The Preparation and Crystal and Molecular Structures of Trichlorobis(methyldiphenylphosphine)vanadium(III) and its Acetonitrile Adduct[‡]

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The complex $[VCl_3(PPh_2Me)_2]$ has been prepared from $[VCl_3(MeCN)_3]$ or $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) and the tertiary phosphine in toluene. In the crystal there are two independent trigonal-bipyramidal molecules with axial phosphine ligands. There is considerable distortion from regular co-ordination polyhedra and mean bond distances are V–Cl, 2.22 and 2.23 Å, and V–P, 2.54 and 2.53 Å. On long reflux of a solution of $[VCl_3(MeCN)_3]$ and PPh_2Me in toluene, the complex $[VCl_3(MeCN)(PPh_2Me)_2]$ is obtained. It contains six-co-ordinate vanadium(III) with meridional V–Cl bonds of average length 2.30 Å. Other bond distances are V–N, 2.140(3) Å and V–P, 2.56 Å (av.).

Complexes of vanadium(III) with tertiary aliphatic phosphines, $[VCl_3(PR_3)_2]$ (R = Me, Et, or Pr^n) have been prepared from VCl_3 and are thought[1] to be trigonal bipyramidal with the phosphines co-ordinated axially. However, triphenylphosphine and tricyclohexylphosphine react with VCl_3 only in melts of the phosphine to give compounds of varying atomic ratios which were thought to be dimers, *e.g.* $[\{VCl_3(PPh_3)\}_2]$. The related complexes $[VX_2(PR_3)_2(\eta^5\text{-}C_5H_5)]$ (X = Cl or Br, R = Me or Et) have been prepared by reacting $[VX_3(thf)_3]$ (thf = tetrahydrofuran) with $[Mg(\eta^5\text{-}C_5H_5)_2]$ and PR_3.[2] These complexes are useful starting materials for the preparation of other vanadium complexes such as $[V(CO)_3(PEt_3)(\eta^5\text{-}C_5H_5)]$. It has been reported that a vanadium(II) dimer, $[\{VCl_2(PEt_3)_2\}_2]$, can be prepared by zinc reduction of $[VCl_3(PEt_3)_2]$ or reaction[3] of PEt_3 with '$VCl_2(thf)_2$,' now known to be a mixed-metal salt, $[\{V_2(\mu\text{-}Cl)_3(thf)_6\}_2][Zn_2Cl_6]$.[4] Furthermore, reaction of this mixed-metal salt with PPh_2Me followed by addition of $LiBH_4$ yields a green solution from which crystals of a bimetallic vanadium(I) polyhydride $[V_2Zn_2H_4(BH_4)_2(PPh_2Me)_4]$ can be isolated.[5] The use of bis(diphenylphosphino)methane (dppm) and $NaBH_4$, instead of PPh_2Me and $LiBH_4$, affords a vanadium(II) dimer with bridging chlorine atoms, bridging dppm, and bidentate tetrahydroborate, $[\{V(\mu\text{-}Cl)(\mu\text{-}dppm)(BH_4)\}_2]$.[6] Therefore, by slightly altering the ligands and reagents a zinc-free product may be obtained from the mixed-metal salt. Recently 1,2-bis(dimethylphosphino)ethane (dmpe) has been reacted with the mixed-metal salt to yield $[VCl_2(dmpe)_2]$.[7]

Before the present work no mononuclear complexes of vanadium(III) with aromatic phosphines had been obtained. The preparations, properties, and molecular structures of $[VCl_3(PPh_2Me)_2]$ and its adduct $[VCl_3(MeCN)(PPh_2Me)_2]$ are reported.[§] During the preparation of this paper the low-temperature (−160 °C) crystal structure and other properties of $[VCl_3(PPh_2Me)_2]\cdot0.4C_5H_{12}$ were published.[8] As indicated below there is generally good agreement with our results.

Experimental

All reactions were carried out under nitrogen with deoxygenated solvents. VCl_3 (B.D.H.) and PPh_2Me (Aldrich Chemical Company) were used as received. Acetonitrile (B.D.H.) was allowed to stand over P_2O_5 for a few days and distilled under nitrogen. Tetrahydrofuran (B.D.H.) was left over $LiAlH_4$ for a few days and then distilled under nitrogen. Toluene (B.D.H.) was left over Na wire for a few days. The wire was removed and the toluene was distilled under nitrogen. n-Pentane (B.D.H.) was washed with portions of concentrated sulphuric acid until there was no colouration of the acid layer after 12 h. It was then washed with portions of 5 mol dm^{-3} $KMnO_4$ (in 3 mol dm^{-3} H_2SO_4), and left to stand over more $KMnO_4$ solution for 2 d after which there was no effervescence with fresh $KMnO_4$. The n-pentane was then washed several times with distilled water and $NaHCO_3$ solution, to remove any residual acid, and distilled under nitrogen. All solvents were stored under nitrogen. $[VCl_3(MeCN)_3]$ and $[VCl_3(thf)_3]$ were prepared from VCl_3 by literature methods.[9,10]

