Synthesis and structural studies of complexes of vanadium(II) and vanadium(III) halides with tertiary phosphines

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Abstract

The vanadium(II) halides $[VCl_2(H_2O)_4]$ and $[V(H_2O)_6]Br_2$, prepared from the metal and the appropriate acid, combine with 1,2-bis(dimethylphosphino)ethane (dmpe) and 1,2-bis(diethylphosphino)ethane (depe) in methanol to give $[VX_2(dmpe)_2]$ and $[VX_2(depe)_2]$ (X = Cl or Br). The iodo complexes were obtained from $[V(MeOH)_6]I_2$, although $[VI_2(depe)_2]$ was not pure. The complexes $[VX_2(dppe)_2]\cdot 2thf$ (X = Cl or Br; dppe = 1,2-bis(diphenylphosphino)ethane) could not be isolated from methanol, but were obtained from tetrahydrofuran (thf). All are typical vanadium(II) complexes, and $[VCl_2(depe)_2]$ and $[VCl_2(dppe)_2]\cdot 2thf$ have *trans* structures. The V–Cl bond distances, 2.445(2) and 2.420(1) Å, respectively, are similar to that in the known complex $[VCl_2(dmpe)_2]$, but the V–P bond distances are longer by approximately 0.06 Å and the P–V–P angles are smaller by *c.* 3°, possibly due to the steric crowding of the more heavily substituted depe and dppe ligands in the equatorial plane. Some new complexes $[VX_3(PR_3)_n]$ (X = Cl or Br, PR_3 = monotertiary phosphine, $n = 2$ or 3) were also prepared from $[VX_3(thf)_3]$.

Introduction

We have recently described a ready synthesis of vanadium(II) compounds suitable to be precursors in further synthesis, starting from vanadium metal [1]. This was a necessary step in our programme to prepare vanadium–dinitrogen complexes, made particularly urgent by the announcement of the vanadium-containing nitrogenases [2] and the existence of ill-defined V^{II} systems which fix nitrogen [3]. Our initial strategy was to use vanadium(II) compounds obtained by electrolytic reduction to prepare vanadium(II) complexes of tertiary phosphines, and thence, by reduction, to bind dinitrogen, but the route from vanadium metal and acid has now proved to be more convenient.

The literature describes complexes of V^{II} with ditertiary phosphines, $[VCl_2(dmpe)_2]$ [4], $[VBr_2(dmpe)_2]$ [5], and $[VBr_2(dippe)_2]\cdot\frac{3}{2}thf$ [5] (dmpe = $Me_2PCH_2CH_2PMe_2$, dippe = $Pr^i_2PCH_2CH_2PPr^i_2$, thf = tetrahydrofuran), obtained via reduction of $[VX_3(thf)_3]$ (X = Cl or Br) in the presence of the phosphine. From $[VCl_2(dmpe)_2]$, $[VX_2(dmpe)_2]$ (X = Me, CN, SCN, etc.) were obtained by metathesis [6]. The reduction of $[VCl_3(thf)_3]$ directly does not give $VCl_2(thf)_2$ as first thought, but $[V_2(thf)_6(\mu\text{-}Cl)_3]^{2+}$ [7, 8], which has also been used to prepare vanadium(II) species, such as $[V(BH_4)_2(dmpe)_2]$ [9], $[V_2(BH_4)_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2]$ [10] and $[V_2(BH_4)_2(\mu\text{-}Cl)_2(\mu\text{-}dmpm)_2]$ [11] (dppm = $Ph_2PCH_2PPh_2$, dmpm = $Me_2PCH_2PMe_2$). Finally, $[V(dppe)_3][V(CO)_6]_2$ is obtainable from $[V(CO)_6]$ [12]. Clearly there is no general, simple route to vanadium(II) phosphine complexes.

On the other hand, several vanadium(III) phosphine compounds are known. They are generally available from $[VCl_3(thf)_3]$, and include $[VCl_3(dmpe)(thf)]$ [13], $[VCl_3(PMe_2Ph)_2]$ [14], $[VCl_3(PMe_2Ph)_2]\cdot 0.4thf$ [15], $[VCl_3(PMe_2Ph)_2(MeCN)]$ [14], $[VCl_3(PR_3)_2]$ (R = Me, Et, or Pr^n) [16], $[V(NCS)_3(PR_3)(MeOH)_2]$ (R_3 = Me_3, Et_3, Pr^n_3, Bu^n_3, or $PhEt_2$) [17] and $V(NCS)_3(depe)_{1/2}(MeOH)_2$ [17]. This list excludes organometallic compounds such as cyclopentadienyl complexes, and some more complicated species [18]. We have extended the basic series to include some further phosphines.

Results and discussion

We used $VCl_2\cdot 4H_2O$ and $VBr_2\cdot 6H_2O$ prepared from vanadium metal and the appropriate acid as the main source of vanadium(II) [1, 19] for the range of com-

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pounds *trans*-$[VX_2(diphosphine)_2]$ (X = Cl, Br or I; diphosphine = dmpe, depe or dppe) given in Table 1. The iodo derivatives were prepared from $[V(MeOH)_6]I_2$, itself obtained from $VCl_2 \cdot 4H_2O$ as before [20]. To prepare the dppe derivatives it was necessary first to dehydrate the chloride and bromide by reaction with alcohols and triethylorthoformate, followed by treatment with tetrahydrofuran (thf) to yield substances of the approximate formulation $VX_2(MeOH)(thf)$. Whatever their precise structures, these are useful intermediates in the preparation of the vanadium(II)–dppe complexes.

Of the complexes $[VX_2(diphosphine)_2]$ (X = Cl, Br or I; diphosphine = dmpe, depe or dppe), $[VCl_2(depe)_2]$ and $[VCl_2(dppe)_2]$ have been structurally characterised. The species $[V(dmpe)_3](BF_4)_2$, obtained from $[V(H_2O)_6](BF_4)_2$, and $VCl_2(dppm)$, have yet to be structurally characterised. The compounds $[VX_2(diphosphine)_2]$ have the expected IR and UV spectra. Some spectral assignments for the complexes are given in Table 1, together with magnetic properties.

