, separated from neighbouring ones by normal van der Waals interactions. The molecule contains a precise plane of mirror symmetry with the vanadium atom, the three chlorine atoms and the OPPh part of the phosphine oxide ligand lying in the mirror plane as shown in Fig. 1. The phenyl groups of the P(5) ligands lie over the phosphine oxide in a compact manner, with one of the C(47) hydrogen atoms pointing into the centre of the C(51)–C(56) ring. The coordination of the vanadium atom is distorted only slightly from octahedral geometry by steric interactions. Atomic coordinates (for all but the hydrogen atoms) are in Table 2 and selected molecular dimensions in Table 3.

There are few complexes of vanadium with which to compare our structure: [$VCl_3(NCMe)(PMePh_2)_2$][2] appears to be the

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† *trans,mer*-Trichlorobis(dimethylphenylphosphine)(dimethylphenylphosphine oxide-κ*O*)vanadium(III) and *mer*-[1,2-bis(diethylphosphino)ethane]trichloro(dimethylphenylphosphine oxide-κ*O*)-vanadium(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp xviii–xxii.

Table 1 Analysis and spectroscopic characterisation of the complexes

Complex	Colour	Elemental analysis[a] (%) C	H	N	$10^6\Lambda^b$/ohm^{-1} cm^2 mol^{-1}	μ_{eff}	IR bands[c]/cm^{-1}	Electronic bands[d] λ_{max}/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}
$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$[e]	Salmon-pink	48.6	5.6	0.0	72.1	2.7	1120s, ν(P=O)	458(sh)	250
		(49.0)	(5.6)	(0.0)					
$[VCl_3(OPMe_2Ph)(bipy)]$	Yellow	46.3	4.4	5.7	10.1	2.8	1100s, ν(P=O)	400	400
		(46.2)	(4.1)	(6.0)			1450–1600s, ν(N=C)	478(sh)	260
$[VCl_3(OPMe_2Ph)(tmen)]\cdot 0.5CH_2Cl_2$	Purple	37.0	6.7	5.5	21.6	2.8	2400–2600m, ν(N–Me)	440	310
		(37.0)	(6.0)	(6.0)			1100s, ν(P=O)		
$[VCl_3(OPMe_2Ph)(depe)]$	Green	41.9	7.0	0.0	22.0	2.8	1100s, ν(P=O)	406(sh)	296
		(41.7)	(6.8)	(0.0)				740	40
$[PHMe_2Ph][VCl_4(OPMe_2Ph)]$	Pink	39.7	5.2	0.0	121.0	2.7	2430m, ν(P–H)	416	224
		(39.5)	(4.7)	(0.0)			1100s, ν(P=O)		
$[V(S_2CNEt_2)_3]$	Orange	36.2	6.7	8.5					
		(36.4)	(6.1)	(8.5)					
$[VCl_2(dmpe)_2]$	Red	34.3	7.5	0.0					
		(34.2)	(7.7)	(0.0)					

[a] Calculated values shown in parentheses. [b] Measured in nitromethane. [c] Nujol mull. [d] Solvent is CH_2Cl_2. [e] Cl 18.5 (18.1).

Table 2 Final atomic coordinates (fractional × 10^4) for $[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
V	841.0(6)	2500	2411(1)
Cl(1)	1663.0(9)	2500	886(2)
Cl(2)	88(1)	2500	4122(3)
Cl(3)	226(1)	2500	364(3)
O(4)	1371(2)	2500	4106(5)
P(4)	1554(1)	2500	5725(2)
C(41)	2317(4)	2500	5774(8)
C(42)	2621(4)	2500	7092(10)
C(43)	3206(4)	2500	7111(12)
C(44)	3504(4)	2500	5767(12)
C(45)	3207(4)	2500	4457(11)
C(46)	2622(4)	2500	4454(9)
C(47)	1299(4)	1478(6)	6728(7)
P(5)	812.3(7)	655(1)	2229(2)
C(51)	1254(3)	−23(4)	3527(6)
C(52)	1027(3)	−694(5)	4521(7)
C(53)	1367(4)	−1165(6)	5524(8)
C(54)	1941(4)	−981(6)	5533(10)
C(55)	2183(4)	−332(6)	4537(10)
C(56)	1827(3)	145(5)	3552(8)
C(57)	100(3)	144(6)	2392(9)
C(58)	1061(4)	193(5)	451(7)