Magnetic susceptibilities at room temperature were determined on a balance obtained from Johnson Matthey Equipment Ltd. and calibrated with $Hg[Co(NCS)_4]$. The sample tube was filled under a nitrogen atmosphere. Diffuse-reflectance and solution spectra of samples in sealed cells were recorded on a Beckman Acta M IV spectrophotometer.

Preparation of Trichlorobis(methyldiphenylphosphine)vanadium(III).—This complex was prepared from both $[VCl_3(MeCN)_3]$ and $[VCl_3(thf)_3]$.

A green suspension of $[VCl_3(MeCN)_3]$ (0.55 g, 1.96 mmol) in deoxygenated toluene (50 cm^3) was prepared. To this, methyldiphenylphosphine (1.25 cm^3, 6.24 mmol) was added and a red solution formed immediately together with a small amount of white precipitate which is thought to be an impurity present in the phosphine. The precipitate was filtered off and the red solution kept below 0 °C in a refrigerator for two weeks. This gave a low yield (6%) of red *crystals* which were isolated by decanting the mother-liquor, dried under vacuum, and stored under nitrogen.

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[‡] *Supplementary data available* (No. SUP 56575, 4 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

[§] Presented at the British Crystallographic Spring Meeting, University of Bristol, April 1985.

Table 1. Analytical[a] and physical data for the vanadium(III) complexes

			Electronic spectra[c]/cm^{-1}				Analyses(%)		
Complex	Colour	ν(CN)[b]/cm^{-1}	Reflectance	Solution[e]	Assignment[f]	$\mu_{eff.}$/B.M.[d]	C	H	N
$[VCl_3(PPh_2Me)_2]$	Red	—	5 210s	5 350 (43)	$^3A_1'',{}^3A_2'', \longleftarrow {}^3A_2'$	2.77	[g]57.0	4.8	—
			7 250s	7 690 (24)	$^2E''(F) \longleftarrow {}^3A_2'$		(56.0)	(4.7)	—
			14 300w	—	$^1E'', {}'E' \longleftarrow {}^3A_2'$				
			20 000s	20 000 (135)	$^3E''(F) \longleftarrow {}^3A_2'$				
			26 900s	—	$^3E''(P),{}^3A_2'(P) \longleftarrow {}^3A_2'$				
$[VCl_3(MeCN)(PPh_2Me)_2]$	Green	2 323w	14 700s	14 140 (39)[h]	$^3T_{2g} \longleftarrow {}^3T_{1g}$	2.64	[i]55.3	4.9	2.4
		2 298m	22 000s	20 410(sh)	$^3T_{1g}(P) \longleftarrow {}^3T_{1g}$		(55.2)	(4.9)	(2.3)
			26 300s	31 950 (1 900)	$^3A_{2g} \longleftarrow {}^3T_{1g}$				

[a] Calculated values given in parentheses. [b] As Nujol mull. [c] Range 5 000—33 000 cm^{-1}. [d] Measured at 295 K; B.M. = 0.927 × 10^{-23} A m^2. [e] Toluene solution of $[VCl_3(PPh_2Me)_2]$; acetonitrile solution of $[VCl_3(MeCN)(PPh_2Me)_2]$; ε(dm^3 mol^{-1} cm^{-1}) in parentheses. [f] Assignments follow those made in ref. 13 for $[VCl_3(NMe_3)_2]$. [g] From $[VCl_3(MeCN)_3]$; from $[VCl_3(thf)_3]$ C, 56.9; 57.1; H, 4.8; 4.9%. [h] Solvolysis of $[VCl_3(MeCN)(PPh_2Me)_2]$ may occur. [i] Analyses of some apparently pure samples gave equally good C and H analyses but low nitrogen analyses.