No $[VCl_2(PR_3)_4]$ complexes were isolated from this route, though we have prepared $[VCl_2(PMe_3)_4]$ by reduction of $[VCl_3(thf)_3]/PMe_3$ mixtures with Na/Hg. We have no evidence yet of N_2 uptake of any of these experiments.

We attempted to synthesise dinitrogen and carbonyl complexes from $[VX_2(diphosphine)_2]$ by reduction with reagents such as sodium amalgam and potassium naphthalene under the appropriate cover gas. For example, $[VCl_2(depe)_2]$ and sodium amalgam under CO (6 atm) yielded a yellow oil which had four bands between 1700 and 2000 cm^{-1} which appeared to be due to $\nu(CO)$. The strongest peak was at *c.* 1800 cm^{-1}. This does not correspond to the reported spectrum of $[V(CO)_2(dmpe)_2]$ [21]. The oil could not be characterised. Similarly, reduction of $[VCl_2(dmpe)_2]$ with sodium amalgam under dinitrogen (8 atm) yielded an oil which had a strong IR band at 1740 cm^{-1}; presumably assignable to $\nu(NN)$. However, microanalyses repeatedly showed negligible nitrogen content, and we were unable to characterise any dinitrogen complexes or their decomposition products.

We now know that reduction of $[VCl_3(thf)_3]$ with sodium and catalytic quantities of naphthalene under N_2 yields *cis*- and *trans*-$[V(N_2)_2(dmpe)_2]^-$ which have been well characterised spectroscopically in solution and which have IR bands at 1674 and 1791 cm^{-1}, and at 1759 cm^{-1}, respectively [22]. Recently, the structure of *trans*-$[V(N_2)_2(dppe)_2]^-$ has been confirmed by a single crystal X-ray study [23]. These vanadium(−I) complexes

TABLE 1. Analyses, magnetic properties and diffuse reflectance spectra of new vanadium(II) complexes

Complex and colour	Analyses[a]		Temp. (K)	μ_{eff}[b]	Magnetic properties		Diffuse reflectance spectra (cm^{-1})		
	C	H			θ[b] (°)	$10^6 \chi_D$[c] ($cm^3\ mol^{-1}$)	$^4A_{2g} \rightarrow {}^4T_{2g}$	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$[d]
$[VCl_2(dmpe)_2]$	32.7	6.6	295	3.7[e]			14200m,b	19800s	28000s
Red–orange	(34.2)	(7.6)	90						24700sh
$[VBr_2(dmpe)_2]$	28.0	5.7	295	3.94	4	332	13100m,vb	19600s	25600sh
Red–maroon	(28.2)	(6.3)	90	3.88					
$[VI_2(dmpe)_2]$	24.6	5.6	295	3.99	3	360	12600m	19600s	28000s
Maroon	(23.8)	(5.3)	90	3.92			14100sh		25300sh
$[V(dmpe)_3](BF_4)_2$	32.8	7.4	295						
Dark red	(32.0)	(7.2)	90						
$[VCl_2(depe)_2]$	44.6	8.7	295	3.98	−1	406	12700m	17500s	28600s
Blue–purple	(45.0)	(9.0)	90	4.00					25600sh
$[VBr_2(depe)_2]$	39.3	7.5	295	3.91	−4	427	12300m	17600s	25600s
Purple	(38.5)	(7.7)	90	3.98			11400m		
$[VI_2(depe)_2]$	36.6	7.3	295				11800m,vb	17500m	27000s
Light purple	(33.5)	(6.7)[f]	90						
$[VCl_2(dppe)_2] \cdot 2thf$	68.4	5.7	295	3.86	−3	581	12000w	14900m,vb	27400s
Yellow–green	(67.7)	(6.0)	90	3.91					24400sh
$[VBr_2(dppe)_2] \cdot 2thf$	62.0	5.3	295	4.02	3	602	11800w	14800m,vb	27800s
Green	(62.6)	(5.5)	90	3.96				19800sh	25000sh
$VCl_2(dppm)$	59.8	5.1	295						
Green	(59.0)	(4.7)	90						

[a]Calculated values in parentheses. [b]Calculated from $\mu_{eff} = 2.828(\chi_A T)^{1/2}$ and the Curie–Weiss Law, $\chi_A^{-1} \propto (T + \theta)$. [c]Diamagnetic correction. [d]Positions uncertain because of background absorption increasing to higher cm^{-1}. [e]From ref. 4, in toluene at 25 °C. [f]Calculated for $[VI_2(depe)_{2.5}]$: C, 36.6; H, 7.4%.

have been isolated as sodium salts by working at low temperature, and they lose dinitrogen *in vacuo*. This is despite the fact that other workers had suggested previously that N_2 uptake under these conditions does not occur [21]. We have repeated these preparations and have obtained similar IR spectra. The complexed dinitrogen is extremely labile, and is lost on drying the compounds *in vacuo* and even in the presence of $[PPh_4]Br$, which we added in order to isolate tetraphenylphosphonium salts. Why a dinitrogen complex with such extremely low values of ν(NN) should bind dinitrogen so weakly is still unclear. It seems unlikely that such a dinitrogen complex, because of its extreme sensitivity and lability, and low oxidation state, should be a good model for dinitrogen binding in nitrogenase.

Our new compounds of vanadium(III) are $[VCl_3(PR_2Ph)_3]$ (R = Me or Pr^n), $[VCl_3(PEt_2Ph)_2]$ and $[VBr_3(PR_2Ph)_2]$ (R = Me or Et). We have previously shown [24] in the system $[ReCl_3(PR_2Ph)_n]$ ($n = 2$ or 3) that the value of n depends in a systematic way on R, being 2 for any R bigger than methyl. It is tempting to apply the same rule here; thus bromides give lower coordination numbers than chlorides, and with the chlorides, $n = 3$ for R = Me and $n = 2$ for R = Et. Unfortunately, for R = Pr^n, n is also equal to 3. This must mean that packing of the alkyl chains within the coordination sphere as well as the absolute bulk of R is an influence on n. More work is required to clarify this point.