Table 3 Selected molecular dimensions (lengths in Å, angles in °) in $[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ with e.s.d.s in parentheses; an asterisk represents an e.s.d. of less than 0.05°

(*a*) About the V atom			
V–Cl(1)	2.361(2)	V–O(4)	1.966(5)
V–Cl(2)	2.339(3)	V–P(5)	2.547(2)
V–Cl(3)	2.339(2)		
Cl(1)–V–Cl(2)	174.4(1)	Cl(1)–V–P(5)	89.1*
Cl(1)–V–Cl(3)	92.3(1)	Cl(2)–V–P(5)	91.3*
Cl(2)–V–Cl(3)	93.3(1)	Cl(3)–V–P(5)	86.1*
Cl(1)–V–O(4)	86.6(2)	O(4)–V–P(5)	93.8*
Cl(2)–V–O(4)	87.7(2)	P(5)–V–P(5′)	172.0(1)
Cl(3)–V–O(4)	178.9(2)		
(*b*) In the ligands			
O(4)–P(4)	1.520(5)	P(5)–C(51)	1.818(6)
P(4)–C(41)	1.781(9)	P(5)–C(57)	1.812(7)
P(4)–C(47)	1.776(7)	P(5)–C(58)	1.819(6)
V–O(4)–P(4)	157.4(4)	V–P(5)–C(51)	117.1(2)
O(4)–P(4)–C(41)	107.8(3)	V–P(5)–C(57)	114.0(3)
O(4)–P(4)–C(47)	113.2(3)	V–P(5)–C(58)	113.4(2)
C(41)–P(4)–C(47)	108.8(3)	C(51)–P(5)–C(57)	105.6(3)
C(47)–P(4)–C(47′)	104.8(4)	C(51)–P(5)–C(58)	101.9(3)
		C(57)–P(5)–C(58)	103.2(4)

Primed atoms are related by reflection through the symmetry plane in the molecule.

only other octahedrally co-ordinated phosphine complex of vanadium(III), and the only vanadium–phosphine oxide complex (other than the one reported later in this paper) is the square-based pyramidal, vanadium(IV) species $[VCl_2O(OPPh_3)_2]$.[3] In this last complex the V–O (phosphine oxide) distances are *ca.* 1.99 Å which are surprisingly slightly longer than the 1.966 Å in our complex. In general the POM angle in phosphine oxide complexes varies widely[4] through *ca.* 123–180° and our value of 157.4(4)° is in the centre of this range. The P–C bonds, mean 1.778(2) Å in our complex, are, as expected, rather shorter than those in the phosphine ligand, mean 1.814(2) Å.

In the crystals of $[VCl_3(NCMe)(PMePh_2)_2]$[2] the two V–P distances are quite different, 2.540(1) and 2.574(1) Å [mean 2.557(17) Å], and the three V–Cl lengths show a range of 2.269(1)–2.320(1) Å. Our V–P distance is 2.547(2) Å which is slightly shorter than the mean value observed in the acetonitrile complex, presumably since our PMe_2Ph ligand is a more electron-releasing σ donor. This greater electron-releasing nature of the PMe_2Ph ligand is reflected in the V–Cl lengths which are increased slightly in comparison with those in the V–$PMePh_2$ complex; our results show a V–Cl range 2.339(2)–2.361(2) Å, mean 2.346(7) Å.

Studies on solutions of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ reveal that the identity of this compound is markedly changed in thf. In particular, conductivity measurements show that it behaves essentially as a 1:1 electrolyte, indicating extensive dissociation of one chloro-group in solution. Furthermore solution EPR measurements indicate that a complicated series of species is formed, most of which we have been unable to identify. However, the major species (*ca.* 50%) has g_{av} = 1.980, and besides the coupling to the vanadium [A_{av}(V) = 9.6 mT], each line is further split into a doublet indicating that there is further coupling to only one phosphorus [A_{av}(P) = 3.2 mT] (Table 4). There is no set of signals attributable to a bis(phosphine) complex. Thus in solution we propose that the dominant species is that shown in Fig. 2. It is important to stress, however, that our confidence limits on the concentrations of the solution species in Table 4, as detected by EPR spectroscopy, are no better than ±10%.