Table 2. Positional parameters with estimated standard deviations in parentheses for $[VCl_3(PPh_2Me)_2]$

Atom	x	y	z	Atom	x	y	z
V(1)	0.744 12(8)	0.198 44(7)	0.054 35(6)	C(125)	0.704 5(9)	−0.192 0(6)	0.055 6(5)
V(2)	0.703 01(8)	0.767 40(7)	0.461 59(6)	C(126)	0.712 7(7)	−0.084 5(6)	0.036 2(4)
Cl(11)	0.771 3(2)	0.349 4(1)	−0.037 1(1)	C(131)	0.710 4(5)	0.153 8(5)	−0.141 9(3)
Cl(12)	0.878 0(2)	0.094 0(1)	0.124 5(1)	C(132)	0.748 0(6)	0.233 1(6)	−0.204 2(4)
Cl(13)	0.571 7(2)	0.149 6(2)	0.071 8(1)	C(133)	0.687 3(9)	0.264 5(7)	−0.273 0(5)
Cl(21)	0.638 5(2)	0.644 9(1)	0.409 5(1)	C(134)	0.586 4(8)	0.216 6(7)	−0.277 8(5)
Cl(22)	0.841 1(1)	0.735 5(1)	0.549 22(9)	C(135)	0.551 5(7)	0.143 5(7)	−0.216 9(5)
Cl(23)	0.628 6(2)	0.926 7(1)	0.420 9(1)	C(136)	0.609 9(6)	0.109 1(6)	−0.150 0(4)
P(11)	0.744 6(1)	0.290 4(1)	0.163 17(9)	C(201)	0.917 6(5)	0.694 2(4)	0.339 4(3)
P(12)	0.788 5(1)	0.108 6(1)	−0.051 90(9)	C(202)	0.903 4(7)	0.653 7(6)	0.276 2(4)
P(21)	0.840 4(1)	0.809 4(1)	0.349 23(9)	C(203)	0.965 7(8)	0.563 5(6)	0.274 1(4)
P(22)	0.570 5(1)	0.702 1(1)	0.575 28(9)	C(204)	1.037 6(7)	0.514 4(6)	0.331 5(5)
C(11)	0.717 4(6)	0.203 9(5)	0.259 0(4)	C(205)	1.048 7(7)	0.553 4(6)	0.393 2(4)
C(12)	0.931 8(5)	0.132 8(5)	−0.081 4(4)	C(206)	0.989 2(7)	0.641 7(5)	0.397 6(4)
C(21)	0.768 7(6)	0.861 7(5)	0.257 4(4)	C(211)	0.946 5(5)	0.903 2(4)	0.349 6(3)
C(22)	0.597 7(6)	0.562 8(5)	0.617 6(4)	C(212)	0.931 4(5)	0.975 5(5)	0.392 5(4)
C(101)	0.655 9(5)	0.405 0(4)	0.159 3(3)	C(213)	1.013 8(6)	1.047 6(5)	0.392 2(4)
C(102)	0.671 6(6)	0.468 5(5)	0.207 9(4)	C(214)	1.108 6(6)	1.046 9(5)	0.350 0(4)
C(103)	0.601 5(6)	0.553 2(5)	0.206 3(4)	C(215)	1.125 8(6)	0.977 5(5)	0.306 7(4)
C(104)	0.513 3(7)	0.574 5(5)	0.155 3(4)	C(216)	1.044 3(6)	0.905 7(5)	0.307 3(4)
C(105)	0.496 2(7)	0.513 6(6)	0.106 2(4)	C(221)	0.588 0(5)	0.762 4(5)	0.654 5(3)
C(106)	0.566 9(6)	0.427 6(5)	0.108 4(4)	C(222)	0.584 9(6)	0.870 8(5)	0.635 9(4)
C(111)	0.883 9(5)	0.337 8(4)	0.167 5(3)	C(223)	0.596 7(7)	0.920 9(5)	0.694 1(4)
C(112)	0.914 7(5)	0.426 2(5)	0.110 6(3)	C(224)	0.615 9(6)	0.863 3(6)	0.769 2(4)
C(113)	1.022 0(6)	0.461 9(5)	0.107 4(4)	C(225)	0.623 2(6)	0.756 6(6)	0.788 8(4)
C(114)	1.098 7(6)	0.407 8(6)	0.161 2(4)	C(226)	0.608 7(6)	0.704 8(5)	0.731 7(4)
C(115)	1.069 3(6)	0.321 0(5)	0.218 1(4)	C(231)	0.422 0(5)	0.716 3(5)	0.555 2(3)
C(116)	0.961 4(5)	0.284 8(5)	0.221 3(4)	C(232)	0.352 1(7)	0.632 6(6)	0.572 6(5)
C(121)	0.777 1(5)	−0.034 1(4)	−0.026 6(3)	C(233)	0.239 3(6)	0.648 5(7)	0.558 7(6)
C(122)	0.830 8(6)	−0.093 3(6)	−0.069 5(4)	C(234)	0.196 1(6)	0.743 8(7)	0.526 3(5)
C(123)	0.819 4(8)	−0.200 7(5)	−0.047 4(5)	C(235)	0.262 6(6)	0.829 3(7)	0.507 1(5)
C(124)	0.757 3(9)	−0.248 5(6)	0.013 0(5)	C(236)	0.374 6(6)	0.814 3(6)	0.522 1(4)