The structures of $[VCl_2(depe)_2]$ (Fig. 1, Tables 2 and 3) and of $[VCl_2(dppe)_2]$ (Figs. 2 and 3, Tables 4 and 5) have a *trans*-octahedral geometry very similar to that already reported for $[VCl_2(dmpe)_2]$ (Table 6). There is a slight lengthening in V–P distances (~0.06 Å) from the last compound and the acute P–V–P angles are significantly smaller (~3°), which may reflect the minimal steric demands of dmpe. The short C–CH_3 and C–C distances in the depe compound (*c.* 1.3 Å) are between atoms with large thermal ellipsoids, and may arise from a combination of disorder and thermal motion. This is not an uncommon problem in such compounds; for example, a small amount of disorder/

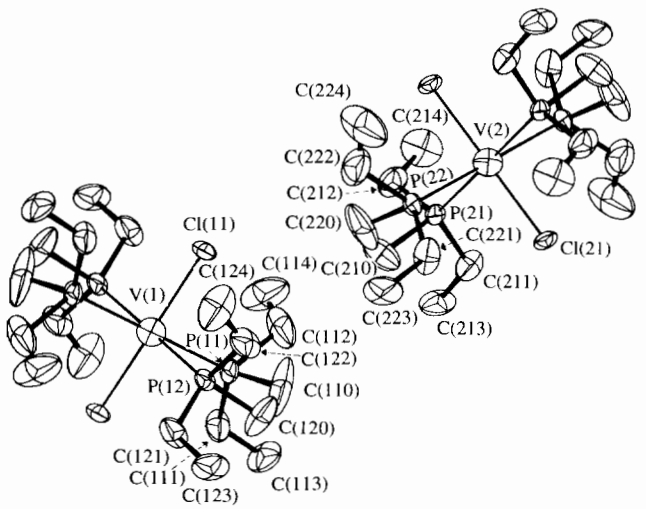

Fig. 1. Molecular structure with atom numbering scheme for the two independent molecules of $[VCl_2(depe)_2]$.

TABLE 2. Final atomic coordinates for non-hydrogen atoms in $[VCl_2(depe)_2]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
V(1)	0	0.500	1.000
V(2)	0.500	0.500	0.500
Cl(11)	0.2474(2)	0.5028(2)	0.0814(1)
Cl(21)	0.2516(2)	0.5050(2)	0.5819(1)
P(11)	0.0820(2)	0.6717(2)	0.8862(1)
P(12)	0.1907(2)	0.3555(2)	0.9228(1)
P(21)	0.3800(2)	0.3604(2)	0.4214(1)
P(22)	0.3286(2)	0.6757(2)	0.3881(1)
C(110)	0.179(2)	0.587(1)	0.8166(7)
C(111)	0.228(1)	0.7676(8)	0.9046(6)
C(112)	−0.070(2)	0.778(2)	0.8117(8)
C(113)	0.304(1)	0.850(1)	0.8373(6)
C(114)	−0.202(2)	0.851(2)	0.8278(9)
C(120)	0.278(1)	0.474(1)	0.8423(6)
C(121)	0.384(1)	0.2514(9)	0.9679(5)
C(122)	0.101(1)	0.2683(9)	0.8635(6)
C(123)	0.510(1)	0.184(1)	0.9195(6)
C(124)	0.027(2)	0.165(1)	0.9072(8)
C(210)	0.233(1)	0.475(1)	0.3421(5)
C(211)	0.241(1)	0.2563(8)	0.4675(5)
C(212)	0.512(1)	0.2717(9)	0.3602(5)
C(213)	0.148(1)	0.1902(9)	0.4194(6)
C(214)	0.639(1)	0.162(1)	0.4055(8)
C(220)	0.277(2)	0.594(1)	0.3146(7)
C(221)	0.139(1)	0.773(1)	0.4078(6)
C(222)	0.423(2)	0.773(2)	0.3107(8)
C(223)	0.017(1)	0.855(1)	0.3419(7)
C(224)	0.525(2)	0.849(2)	0.3237(9)

TABLE 3. Selected bond distances (Å) and angles (°) for $[VCl_2(depe)_2]$ with e.s.d.s in parentheses

V(1)–Cl(11)	2.445(2)	P(21)–C(212)	1.797(9)
V(1)–P(11)	2.558(2)	P(22)–C(220)	1.80(2)
V(1)–P(12)	2.563(2)	P(22)–C(221)	1.749(9)
V(2)–Cl(21)	2.444(2)	P(22)–C(222)	1.771(14)
V(2)–P(21)	2.563(2)	C(110)–C(120)	1.296(15)
V(2)–P(22)	2.553(2)	C(111)–C(113)	1.500(13)
P(11)–C(110)	1.768(13)	C(112)–C(114)	1.25(2)
P(11)–C(111)	1.777(10)	C(121)–C(123)	1.499(14)
P(11)–C(112)	1.800(12)	C(122)–C(124)	1.43(2)
P(12)–C(120)	1.898(10)	C(210)–C(220)	1.38(2)
P(12)–C(121)	1.781(8)	C(211)–C(213)	1.501(14)
P(12)–C(122)	1.782(11)	C(212)–C(214)	1.464(13)
P(21)–C(210)	1.858(8)	C(221)–C(223)	1.496(13)
P(21)–C(211)	1.794(9)	C(222)–C(224)	1.32(3)
Cl(11)–V(1)–P(11)	91.11(6)	Cl(21)–V(2)–P(21)	90.33(6)
Cl(11)–V(1)–P(12)	90.33(6)	Cl(21)–V(2)–P(22)	90.86(5)
P(11)–V(1)–P(12)	78.80(6)	P(21)–V(2)–P(22)	78.88(6)