Table 4 EPR spectral characteristics of phosphine oxide complexes

Complex	g_{av} [a]	$A_{av}(V)$ [b]/mT	$A_{av}(P)$ [b]/mT	Approximate proportion [c] (%)
$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$	1.980	9.6	3.2 [d]	50
$[VCl_3(OPMe_2Ph)(depe)]$	1.981	8.9	2.6 [e]	60
	1.969	11.1		40
$[VCl_3(OPMe_2Ph)(bipy)]$	1.980	10.0		25
	1.976	10.4		25
	1.969	11.1		50
$[PHMe_2Ph][VCl_4(OPMe_2Ph)]$	1.987	9.7		30
	1.972	10.7		30
	1.969	11.1		30

[a] Error = ±0.002. [b] Error = ±0.1. [c] Error = ±10%. [d] Coupling to one phosphorus atom (doublet pattern). [e] Coupling to two phosphorus atoms (triplet pattern).

Table 5 Final atomic coordinates (fractional $\times 10^4$) for $[VCl_3(OPMe_2Ph)(depe)]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
V	1602.6(5)	25.3(7)	0
C(11)	702(7)	−2600(7)	1282(5)
C(12)	1266(9)	−2262(10)	1966(6)
C(13)	2349(9)	−3186(8)	393(8)
C(14)	2205(11)	−4560(9)	540(9)
P(1)	1307(1)	−2210(1)	384(1)
C(1x)*	677(9)	−2913(8)	−445(7)
C(1y)*	29(15)	−2472(32)	90(12)
C(2)	−124(6)	−2085(8)	−733(5)
P(2)	347(1)	−550(2)	−981(1)
C(21)	703(6)	−686(8)	−1989(4)
C(22)	1120(6)	451(9)	−2335(4)
C(23)	−734(5)	398(10)	−996(5)
C(24)	−1580(6)	−47(14)	−1491(7)
Cl(3)	365(1)	504(1)	887(1)
Cl(4)	2734(1)	−812(1)	−841(1)
Cl(5)	1683(1)	2060(1)	−478(1)
O(6)	2634(3)	229(3)	845(2)
P(6)	3391.7(9)	1183(1)	1020(1)
C(61)	4152(4)	638(5)	1799(3)
C(62)	3790(4)	−283(6)	2295(4)
C(63)	4356(5)	−670(6)	2917(4)
C(64)	5249(5)	−185(7)	3035(4)
C(65)	5612(5)	708(7)	2548(4)
C(66)	5049(4)	1117(5)	1932(4)
C(67)	2872(6)	2573(6)	1368(5)
C(68)	4146(5)	1522(7)	217(4)

Atoms C(1x) and C(1y) have site occupancy factors of 0.7 and 0.3 respectively.

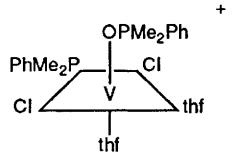


Fig. 2 Proposed structure of solvento-species formed upon dissolution of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ in thf

Reactions of $[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ *and Structure of mer*-$[VCl_3(OPMe_2Ph)(depe)]$.—The reactions of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ fall into two distinct categories: those involving loss of the phosphine oxide ligand, and those in which the phosphine oxide is retained. These reactions are summarised in Scheme 1.

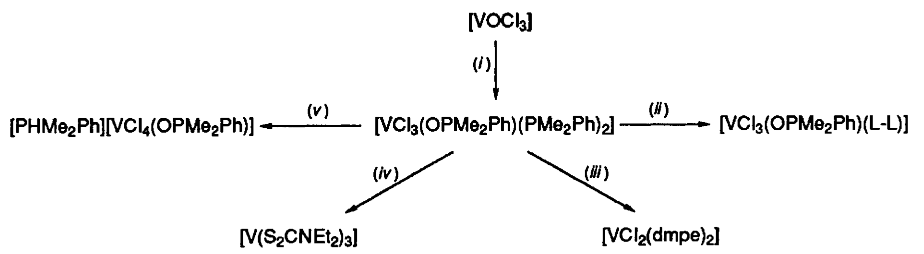
Loss of the phosphine oxide ligand only occurs in two reactions of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$: with an excess of $SiMe_3(S_2CNEt_2)$, to give the known $[V(S_2CNEt_2)_3]$,[5] characterised by comparison with an authentic sample of this material, and reduction in the presence of $Me_2PCH_2CH_2PMe_2$ (dmpe) to give $[VCl_2(dmpe)_2]$, again characterised by comparison with an authentic sample prepared by the literature method.[6] The reaction of anhydrous HCl with *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ rapidly precipitated pink $[PHMe_2Ph][VCl_4(OPMe_2Ph)]$. This material, with a characteristic ν(P–H) 2430 cm^{-1} stretch in the infrared spectrum, can be a contaminant of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ during its preparation, unless rigorously dry glassware and reagents are used.