A purple solution of $[VCl_3(thf)_3]$ (0.96 g, 2.57 mmol) in deoxygenated toluene (50 cm^3) was prepared. To this, methyldiphenylphosphine (1.54 cm^3, 7.71 mmol) was added to give a red solution which contained a small amount of white precipitate which was filtered off. The solvent was evaporated from the red filtrate under vacuum to give a red gel. Deoxygenated n-pentane (50 cm^3) was added to the red gel. A pink microcrystalline precipitate formed which was stirred for 1 h, filtered off, and dried under vacuum. This gave a high yield (88%) of a pink *powder* which was stored under nitrogen.

Preparation of (Acetonitrile)trichlorobis(methyldiphenylphosphine)vanadium(III).—A green suspension of $[VCl_3(MeCN)_3]$ (1.40 g, 5.00 mmol) in deoxygenated toluene (75 cm^3) was prepared as before. Methyldiphenylphosphine (3.00 cm^3, 15.0 mmol) was added to give a red solution. The mixture was refluxed and the solution gradually became dark green. After 10 h under reflux the solution was allowed to cool very slowly. Green *crystals* formed which were filtered off, dried under vacuum, and stored under nitrogen (yield 40%).

When a solution of $[VCl_3(thf)_3]$ (0.48 g, 1.28 mmol) in deoxygenated toluene (60 cm^3) was added to methyldiphenylphosphine (0.8 cm^3, 4.0 mmol) a dark red solution resulted which remained unchanged after 10 h under reflux. The spectrum was the same as that of a solution in toluene of $[VCl_3(PPh_2Me)_2]$ prepared from $[VCl_3(MeCN)_3]$ as above.

The analytical and physical data obtained for these complexes are given in Table 1.

Table 3. Positional parameters with estimated standard deviations in parentheses for [$VCl_3(MeCN)(PPh_2Me)_2$]

Atom	*x*	*y*	*z*
V	0.658 85(5)	0.264 77(4)	0.462 26(3)
Cl(1)	0.706 65(9)	0.415 30(7)	0.511 74(6)
Cl(2)	0.817 07(9)	0.183 70(9)	0.500 32(6)
Cl(3)	0.568 99(9)	0.133 05(7)	0.400 60(6)
P(1)	0.735 58(7)	0.306 54(7)	0.340 39(5)
P(2)	0.586 60(8)	0.205 89(7)	0.583 94(5)
N	0.508 4(2)	0.335 0(2)	0.418 4(2)
C(1)	0.781 2(4)	0.200 3(3)	0.291 6(3)
C(2)	0.615 0(4)	0.077 4(3)	0.600 9(3)
C(3)	0.431 9(3)	0.370 7(3)	0.387 9(2)
C(4)	0.336 0(4)	0.417 9(4)	0.349 0(3)
C(111)	0.853 7(3)	0.386 9(3)	0.344 7(2)
C(112)	0.871 6(3)	0.443 0(3)	0.282 5(2)
C(113)	0.963 2(3)	0.501 8(3)	0.286 7(2)
C(114)	1.037 8(3)	0.504 3(3)	0.351 9(3)
C(115)	1.022 0(3)	0.448 7(4)	0.413 2(2)
C(116)	0.930 1(3)	0.389 3(3)	0.410 3(2)
C(121)	0.634 9(3)	0.364 1(3)	0.270 9(2)
C(122)	0.608 6(3)	0.458 9(4)	0.280 1(3)
C(123)	0.528 5(4)	0.502 5(4)	0.229 3(4)
C(124)	0.472 3(4)	0.452 0(6)	0.170 3(4)
C(125)	0.495 4(5)	0.356 5(7)	0.163 3(3)
C(126)	0.575 9(4)	0.312 0(5)	0.212 0(3)
C(211)	0.640 1(3)	0.255 6(3)	0.677 8(2)
C(212)	0.742 4(4)	0.297 7(3)	0.690 3(2)
C(213)	0.787 5(4)	0.328 2(4)	0.762 8(2)
C(214)	0.732 2(4)	0.319 1(4)	0.826 6(2)
C(215)	0.630 5(4)	0.277 1(4)	0.812 1(2)
C(216)	0.584 2(3)	0.245 4(3)	0.740 6(2)
C(221)	0.439 6(3)	0.218 5(3)	0.577 4(2)
C(222)	0.368 5(4)	0.140 0(3)	0.568 0(3)
C(223)	0.257 6(4)	0.154 8(4)	0.556 3(3)
C(224)	0.214 7(4)	0.248 0(5)	0.553 1(3)
C(225)	0.283 8(4)	0.324 6(4)	0.562 7(3)
C(226)	0.394 3(3)	0.311 1(3)	0.574 2(2)