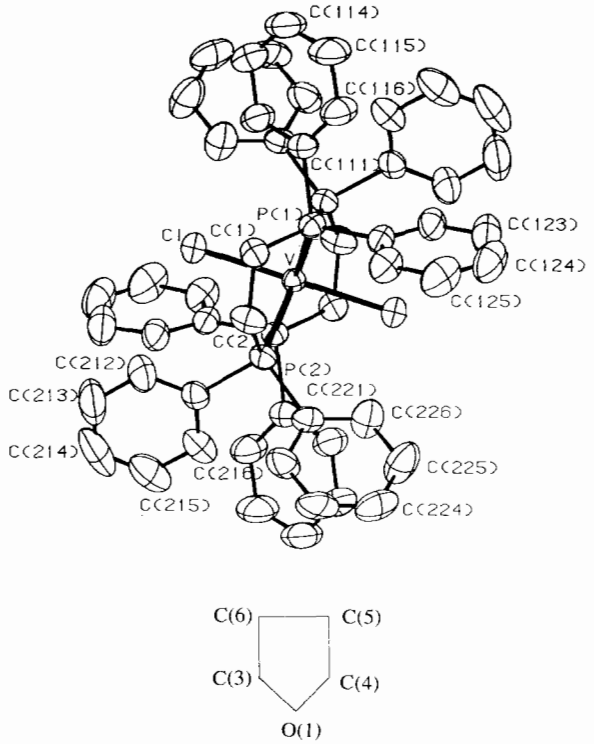

Fig. 2. Molecular structure with atom numbering scheme for $[VCl_2(dppe)_2]\cdot 2thf$.

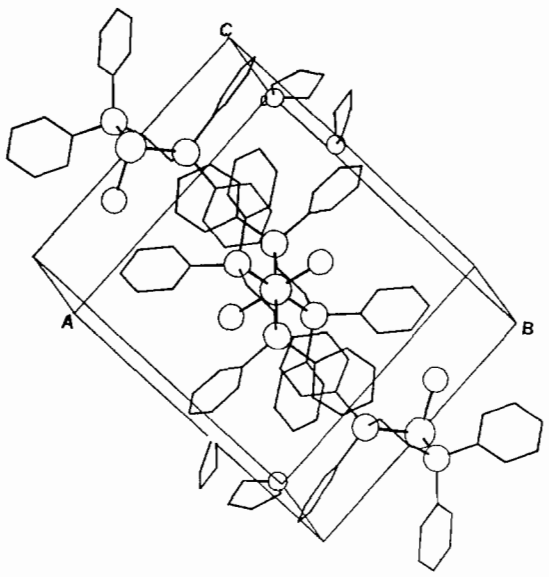

Fig. 3. Packing diagram of $[VCl_2(dppe)_2]\cdot 2thf$ showing solvent molecules.

high thermal motion also occurred for one of the two crystallographically independent molecules in $[VCl_2(dmpe)_2]$ leading to artificially low C–C distances between some of the dmpe methylene carbons [6].

The M–Cl and M–P distances in the complexes *trans*-$[MCl_2(dmpe)_2]$ (M = Ti, V, low-spin Fe, or low-spin Cr) [4, 25] have been reported to show a decrease consistent with the decline in M^{II} radii along the series. The effect is, however, greater for the phosphorus bonds (>0.3 Å) than the chlorine (<0.1 Å). High-spin Mn^{II} does not fit in to this, which is attributed to the greater radius of high-spin Mn^{II} compared to low-spin Mn^{II}.

TABLE 4. Final atomic coordinates for non-hydrogen atoms in $[VCl_2(dppe)_2]\cdot 2thf$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
V	0.500	0.500	0.500
Cl	0.6690(1)	0.4436(1)	0.4368(1)
P(1)	0.4703(1)	0.6122(1)	0.3821(1)
P(2)	0.3830(1)	0.3861(1)	0.4068(1)
C(1)	0.4333(5)	0.5318(4)	0.2985(3)
C(2)	0.4331(5)	0.4207(4)	0.3134(3)
C(111)	0.3567(4)	0.7078(4)	0.3636(3)
C(112)	0.3614(5)	0.7727(5)	0.3034(4)
C(113)	0.2720(6)	0.8379(5)	0.2864(4)
C(114)	0.1759(6)	0.8391(5)	0.3274(4)
C(115)	0.1696(6)	0.7759(6)	0.3864(4)
C(116)	0.2598(5)	0.7089(5)	0.4051(3)
C(121)	0.6027(4)	0.6794(4)	0.3615(3)
C(122)	0.6864(5)	0.6408(5)	0.3189(4)
C(123)	0.7892(6)	0.6924(7)	0.3106(4)
C(124)	0.8078(6)	0.7833(6)	0.3454(4)
C(125)	0.7253(6)	0.8220(5)	0.3881(4)
C(126)	0.6227(5)	0.7719(5)	0.3966(3)
C(211)	0.2247(4)	0.4008(4)	0.3997(3)
C(212)	0.1665(5)	0.3828(4)	0.4643(3)
C(213)	0.0456(5)	0.3932(5)	0.4626(4)
C(214)	−0.0151(5)	0.4254(5)	0.3971(5)
C(215)	0.0412(6)	0.4441(6)	0.3339(4)
C(216)	0.1616(5)	0.4307(5)	0.3343(3)
C(221)	0.4033(5)	0.2513(4)	0.4053(3)
C(222)	0.3115(5)	0.1851(4)	0.3909(4)
C(223)	0.3316(7)	0.0842(5)	0.3912(5)
C(224)	0.4402(7)	0.0468(5)	0.4051(4)
C(225)	0.5311(6)	0.1102(5)	0.4193(4)
C(226)	0.5138(5)	0.2116(4)	0.4201(4)
O(1)	0.0149(7)	0.0843(6)	0.3367(4)
C(3)	−0.065(1)	0.1551(8)	0.3102(6)
C(4)	−0.007(1)	0.069(1)	0.4090(6)
C(5)	−0.112(1)	0.105(1)	0.4244(7)
C(6)	−0.1560(9)	0.153(1)	0.3570(7)