The reactions of potentially bidentate ligands L–L such as bipy, tmen or depe with *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ give $[VCl_3(OPMe_2Ph)(L\text{–}L)]$. For the complex $[VCl_3(OPMe_2Ph)(depe)]$ the structure has been established in the solid state by X-ray crystallography.

Analogous to the crystal structure of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$, in the crystals of $[VCl_3(OPMe_2Ph)(depe)]$ the complex is a discrete monomer, separated from neighbouring molecules by normal van der Waals distances. The co-ordination of the vanadium atom has a slightly distorted octahedral geometry, with the three chlorine atoms in a meridional arrangement, all *cis* to the phosphine oxide ligand, as shown in Fig. 3. One of the methylene groups of the diphosphine ligand is disordered over two sites with occupancy factors of *ca.* 0.7 and 0.3. Also the large thermal parameters of some of the carbon atoms in the ethyl groups suggest that here too there is some corresponding disorder. Atomic coordinates for *mer*-$[VCl_3(OPMe_2Ph)(depe)]$ are in Table 5 and molecular dimensions in Table 6.

Comparison of the structures and dimensions in $[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ and $[VCl_3(OPMe_2Ph)(depe)]$ reveals some interesting differences. Although the V–Cl distances are similar [2.339–2.361 Å (PMe_2Ph complex) and 2.317–2.352 Å (depe complex)], the V–O distance for the depe complex is considerably longer (2.049 Å) than in the PMe_2Ph species (1.966 Å). However, this probably represents the nature of the *trans* ligand, being a chlorine atom in the latter complex and a phosphorus atom in the depe complex. The change of donor atom *trans* to the phosphine oxide may also account for the very different VOP angle [157.4° (PMe_2Ph complex) and 134.6° (depe complex)], and P–O distances [1.520 Å (PMe_2Ph complex) and 1.502 Å (depe complex)]. Certainly the V–P distances seem to reflect the nature of the *trans* ligand. In *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ the V–P distance is 2.547 Å whereas in *mer*-$[VCl_3(OPMe_2Ph)(depe)]$ the V–P distances are 2.538 (*trans* to Cl) and 2.501 Å (*trans* to O).

As we saw for *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$, the solution behaviour of $[VCl_3(OPMe_2Ph)(L\text{–}L)]$ does not reflect the solid-state structure. The solution EPR spectrum of $[VCl_3(OPMe_2Ph)(depe)]$ shows two sets of signals. The predominant species (*ca.* 60%) centred at g_{av} = 1.981 shows coupling to the vanadium atom [$A_{av}(V)$ = 8.9 mT], with each line further split into a triplet due to coupling to two essentially equivalent phosphorus atoms [$A_{av}(P)$ = 2.6 mT]. This appears to be the



Scheme 1 Preparation and reactions of *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$]. (*i*) PMe_2Ph; (*ii*) L–L = bipy, tmen or depe; (*iii*) MgEtBr, dmpe; (*iv*) $SiMe_3(S_2CNEt_2)$; (*v*) HCl

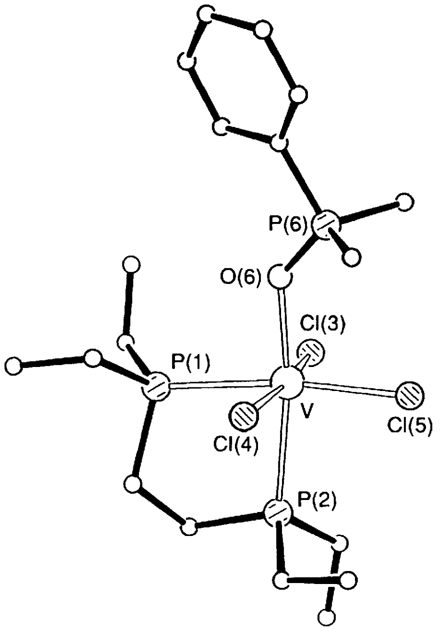


Fig. 3 A view of *mer*-[$VCl_3(OPMe_2Ph)$(depe)]