X-Ray Structure Determination of [$VCl_3(PPh_2Me)_2$].—Crystals, prepared from [$VCl_3(MeCN)_3$] as described above, were sealed under nitrogen in Lindemann capillaries.

Crystal data. $C_{26}H_{26}Cl_3P_2V$, M = 557.75, triclinic, a = 12.003(2), b = 13.744(2), c = 17.751(4) Å, α = 74.00(2), β = 89.19(2), γ = 88.07(1)°, U = 2 710.9 Å^3 (by least-squares refinement of 25 automatically centred reflections, λ = 0.710 69 Å), space group $P\bar{1}$, Z = 4, D_c = 1.367 g cm^{-3}. Red, air-sensitive tablets, approximate dimensions 0.3 × 0.3 × 0.1 mm, $F(000)$ = 1 144, μ(Mo-K_α) = 7.81 cm^{-1}.

Data collection and processing.[11] Enraf-Nonius CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.70 + 0.35 tan θ, ω scan speed 3.33° min^{-1}, graphite-monochromated Mo-K_α radiation; 9 327 unique reflections (all h positive, $1 \leqslant \theta \leqslant 25°$) yielding 5 175 reflections with $I \geqslant 3\sigma(I)$.

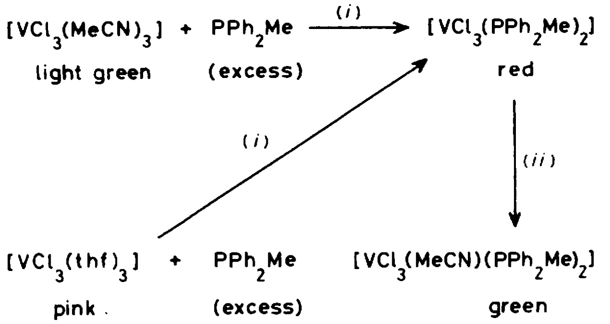
Structure analysis and refinement. Direct methods (V, Cl, and P atoms) followed by normal heavy-atom procedures. Full-matrix isotropic refinement of all non-hydrogen atoms with hydrogens in calculated positions until convergence at R = 0.099 followed by application of absorption correction. Full-matrix anisotropic refinement of all non-hydrogen atoms, hydrogens fixed as before, converged at R = 0.052, R' = 0.067. The weighting scheme $w = \mathrm{Lp}/[\sigma^2(I) + (0.07I)^2]^{\frac{1}{2}}$ where I = raw intensity gave satisfactory agreement analyses. Throughout, the 001 reflection was omitted. Programs, computers, and scattering factor data are given in ref. 11. Atomic co-ordinates are given in Table 2.

X-Ray Structure Determination of [$VCl_3(MeCN)(PPh_2Me)_2$].—Crystals were prepared as described previously and sealed under nitrogen in Lindemann capillaries.

Crystal data. $C_{28}H_{29}Cl_3NP_2V$, M = 598.8, monoclinic, a = 12.359(3), b = 13.816(1), c = 17.654(3) Å, β = 98.31(2)°, U = 2 982.8 Å^3 (by least-squares refinement of 25 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$ (alt. $P2_1/c$ no. 14), Z = 4, D_c = 1.333 g cm^{-3}. Green, air-sensitive tablets, approximate dimensions 0.2 × 0.2 × 0.1 mm, $F(000)$ = 1 204, μ(Mo-K_α) = 7.16 cm^{-1}.

Data collection and processing.[11] Enraf-Nonius CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.80 + 0.35 tanθ, ω scan speed 3.33° min^{-1}, graphite-monochromated Mo-K_α radiation; 4 669 unique reflections measured ($1 \leqslant \theta \leqslant 25°$) yielding 3 737 with $I \geqslant 2.58\sigma(I)$.