TABLE 5. Selected bond distances (Å) and angles (°) for $[VCl_2(dppe)_2]\cdot 2thf$ with e.s.d.s in parentheses

V–Cl	2.420(1)	P(1)–C(121)	1.821(5)
V–P(1)	2.574(1)	P(2)–C(2)	1.842(5)
V–P(2)	2.558(1)	P(2)–C(211)	1.818(5)
P(1)–C(1)	1.853(5)	P(2)–C(221)	1.824(5)
P(1)–C(111)	1.841(5)	C(1)–C(2)	1.514(8)
Cl–V–P(1)	82.82(4)	C(1)–P(1)–C(121)	106.10(3)
Cl–V–P(2)	85.19(4)	C(111)–P(1)–C(121)	101.9(2)
P(1)–V–P(2)	78.09(4)	C(2)–P(2)–C(211)	106.3(2)
C(1)–P(1)–C(111)	98.20(2)	C(2)–P(2)–C(221)	100.9(2)
		C(211)–P(2)–C(221)	103.5(2)
		P(1)–C(1)–C(2)	115.9(4)
		P(2)–C(2)–C(1)	114.1(1)

TABLE 6. Bond distances (Å) and angles (°) in the $[VCl_2(diphosphine)_2]$ complexes

	$[VCl_2(dmpe)_2]$[a]	$[VCl_2(depe)_2]$	$[VCl_2(dppe)_2]\cdot 2thf$
V–Cl	2.446(4)	2.445(2)	2.420(1)
	2.434(4)	2.444(2)	
V–P	2.495(5)	2.558(2)	2.574(1)
	2.501(5)	2.563(2)	2.558(1)
	2.499(5)	2.563(2)	
	2.500(5)	2.553(2)	
P–V–P	81.6(2)	78.80(6)	78.09(4)
	81.3(2)	78.88(8)	

[a]Ref. 4.

Two comments appear apposite here. First, we have good data on high-spin and low-spin Fe^{II} complexes of the form $[FeCl_2(diphosphine)_2]$ [25]. In this case, the Fe–P bond length varies dramatically between the high-spin and low-spin forms (*c.* 0.3 Å), whereas Fe–Cl changes by less than 0.03 Å. This defies a simple radius explanation. Second, in the heavy metal series *mer*-$[MCl_3(PMe_2Ph)_3]$ (M = W, Re, Os, or Ir), M–P distances of the same kind also seem to be radius dependent, whereas M–Cl distances of the same kind are invariant [26]. There is some fundamental difference between Cl and P which causes this but we have yet to determine what it might be.

Experimental

All reactions were carried out under dinitrogen with dry deoxygenated solvents. Solvents were volatilised and solids dried under oil pump vacuum. Yields were of the order of 60%. The diphosphines bis(1,2-dimethylphosphino)methane, bis(1,2-diethylphosphino)ethane, bis(1,2-diphenylphosphino)ethane and bis(1,2-dimethylphosphino)ethane were prepared by standard methods [27].

The compounds $[V(H_2O)_4Cl_2]$ and $[V(H_2O)_6]Br_2$ were prepared [1] from vanadium turnings (99.7% purity, Aldrich) for use directly in the preparations of complexes of dmpe and depe [19]. The iodo-derivatives were obtained from the vanadium(II) species of approximate composition $[V(CH_3OH)_6]I_2$, itself isolated from $VCl_2\cdot 4H_2O$ as described earlier [20]. The complexes $[VCl_2(dppe)_2]\cdot 2thf$ and $[VBr_2(dppe)_2]\cdot 2thf$ could not be obtained from the hydrated halide and dppe in tetrahydrofuran. It was necessary to use the new anhydrous compounds which we tentatively formulate as $VCl_2(MeOH)(thf)$ and $VBr_2(MeOH)(thf)$. They were isolated in attempts to prepare $VX_2\cdot n thf$ from the hydrated halides, and although their analyses do not agree well with this formulation, dppe complexes of vanadium(II) chloride and bromide with satisfactory analyses and other properties were obtained from them. $[VBr_3(thf)_3]$ and $[VCl_3(thf)_3]$ were prepared by the literature methods [28].

Magnetic susceptibilities of samples in sealed tubes were determined between room and liquid nitrogen temperature by the Gouy method. The diffuse reflectance spectra of samples in sealed cells were recorded on a Beckman Acta MIV spectrophotometer. IR spectra of Nujol mulls made up in an inert atmosphere box were recorded on a Perkin-Elmer 577 spectrophotometer.

Dichloro(methanol)(tetrahydrofuran)vanadium

The chloride $[VCl_2(H_2O)_4]$ (4 g, 0.021 mol) was dissolved in ethanol (30 cm^3) in the presence of triethylorthoformate (30 cm^3). The blue-green solution was stirred for 2 h and then evaporated to dryness, to yield a green solid which was washed with petroleum ether (75 cm^3) to remove any ethyl formate and dried. The solid was dissolved in methanol to give a purple solution which was stirred for 2 h, and then evaporated to dryness. The green powder obtained was dissolved in thf (100 cm^3) to give a green solution which was allowed to stand for several hours before the solvent was removed under reduced pressure to give a green solid which was dissolved in thf (100 cm^3). After 1 h a light green solid separated and it was filtered off and dried. *Anal.* Found: C, 23.3; H, 4.7. Calc. for $C_5H_{12}Cl_2O_2V$: C, 26,6; H, 5.4%. IR: ν(OH) 3350, ν(CO) 1037, δ(OH) 920, ν(VCl) 290 cm^{-1}.