Fig. 4 The proposed solution species formed upon dissolution of *mer*-[$VCl_3(OPMe_2Ph)$(depe)] in thf

Table 6 Selected molecular dimensions (lengths in Å, angles in °) in [$VCl_3(OPMe_2Ph)$(depe)] with e.s.d.s in parentheses

(*a*) About the V atom			
V–P(1)	2.538(2)	V–Cl(4)	2.317(2)
V–P(2)	2.501(2)	V–Cl(5)	2.351(2)
V–Cl(3)	2.352(2)	V–O(6)	2.049(4)
P(1)–V–P(2)	80.0(1)	Cl(3)–V–Cl(5)	93.2(1)
P(1)–V–Cl(3)	85.6(1)	Cl(4)–V–Cl(5)	96.6(1)
P(2)–V–Cl(3)	89.1(1)	P(1)–V–O(6)	91.7(1)
P(1)–V–Cl(4)	84.2(1)	P(2)–V–O(6)	171.7(1)
P(2)–V–Cl(4)	87.3(1)	Cl(3)–V–O(6)	91.4(1)
Cl(3)–V–Cl(4)	169.7(1)	Cl(4)–V–O(6)	90.7(1)
P(1)–V–Cl(5)	171.6(1)	Cl(5)–V–O(6)	96.6(1)
P(2)–V–Cl(5)	91.7(1)		
(*b*) In the ligands			
P(1)–C(11)	1.807(8)	P(2)–C(21)	1.807(7)
P(1)–C(13)	1.788(9)	P(2)–C(23)	1.814(7)
P(1)–C(1x)	1.836(10)	P(2)–C(2)	1.834(7)
P(1)–C(1y)	1.862(16)		
V–P(1)–C(11)	121.3(2)	V–P(2)–C(21)	118.5(2)
V–P(1)–C(13)	115.7(3)	V–P(2)–C(23)	116.3(3)
V–P(1)–C(1x)	105.6(3)	V–P(2)–C(2)	108.4(2)
V–P(1)–C(1y)	103.2(9)		
C(11)–P(1)–C(13)	103.2(4)	C(21)–P(2)–C(23)	104.9(4)
C(11)–P(1)–C(1x)	110.3(5)	C(21)–P(2)–C(2)	104.3(4)
C(11)–P(1)–C(1y)	75.9(7)		
C(13)–P(1)–C(1x)	98.4(7)	C(23)–P(2)–C(2)	102.7(4)
C(13)–P(1)–C(1y)	132.8(13)		
O(6)--P(6)	1.502(4)	P(6)–C(67)	1.770(7)
P(6)–C(61)	1.802(6)	P(6)–C(68)	1.770(7)
V–O(6)–P(6)	134.6(2)		
O(6)–P(6)–C(61)	109.4(2)	C(61)–P(6)–C(67)	105.3(3)
O(6)–P(6)–C(67)	111.5(3)	C(61)–P(6)–C(68)	107.6(3)
O(6)–P(6)–C(68)	113.5(3)	C(67)–P(6)–C(68)	109.1(4)

same species as observed in the solid state, containing the bidentate depe ligand. Clearly the inequivalence of the phosphorus atoms observed in the solid-state structure is insufficient to be resolved in the EPR spectrum. However, we cannot rule out the possibility that in solution the alternative isomer (where each phosphorus atom is *trans* to a chlorine atom) is the major species. The minor component of the mixture shows no phosphorus coupling (Table 4). It is important to appreciate that for complexes of the type [$VCl_3(OPMe_2Ph)$(L–L)] shown in Table 4 it is only the depe complex whose co-ordination environment we can probe by EPR spectroscopy, by monitoring the coupling to the vanadium-bound phosphorus atoms. This makes any analysis of the solution species difficult for all samples except the depe complex. However, for *mer*-[$VCl_3(OPMe_2Ph)$(depe)] two important points can be made from the data collected in Table 4. First, the minor signal [g_{av} = 1.969, A_{av}(V) = 11.1 mT] is also observed in the spectra of all the other complexes of this type, and on this basis we tentatively assign this signal to [$VCl_3(OPMe_2Ph)(thf)_2$]. Secondly, we see no signals attributable to a species in which the depe ligand is acting as a monodentate ligand with a pendant phosphorus atom. Thus in solution [$VCl_3(OPMe_2Ph)$(depe)] exists as the two species shown in Fig. 4. Finally it should be noted that the conductivity measurements on [$VCl_3(OPMe_2Ph)$(L–L)] give low molar conductivities, but they do indicate significant formation of ionic species in solution. The complexity of the solution behaviour of these systems, as illustrated by EPR spectroscopy, precludes detailed analysis of the complexes by conductivity.