Structure analysis and refinement. Direct methods (V and Cl atoms) followed by normal heavy-atom methods. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions. The weighting scheme $w = \mathrm{Lp}/[\sigma^2(I) + (0.05I)^2]^{\frac{1}{2}}$ where I = raw intensity gave satisfactory agreement analyses. The 30$\bar{1}$ reflection was omitted because of extinction. Final R and R' values were 0.043 and 0.064 respectively. Programs and computers used and sources of scattering factor data are given in ref. 11. Atomic co-ordinates are given in Table 3.



Scheme. (*i*) toluene; (*ii*) MeCN, reflux, 10 h

Results and Discussion

The preparation of [$VCl_3(PPh_2Me)_2$] from [$VCl_3(MeCN)_3$] and reaction to give the acetonitrile adduct are outlined in the Scheme. [$VCl_3(PPh_2Me)_2$] may also be prepared from [$VCl_3(thf)_3$]. However, the colour of the solution of [$VCl_3(PPh_2Me)_2$] prepared in this way remained unchanged after refluxing in toluene for 10 h which suggests that tetrahydrofuran cannot form an adduct with [$VCl_3(PPh_2Me)_2$].

There are two independent molecules in the crystals of [$VCl_3(PPh_2Me)_2$]. Each has a trigonal-bipyramidal structure with the phosphines co-ordinated in the axial positions (Figure 1). The V–Cl bond distances in the two molecules are the same within experimental error, and within each molecule one V–Cl distance (*ca.* 2.19 Å) is markedly shorter than the other two which are approximately equal (*ca.* 2.24 Å). The Cl–V–Cl bond angles (115.7—125.5°) show some distortion from the expected 120° (Table 4). The corresponding angles are 118.1 and 121.0° (two) in [$VCl_3(NMe_3)_2$], the only other trigonal-bipyramidal complex of vanadium(III) which has been structurally character-

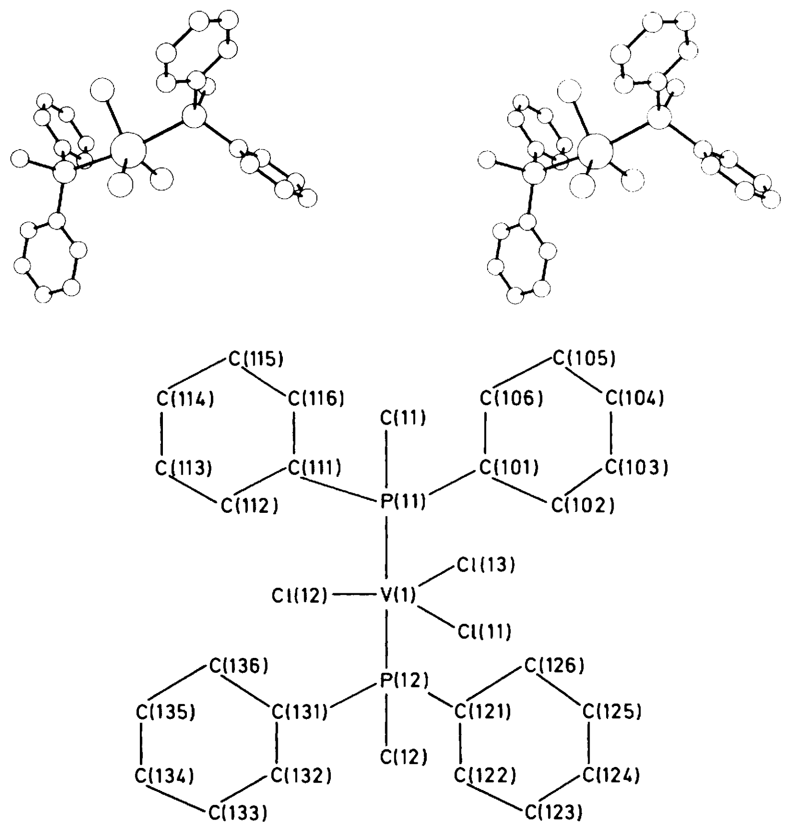


Figure 1. Atom numbering scheme and stereoscopic pair for [$VCl_3(PPh_2Me)_2$]