Dibromo(methanol)(tetrahydrofuran)vanadium

The bromide $[V(H_2O)_6]Br_2$ (1.5 g) was dissolved in a mixture of ethanol (30 cm^3) and triethylorthoformate (30 cm^3). The blue–green solution was stirred for 2 h and then evaporated to dryness, to yield a green solid which was washed with petroleum ether (75 cm^3) and dried. The green solid was dissolved in methanol to give a purple solution which was stirred for 2 h. Then the solvent was removed *in vacuo* to yield a green powder which was dissolved in thf (100 cm^3) to give a green solution. After several hours the solvent was removed *in vacuo* yielding a green solid which was again dissolved in thf (100 cm^3). After 1 h the light green solid which separated was filtered off and dried. *Anal.* Found: C, 22.9; H, 4.2. Calc. for $C_5H_{12}Br_2O_2V$: C, 19.1; H, 3.84%. IR: ν(OH) 3300, ν(CO) 1025, ν(VBr) 265 cm^{-1}.

Bis[1,2-bis(dimethylphosphino)ethane]dichlorovanadium(II)

To a purple solution of $[VCl_2(H_2O)_4]$ (1.3 g, 6.7 mmol) in methanol (20 cm^3) was added dmpe (2 cm^3, 13.3 mmol). The resulting dark purple solution was

placed at −20 °C for 48 h and the red–orange crystals which appeared were filtered off, washed with hexane and dried.

Bis[1,2-bis(dimethylphosphino)ethane]dibromovanadium(II)

The bromide $[V(H_2O)_6]Br_2$ (1.27 g, 4 mmol) was dissolved in methanol (20 cm^3) to give a dark purple solution. On addition of dmpe (1.2 cm^3, 8 mmol) the solution became opaque and it was left at −20 °C for 12 h. The maroon crystals, which had separated leaving a blue solution, were filtered off, washed with hexane and dried.

Bis[1,2-bis(dimethylphosphino)ethane]diiodovanadium(II)

The iodide $[V(CH_3OH)_6]I_2$ (0.4 g, 0.8 mmol) was dissolved in methanol (20 cm^3) to give a purple solution. When dmpe (0.25 cm^3, 1.6 mmol) was added the solution darkened and after the solution had been cooled to −20 °C for approximately 1 h, maroon crystals separated. These were filtered off, washed with hexane and dried.

Tris[1,2-bis(dimethylphosphino)ethane]vanadium(II) tetrafluoroborate

On the addition of dmpe (1 cm^3, 6.25 mmol) to $[V(H_2O)_6](BF_4)_2$ (0.52 g, 1.56 mmol) dissolved in methanol (40 cm^3) the purple solution became a deep blue. After two weeks at −20 °C a dark red solid crystallised. This was filtered off and dried.

Bis[1,2-bis(diethylphosphino)ethane]dichlorovanadium(II)

The addition of depe (1 cm^3, 4.85 mmol) to $[VCl_2(H_2O)_4]$ (0.48 g, 2.22 mmol) dissolved in methanol (20 cm^3) produced a dark purple solution which was placed at −20 °C for 12 h, whereupon blue–purple needle crystals were obtained. These were filtered off, washed with diethyl ether and dried.

Bis[1,2-bis(diethylphosphino)ethane]dibromovanadium(II)

On the addition of depe (1.5 cm^3, 7.28 mmol) to $[V(H_2O)_6]Br_2$ (1.12 g, 3.53 mmol) dissolved in methanol (20 cm^3) the purple solution darkened and within minutes purple crystals appeared. These crystals were filtered off, washed with diethyl ether and dried.

Bis[1,2-bis(diethylphosphino)ethane]diiodovanadium(II)

To $[V(CH_3OH)_6]I_2$ (3.52 g, 7.08 mmol) dissolved in methanol (20 cm^3), depe (2.6 cm^3, 0.012 mol) was added. The purple solution darkened and the fine light purple crystals which separated after 1 h were filtered off, washed with methanol and dried. Poor analyses were obtained for this complex.

Bis[1,2-bis(diphenylphosphino)ethane]dichlorovanadium(II) tetrahydrofuran (1/2)

To a suspension of light green $VCl_2(CH_3OH)(thf)$ (2.05 g, 9.07 mmol) in thf (50 cm^3) was added a solution of dppe (7.2 g, 0.0184 mmol) in thf (20 cm^3). After heating for 8 h under reflux the suspension was cooled, filtered, and the green filtrate concentrated to half volume under reduced pressure. The green crystals which appeared after 72 h at −20 °C were filtered off and dried. They proved suitable for structure determination.

Bis[1,2-bis(diphenylphosphino)ethane]dibromovanadium(II) tetrahydrofuran (1/2)

A solution of dppe (3.27 g, 8.12 mmol) in thf (20 cm^3) was added to a green suspension of $VBr_2(CH_3OH)(thf)$ (1.28 g, 4.06 mmol) in thf (130 cm^3). After 3 h under reflux a green solution was obtained. This was concentrated to one-third volume and kept at −20 °C for 1 week. The green solid which appeared was filtered off and dried.

1,2-Bis(diphenylphosphino)methanedichlorovanadium(II)

To a green suspension of $VCl_2(CH_3OH)(thf)$ (0.76 g, 3.36 mmol) in thf (130 cm^3) a solution of dppm (2.76 g, 6.88 mmol) in thf (20 cm^3) was added. After 8 h under reflux, the suspension was filtered and the green filtrate was concentrated to half volume. After several weeks at −20 °C a green solid separated. This was filtered off and dried.

Trichlorotris(dimethylphenylphosphine)vanadium(III)

To a purple solution of $[VCl_3(thf)_3]$ (0.37 g, 0.99 mmol) in toluene (25 cm^3) was added PMe_2Ph (0.4 cm^3, 2.89 mmol). The dark red–brown solution obtained was left at −20 °C for 3 weeks, after which a red microcrystalline solid had formed. This was filtered off and dried *in vacuo* to give a red–orange powder. The green filtrate was discarded. *Anal.* Found: C, 48.0; H, 5.6. Calc. for $C_{24}H_{33}Cl_3P_3V$: C, 50.4; H, 5.8%.