Having established the synthesis, reactivity and structure (both in the solid state and in solution) of *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$], together with the structure of one of the two reaction products, *mer*-[$VCl_3(OPMe_2Ph)$(depe)], we will, in the following paper, discuss the kinetics and mechanism of the reactions of *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$] with bipy and depe.

Experimental

All manipulations were routinely performed under an atmosphere of dinitrogen, using standard Schlenk and syringe tech-

Table 7 Crystal data

Compound	[VCl$_3$(OPMe$_2$Ph)(PMe$_2$Ph)$_2$]	[VCl$_3$(OPMe$_2$Ph)(depe)]
Formula	$C_{24}H_{33}Cl_3OP_3V$	$C_{18}H_{35}Cl_3OP_3V$
M	587.7	517.7
Crystal system	Orthorhombic	Orthorhombic
a/Å	23.344(2)	13.851(2)
b/Å	13.771(2)	10.811(1)
c/Å	9.015(1)	17.192(2)
U/Å^3	2897.9	2574.5
Space group	*Pnma* (no. 62)	*Pna*2$_1$ (no. 33)
Z	4	4
D_c/g cm^{-3}	1.347	1.335
F(000)	1216	1080
μ(Mo-Kα)/cm^{-1}	7.9	8.8

Table 8 Experimental details of the X-ray analyses

Compound	[VCl$_3$(OPMe$_2$Ph)(PMe$_2$Ph)$_2$]	[VCl$_3$(OPMe$_2$Ph)(depe)]
Crystal colour, shape	Red-brown plates	Green shards
Crystal size/mm	0.06 × 0.60 × 0.70	0.05 × 0.20 × 0.95
Mounting	Glass fibre, coated with silicone grease	Glass fibre, coated with epoxy resin
On CAD4 diffractometer:		
For cell dimensions, 25 reflections with θ/°	10–11	10–11
θ_{max} for data collection/°	23	23
No. of independent reflections	2109	1853
No. of reflections with $I > 2\sigma_I$	1443	1766
During processing, corrections made for		
Lorentz polarisation	Yes	Yes
Deterioration	Yes	Yes
Absorption	Yes	Yes
Negative intensities	No	Yes
Structure solved by	Automated Patterson routines	Patterson, electron-density and difference maps
Final R (ref. 9)	0.065	0.036
Final R' (ref. 9)	0.067	0.041
No. of reflections in refinement	1669	1853
with $I > n\sigma_I$, where n	1	0
Weighted $w = (\sigma_F^2 + gF^2)^{-1}$ where g	0.0032	0.0022
Highest peak in final difference map/e Å^{-3}	0.5	0.4

niques as appropriate. Solvents were freshly distilled from the appropriate drying agent immediately prior to use. Infrared spectra were recorded using a Perkin-Elmer 883 spectrometer, visible absorption spectra on a Philips Analytical SP1800 spectrophotometer and EPR spectra using an updated Bruker ER200D spectrometer.

The compound VOCl$_3$ was used as received as were bipy and tmen (all from Aldrich); Et$_2$PCH$_2$CH$_2$PEt$_2$ and Me$_2$PCH$_2$CH$_2$PMe$_2$ were prepared from Cl$_2$PCH$_2$CH$_2$PCl$_2$ by the literature method,[7] and SiMe$_3$(S$_2$CNEt$_2$) was also prepared by the literature procedure.[8]

Trichlorobis(dimethylphenylphosphine)(dimethylphenylphosphine oxide)vanadium.—To a rapidly stirring solution of VOCl$_3$ (0.54 cm^3, 3.1 mmol) in toluene (50 cm^3) was added PMe$_2$Ph (1.9 cm^3, 13.8 mmol). There was an immediate colour change from dark red through green to orange in a very exothermic reaction. Upon stirring the solution for 1 h the salmon-pink product (contaminated with a small amount of oily material) was precipitated. It was removed by filtration, leaving the oily by-product behind, washed with toluene, then diethyl ether and finally dried *in vacuo*. The compound was recrystallised as orange plates from dichloromethane by allowing diethyl ether to diffuse slowly into the solution. Yield = 2.4 g, 72%.