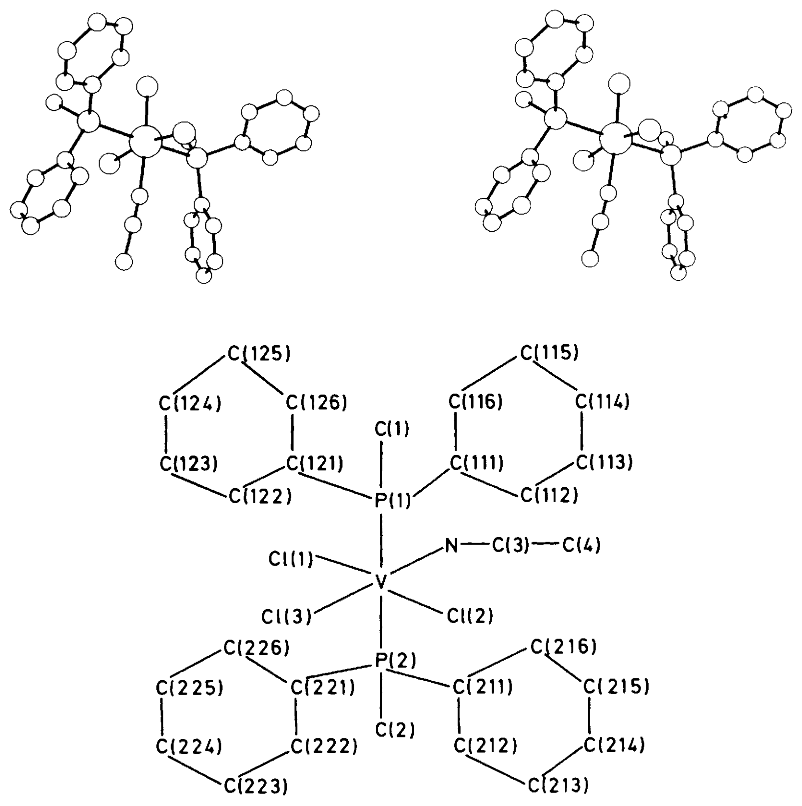


Figure 2. Atom numbering scheme and stereoscopic pair for [$VCl_3(MeCN)(PPh_2Me)_2$]

Table 4. Bond lengths (Å) and angles (°) for $[VCl_3(PPh_2Me)_2]$. Values are given for molecule 1 with equivalent values for molecule 2 alongside

V(1)–Cl(11)	2.232(2)	2.240(2)
V(1)–Cl(12)	2.237(2)	2.238(2)
V(1)–Cl(13)	2.181(2)	2.196(2)
V(1)–P(11)	2.552(2)	2.522(2)
V(1)–P(12)	2.534(2)	2.528(2)
P(11)–C(11)	1.801(6)	1.804(6)
P(11)–C(101)	1.810(6)	1.807(6)
P(11)–C(111)	1.815(6)	1.810(6)
P(12)–C(12)	1.804(7)	1.810(6)
P(12)–C(121)	1.828(6)	1.817(7)
P(12)–C(131)	1.807(6)	1.815(6)

Cl(11)–V(1)–Cl(12)	125.5(1)	123.2(1)
Cl(11)–V(1)–Cl(13)	115.7(1)	117.4(1)
Cl(12)–V(1)–Cl(12)	118.8(1)	119.4(1)
Cl(11)–V(1)–P(11)	91.6(1)	86.9(1)
Cl(11)–V(1)–P(12)	86.4(1)	88.0(1)
Cl(12)–V(1)–P(11)	84.7(1)	91.4(1)
Cl(12)–V(1)–P(12)	86.6(1)	87.5(1)
Cl(13)–V(1)–P(11)	96.0(1)	90.2(1)
Cl(13)–V(1)–P(12)	95.8(1)	96.3(1)
P(11)–V(1)–P(12)	167.8(1)	173.0(1)
C(11)–P(11)–C(101)	103.8(3)	105.5(3)
C(11)–P(11)–C(111)	105.9(3)	104.8(3)
C(101)–P(11)–C(111)	103.2(3)	104.3(3)
C(12)–P(12)–C(121)	105.2(3)	105.8(3)
C(12)–P(12)–C(131)	104.6(3)	105.6(3)
C(121)–P(12)–C(131)	103.3(3)	104.3(3)

Mean C–C bond length in phenyl rings = 1.37(2) Å; range 1.400—1.312 Å.