Trichlorobis(diethylphenylphosphine)vanadium(III)

To a purple solution of $[VCl_3(thf)_3]$ (1.99 g, 5.44 mmol) in toluene (80 cm^3) was added PEt_2Ph. The solution became a deep red colour and, after standing for a few minutes, a white solid appeared. More of this solid appeared on concentration of the solution. The solution was filtered and the solid discarded. The red filtrate was left at −20 °C for 7 days, after which a red–orange solid appeared. This was filtered off and

dried *in vacuo*. *Anal.* Found: C, 49.6; H, 7.0. Calc. for $C_{20}H_{30}Cl_3P_2V$: C, 49.0; H, 6.2%.

Trichlorotris(di-n-propylphenylphosphine)vanadium(III)

To a purple solution of $[VCl_3(thf)_3]$ (0.88 g, 2.37 mmol) in toluene (60 cm^3) was added PPr_2Ph (1.37 g, 7.11 mmol) to give a deep red solution. On standing overnight a white solid formed, which was discarded. The solvent was removed *in vacuo* to leave a red–maroon solid. *Anal.* Found: C, 58.7; H, 7.5. Calc. for $C_{36}H_{57}Cl_3P_3V$: C, 58.7, H, 7.8%.

Tribromobis(dimethylphenylphosphine)vanadium(III)

To a green–brown solution of $[VBr_3(thf)_3]$ (0.82 g, 1.6 mmol) in toluene (50 cm^3) was added PMe_2Ph (0.66 cm^3, 4.8 mmol). The orange–brown solution was stirred overnight and the red–orange precipitate was filtered off and dried *in vacuo*. *Anal.* Found: C, 40.9; H, 5.0. Calc. for $C_{16}H_{22}Br_3P_2V$: C, 40.9, H, 4.7%.

Tribromobis(diethylphenylphosphine)vanadium(III)

To a green–brown solution of $[VBr_3(thf)_3]$ (0.82 g, 1.6 mmol) in toluene (50 cm^3) was added PEt_2Ph (1.04 g, 6.3 mmol). The red–orange solution was stirred for 2 h and the brown–black precipitate discarded. The red–orange filtrate was placed at −20 °C for 12 h to give an orange solid, which was filtered off and dried *in vacuo*. *Anal.* Found: C, 39.0; H, 5.6. Calc. for $C_{20}H_{30}Br_3P_2V$: C, 38.6; H, 4.9%.

Only oils were isolated from reactions of $PEtPh_2$, PPr^nPh_2 and PBu^nPh_2. These were not characterised.

Dichlorotetrakis(trimethylphosphine)vanadium(II)

Trimethylphosphine (1.6 cm^3, *c*. 16 mmol) was added via syringe to $[VCl_3(thf)_3]$ (2.9 g, 7.76 mmol) in thf (100 cm^3). The resulting dark solution of $[VCl_3(PMe_3)_2]$ was stirred for 1 h and transferred to a flask containing 1% Na/Hg (0.97 g of sodium excess). The colour changed immediately to dark blue. Once the solution was completely transferred, PMe_3 (2 cm^3, *c*. 20 mmol) was added. The mixture was stirred overnight at room temperature. The liquor was decanted, filtered through celite and taken to dryness. The extremely air-sensitive product was extracted with thf, the solution filtered, concentrated and layered with hexane, affording a dark brown solid, which was filtered, washed with hexane and dried *in vacuo*. Yield 46%. *Anal.* Found: C, 33.0; H, 8.3. Calc. for $C_{12}H_{36}Cl_2P_4V$: C, 33.8; H, 8.4%. EPR: octet of quintets, $g = 1.971$, $A(^{51}V) = 161$ G; $A(^{31}P) = 24$ G (frozen thf solution at 77 K).

X-ray crystal structure determination of $[VCl_2(depe)_2]$

Crystals prepared as described above were sealed under dinitrogen in Lindemann capillaries. Crystal data: $C_{20}H_{48}Cl_2P_4V$, $M_r = 534.35$, triclinic, $a = 8.012(5)$, $b = 10.762(2)$, $c = 17.374(3)$ Å, $\alpha = 76.65(1)$, $\beta = 89.90(3)$, $\gamma = 78.52(3)°$, $V = 1426.9$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.244$ g cm^{-3}, $F(000) = 570$, graphite-monochromated, Mo Kα radiation ($\lambda = 0.71073$ Å^3), μ(Mo Kα) = 7.52 cm^{-1}.

Data collection and processing

Cell parameters were measured from a lath crystal of dimensions $\sim 0.6 \times 0.15 \times 0.05$ mm using 25 accurately centred reflections obtained in the θ range 14–16° on an Enraf-Nonius CAD4 four-circle diffractometer. The intensities of 6016 reflections were measured by the $\omega/2\theta$ scan method for a hemisphere of the reciprocal lattice in the range $1 \leqslant \theta \leqslant 26°$, $0 \leqslant h \leqslant 9$, $-13 \leqslant k \leqslant 13$, and $-21 \leqslant l \leqslant 21$. The 4 0 0 reflection was monitored hourly and it showed negligible decay of 0.4%. After application of the Lorentz and polarisation corrections, 3922 reflections were considered as observed, having $I \geqslant 3\sigma(I)$.

Structure solution and refinement

An empirical absorption correction was applied with minimum and maximum corrections of 0.874 and 0.998. From the Patterson map the positions were obtained of two independent vanadium atoms on centres of symmetry with their associated chlorine atoms. Normal heavy atom methods produced the remainder of the structure, which converged very slowly to $R = 0.13$; hydrogen atoms were included in the calculation in calculated positions ($d_H = 1.0$ Å). Full anisotropic refinement by full matrix least-squares slowly converged to $R = 0.081$ using a weighting scheme [29], $w^{-1} = [(\sigma(F))^2 + (0.05F)^2 + 5.0]$.