[1,2-*Bis(diethylphosphino)ethane*]*trichloro(dimethylphenylphosphine oxide)vanadium.*—To a solution of *trans,mer*-[VCl$_3$(OPMe$_2$Ph)(PMe$_2$Ph)$_2$] (0.53 g, 0.9 mmol) in toluene (*ca.* 20 cm) was added depe (0.22 g, 1.1 mmol). The solution turned green rapidly and was stirred for 1 h. The solvent was removed *in vacuo*, and the resulting oil was dissolved in the minimum of dichloromethane; addition of a large excess of hexane, and leaving at −20 °C for 3 d produced dark green needles of the product. Yield = 0.24 g, 52%. The tmen and bipy analogues were prepared in a similar manner.

Dimethylphenylphosphonium Tetrachloro(dimethylphenylphosphine oxide)vanadium.—To a solution of *trans,mer*-[VCl$_3$(OPMe$_2$Ph)(PMe$_2$Ph)$_2$] (0.62 g, 1.1 mmol) in thf (*ca.* 20 cm^3) was added 5 equivalents of anhydrous HCl [methanol (0.17 cm^3) and chlorotrimethylsilane (0.56 cm^3)]. The solution immediately turned pink and rapidly precipitated the pink product as analytically pure material. Yield = 0.41 g, 81%.

Tris(diethyldithiocarbamato)vanadium.—To a solution of *trans,mer*-[VCl$_3$(OPMe$_2$Ph)(PMe$_2$Ph)$_2$] (0.50 g, 0.9 mmol) in toluene (*ca.* 50 cm^3) was added SiMe$_3$(S$_2$CNEt$_2$) (0.7 cm^3, 3.2 mmol) to form a brown solution immediately. After stirring the solution for 1 h the solvent was removed *in vacuo* to yield a brown solid. Recrystallisation of this crude material from dichloromethane–diethyl ether gave brown cubic crystals. Yield = 0.20 g, 47%.

Crystal Structure Analysis.—The X-ray analysis of *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$] is described; the analysis of *mer*-[$VCl_3(OPMe_2Ph)$(depe)] followed a very similar course. The crystal data for both complexes are in Table 7, and experimental details in Table 8.

Several of the slightly air-sensitive crystals of *trans,mer*-[$VCl_3(OPMe_2Ph)(PMe_2Ph)_2$] were mounted on glass fibres and coated with silicone grease. Photographic examination indicated that some crystals suffered from disorder (with *hkl*, *h* odd reflections having very blurred spots in contrast to the other sharp spots). A crystal with a wholly sharp diffraction pattern was transferred to our Enraf-Nonius CAD4 diffractometer [with monochromated radiation, $\lambda(\text{Mo-K}\bar{\alpha}) = 0.710\,69$ Å] for determination of cell parameters, and measurement of diffraction intensities. During processing these data were corrected for Lorentz-polarisation and absorption (from crystal size and shape measurements) effects and for slight deterioration. The data were entered into the SHELX program system[9] for structure determination. This was achieved from the automated Patterson routines in SHELXS[10] in which the third-best-looking result from PATT was found, through the tangent expansion routine TEXP, to give the correct solution. Refinement by full-matrix least-squares methods was completed with $R = 0.065$ and $R' = 0.067$[9] for all data weighted $w = (\sigma_F^2 + 0.0032\,F^2)^{-1}$.

In the final cycles of refinement all the non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms of the phenyl groups were included in idealised positions with parameters riding on those of their bonded carbon atoms; methyl-group hydrogen atoms were refined with geometrical restraints applied.

In a final difference map there were no features outside the range -0.58 to 0.52 e Å^{-3}. Scattering factors for neutral atoms were taken from ref. 11. Computer programs used in this analysis have been noted above and in Table 4 of ref. 12, and were run on the MicroVAX II computer in this laboratory.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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