Table 5. Bond lengths (Å) and angles (°) for $[VCl_3(MeCN)(PPh_2Me)_2]$

V–Cl(1)	2.300(1)	P(1)–C(1)	1.831(3)
V–Cl(2)	2.269(1)	P(1)–C(111)	1.826(3)
V–Cl(3)	2.320(1)	P(1)–C(121)	1.802(3)
V–P(1)	2.540(1)	P(2)–C(2)	1.826(3)
V–P(2)	2.574(1)	P(2)–C(211)	1.827(3)
V–N	2.140(3)	P(2)–C(221)	1.812(3)
		N–C(3)	1.132(3)
		C(3)–C(4)	1.437(5)

Cl(1)–V–Cl(2)	99.84(4)	Cl(2)–V–N	175.63(7)
Cl(1)–V–Cl(3)	165.25(4)	Cl(3)–V–N	81.60(7)
Cl(2)–V–Cl(3)	94.90(4)	P(1)–V–P(2)	174.61(3)
Cl(1)–V–P(1)	90.54(3)	C(1)–P(1)–C(111)	102.0(1)
Cl(1)–V–P(2)	94.01(3)	C(1)–P(1)–C(121)	105.2(2)
Cl(2)–V–P(1)	87.23(3)	C(111)–P(1)–C(121)	103.3(1)
Cl(2)–V–P(2)	89.14(3)	C(2)–P(2)–C(211)	100.4(1)
Cl(3)–V–P(1)	89.58(3)	C(2)–P(2)–C(221)	105.7(2)
Cl(3)–V–P(2)	86.76(3)	C(211)–P(2)–C(221)	104.4(1)
Cl(1)–V–N	83.65(7)	N–C(3)–C(4)	178.8(4)

Mean C–C bond length in phenyl rings = 1.38(7) Å; range = 1.396—1.345 Å.

ised.[12] Also, in this complex the bonds to the axial trimethylamine ligands are at right angles to the plane containing the chlorine and vanadium atoms, *i.e.* N–V–N = 180°, whereas in the molecules of $[VCl_3(PPh_2Me)_2]$ P–V–P = 167.8 and 173.0°. The greater distortion from the ideal trigonal bipyramid in the phosphine complex is caused by steric effects of the phosphine ligands and crystal packing. The mean V–Cl separations (2.217 and 2.225 Å) are similar to that in $[VCl_3(NMe_3)_2]$ (2.239 Å).[12]

The dimensions of the trigonal-bipyramidal molecules agree well with those determined recently under different conditions (–160 °C) on a crystal obtained by a different procedure. The solid, which was isolated from $[VCl_3(thf)_3]$ and PPh_2Me in toluene, to which pentane had been added, and recrystallised from toluene–pentane, had analyses indicating an average composition $[VCl_3(PPh_2Me)_2]\cdot 0.4C_5H_{12}$. Apparently the crystal chosen for investigation contained a negligible amount of pentane.[8] We have also used a similar method preparatively, but our crystals were obtained from $[VCl_3(MeCN)_3]$ (see Experimental section).

The close correspondence between the solution and reflectance spectra of $[VCl_3(PPh_2Me)_2]$ (Table 1) indicates that the same species is present in solution as in the solid state. The band assignments are based on a previous interpretation of the electronic spectrum of $[VCl_3(NMe_3)_2]$.[13] The effective magnetic moment of 2.77 B.M. confirms the oxidation state and is close to the values reported for $[VCl_3(PEt_3)_2]$ (2.83 B.M. at 298 K)[1] and $[VCl_3(PPh_2Me)_2]\cdot 0.4C_5H_{12}$ (2.78 B.M. in benzene at 295 K).[8]

The acetonitrile adduct has a distorted octahedral structure (Figure 2) with the two phosphine ligands above and below the plane formed by the vanadium and chlorine atoms (the acetonitrile is slightly removed from this plane). The V–Cl bond lengths in the adduct are not uniform because of distortion from octahedral stereochemistry and are longer than in $[VCl_3(PPh_2Me)_2]$. The lengthening of the V–P bonds in $[VCl_3(MeCN)(PPh_2Me)_2]$ (2.540 and 2.574 Å) compared with $[VCl_2(dmpe)_2]$ (2.499 Å)[7] suggests greater back-bonding in the latter as might be expected from the lower oxidation state of the vanadium. The C≡N and C–C bond distances in the co-ordinated acetonitrile [1.132(3) and 1.437(5) Å respectively, Table 5] correspond closely with those in $[VOCl_3(MeCN)]$[14] [C≡N 1.137(2) and C–C 1.445(3) Å].

In the reflectance spectrum of the adduct (Table 1) the band at 26 300 cm^{-1} has been assigned to the $^3A_{2g} \longleftarrow {}^3T_{1g}$ transition[15] which has not been observed in other octahedral vanadium(III) complexes as it was obscured by charge transfer or ligand absorption. The effective magnetic moment of 2.64 B.M. is lower than the spin-only value (2.87 B.M.) but effective magnetic moments of *ca.* 2.7 B.M. have been reported for octahedral vanadium(III) complexes.[16]

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