A difference map revealed electron density peaks of 1.2 electrons closely associated with both chlorine and all four phosphorus atoms (at distances of 0.1–0.6 Å). Other electron density peaks of 0.8 electrons were associated with the carbon atoms. There appeared to be no other atoms in the structure.

A bond scan showed slightly distorted octahedral coordination around each V atom and the dimensions of the two independent centrosymmetric molecules are very similar (Table 3). However, the geometry of the ligands is very distorted with many C–C distances being much shorter than the expected value of 1.54 Å for a single bond, e.g. C(110)–C(120) = 1.296(15) Å and C(210)–C(220) = 1.38(2) Å. In view of the difficulty experienced in the refinement in space group $P\bar{1}$, a refinement was also attempted in space group $P1$. The full anisotropic refinement converged slowly to $R = 0.068$. The lower R value is to be expected because of the increase in the number of parameters but it was obtained at the expense of a much worse molecular geometry. The unsatisfactory nature of the refinement of this compound is not understood and some possible factors

are given in the discussion below. Final atomic parameters are given in Table 2 and selected bond lengths and angles in Table 3. All calculations were performed using the Enraf-Nonius Structure Determination Package [30].

A Delauney reduction of the unit cell failed to indicated a higher symmetry system and the possibility of twinning has also been considered. There is a strong translational coincidence present between the coordinates of the V, Cl and P atoms of the independent molecules, as has been shown using a molecular graphics program. However, the C atoms, especially those of the ethyl groups, do not superimpose as might be the case if twinning were present.

Other factors contributing to the poor refinement results might arise from two possible causes: (i) an unreliable absorption correction by the use of psi data, and (ii) the presence of disorder of the light atoms, especially those of the ethyl group.

As a variant on the absorption correction, the program DIFABS [31] was used which gave results that were not significantly different. Our prime conclusion, therefore, is that positional disorder is the main factor for the distortion of the molecule and hence the high R factor. Table 2 shows that the x and y coordinates of nearly all the carbon atoms are determined to only three decimal places, with the e.s.d. of the terminal methyl groups, on average, about twice those of the methylene groups. The ORTEP diagrams clearly show large thermal vibration ellipsoids associated with many of the carbon atoms and, in particular, the bridge atoms C110, C120 and C210, C220 are quite elongated. It is our experience that when positional disorder is present in a structure there is usually a correlation between the coordinates and the thermal vibration parameters which result in the shortening of the interatomic distances, as Table 3 shows. A 4.0 Å scan around each atom reveals that the molecules are well separated, with all intermolecular carbon–carbon distances greater than 3.75 Å. The structure has therefore a very loose packing allowing the light atoms to adopt a disordered arrangement and whilst this has not given an accurate structure determination, nevertheless the stereochemistry has been established.

X-ray crystal structure determination of $[VCl_2(dppe)_2]\cdot 2thf$

Crystals prepared as above were sealed under nitrogen in Lindemann capillaries. Crystal data: $C_{60}H_{64}Cl_2P_4O_2V$, $M_r = 1062.92$, monoclinic, $a = 11.445(10)$, $b = 13.415(7)$, $c = 17.666(5)$ Å, $\beta = 93.89(5)°$, $V = 2706.0$ Å^3, space group $= P2_1/c$, $Z = 2$, $D_c = 1.304$ g cm^{-3}, $F(000) = 1114$, graphite-monochromated radiation, Mo Kα($\lambda = 0.71073$ Å), μ(Mo Kα) $= 4.335$ cm^{-1}.

Data collection and processing

A crystal of dimensions $0.8 \times 0.8 \times 0.7$ mm was used. Unit cell dimensions were obtained from 25 accurately centred reflections on a CAD4 diffractometer using monochromated Mo Kα radiation in the range $9 \leqslant \theta \leqslant 12°$. The intensities of reflections were measured in the range $1 \leqslant \theta \leqslant 24°$, with the index range $0 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 15$ and $-20 \leqslant l \leqslant 20$. This yielded a total of 4695 reflections of which 2731 with $I \geqslant 3\sigma(I)$ were considered observed. The space group was determined by inspection of the systematic absences occurring for $h0l$ (l odd) and $0k0$ (k odd). The Lorentz and polarisation corrections were applied and correction made for 24% decay in the standard reflection over the data collection period. An empirical absorption correction based on psi data was applied; the minimum correction was 0.873, the maximum correction 0.999 and the average correction 0.936.

Structure solution and refinement

Since there are only two vanadium atoms ($Z = 2$) in the unit cell, these must be sited at centres of symmetry. From the Patterson function, the positions of one chlorine and one phosphorus atom were obtained. Least-squares refinement of these three atoms, followed by an electron density calculation produced the remaining atoms of the structure, and isotropic refinement of all atoms converged at $R = 0.153$. At this stage a difference Fourier map revealed the presence of a solvent thf molecule. After the formula had been adjusted, full isotropic refinement of all atoms converged at $R = 0.093$. The hydrogen atoms were included in fixed calculated positions, $d_H = 1.0$ Å. The program DIFABS [31] was then used to apply an absorption correction (min. $= 0.701$, max. $= 1.147$, av. $= 0.983$). Refinement with the V, Cl, P(1) and P(2) atoms anisotropic and the remainder isotropic converged at $R = 0.078$. After this, full anisotropic refinement of all non-hydrogen atoms converged at $R = 0.049$, $R_w = 0.064$ and S (estimated standard deviation of observation of unit weight) $= 0.991$. The weighting scheme used was $w^{-1} = [\sigma(F)^2 + (0.04F)^2 + 4.0]$ [29]. The highest residual peak in the final difference map was 0.53 electrons and a 4 Å search around the molecule revealed no unusually close contacts. Refinement without the application of DIFABS gave a less satisfactory result. Convergence was achieved at $R = 0.054$, $R_w = 0.069$ and $S = 1.072$. Final atomic parameters are given in Table 4 and selected bond lengths and angles in Table 5.

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