

PREPARATION AND CHARACTERIZATION OF MONO-CYCLOPENTADIENYLVANADIUM DIHALIDE BIS-PHOSPHINE COMPLEXES; CRYSTAL STRUCTURE OF $(\eta^5\text{-C}_5\text{H}_5)\text{VCl}_2(\text{PMe}_3)_2$

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Summary

Mono-cyclopentadienyl complexes $\text{CpVX}_2(\text{PR}_3)_2$ and $\text{Cp}'\text{VX}_2(\text{PR}_3)_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{Me}$; $\text{R} = \text{Me, Et}$; $\text{X} = \text{Cl, Br}$) have been prepared by reaction of $\text{VX}_3(\text{PR}_3)_2$ with CpM ($\text{M} = \text{Na, Tl, SnBu}_3^n, 1/2 \text{ Mg}$) or $\text{Cp}'\text{Na}$. Attempts to prepare analogous complexes with other phosphine ligands, PPh_3 , PPh_2Me , PPhMe_2 , Pcy_3 , DMPE and DPPE failed. Reduction of $\text{CpVCl}_2(\text{PEt}_3)_2$ with zinc or aluminium under CO (1 bar) offers a simple method for the preparation of $\text{CpV}(\text{CO})_3(\text{PEt}_3)$. The crystal structure of the trimethylphosphine complex $\text{CpVCl}_2(\text{PMe}_3)_2$ is reported.

Introduction

Organometallic chemistry of trivalent titanium and vanadium has been centered mainly on metallocene derivatives [1]. Little is known about the mono-cyclopentadienyl derivatives. Available data indicate that they show a tendency to disproportionate to dicyclopentadienyl compounds and complexes without cyclopentadienyl groups [2]. Trivalent CpTi compounds also tend to disproportionate to species with the metal in di- and tetravalent state [3].

The chemistry of CpTi(III) derivatives is based on the halides CpTiX_2 and CpTiX_2L_n as starting materials [4]. Analogous vanadium complexes were not known when we started our research. Recently King et al. [5] reported the preparation of CpVI_2 from $\text{CpV}(\text{CO})_4$ and I_2 .

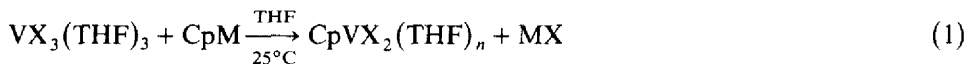
We decided to develop a convenient method to make, starting from readily

available complexes $\text{VX}_3(\text{THF})_3$, mono-cyclopentadienyl vanadium compounds of the type CpVX_2 or CpVX_2L_n (L = stabilizing donor ligand) and to study their chemistry. A preliminary account has been published [6].

Results and discussion

Exploratory studies

A straightforward looking method of introducing one Cp group per vanadium and stabilizing the 12 electron species CpVX_2 by complexation with THF was tried for a range of cyclopentadienylating reagents (eq. 1).



($\text{X} = \text{Cl, Br}$; $\text{M} = \text{Na, Tl, SnBu}_3^n, 1/2 \text{ Mg}$)

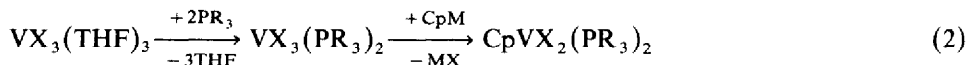
In all cases reaction took place readily, with formation of an intensely coloured purple solution (for $\text{X} = \text{Cl}$: λ_{max} 495 nm; $\epsilon_{\text{max}} \approx 720 \text{ l mol}^{-1} \text{ cm}^{-1}$). Attempts to isolate and identify the purple product failed, due to disproportionation to Cp_2VX and $\text{VX}_3(\text{THF})_3$. Addition of potential stabilizing ligands (dimethoxyethane, nitriles, amines, pyridine, phosphites, phosphines and arsines) after the reaction of $\text{VX}_3(\text{THF})_3$ with CpM gave only disproportionation products Cp_2VX and $\text{VX}_3(\text{THF})_3$ (or VX_3L_n) and no trace of mono-cyclopentadienyl complexes.

The purple solution is not a mixture of Cp_2VX and $\text{VX}_3(\text{THF})_3$. This follows from comparing the UV VIS spectra of the purple reaction product with a 1/1 mixture of Cp_2VX and $\text{VX}_3(\text{THF})_3$; the spectra are not identical. The product is probably not $\text{CpVX}_2(\text{THF})_n$ either, since addition of small trialkylphosphines does not result in the formation of $\text{CpVX}_2(\text{PR}_3)_2$ (vide infra).

The results indicate that the synthesis of CpVX_2 compounds directly from $\text{VX}_3(\text{THF})_3$ will be unlikely. Other complexes VX_3L_n may be better starting materials.

Synthesis of $\text{CpVX}_2(\text{PR}_3)_2$

$\text{VX}_3(\text{THF})_3$ is a convenient starting material for the adducts $\text{VX}_3(\text{PR}_3)_2$ ($\text{R} = \text{Me, Et}$), cf. [7]. Analogous adducts of PPh_3 , PPh_2Me , PPhMe_2 , Pcy_3 and DPPE cannot be made in this manner in THF solution. DMPE gives a green complex, cf. [8], which was isolated for $\text{X} = \text{Cl}$; it analyzed as $\text{VCl}_3(\text{DMPE})(\text{THF})$. Attempts to prepare $\text{CpVCl}_2(\text{DMPE})$ from this adduct were not successful. The phosphine complexes $\text{VX}_3(\text{PR}_3)_2$ ($\text{R} = \text{Me, Et}$) in turn are excellent starting compounds for CpV derivatives; high yields of $\text{CpVX}_2(\text{PR}_3)_2$ (eq. 2) were obtained, especially when $\text{VX}_3(\text{PR}_3)_2$ was prepared and used in situ.



All cyclopentadienylating reagents used (eq. 1) gave good results; Cp_2Mg was used for convenience. Introduction of methyl substituted cyclopentadienyl was possible using $\text{Cp}'\text{Na}$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{Me}$). Pentamethylcyclopentadienyl (Cp^*) derivatives could not be synthesized in this way using Cp^*Li , Cp^*Na or Cp^*MgCl .

Detailed information on the synthesis of the complexes is given in the experimental part. Yields, analytical data, etc. are summarized in Table 1.

TABLE 1

ANALYTICAL DATA FOR $\text{CpVX}_2(\text{PR}_3)_2$ AND $\text{Cp}'\text{VX}_2(\text{PR}_3)_2$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{Me}$)

Compound	Yield (%)	Mol. Weight ^a (calcd.)	M.p. ^b (°C)	Analysis (Found (calcd.) (%))				
				V	Cl	Br	C	H
$\text{CpVCl}_2(\text{PMe}_3)_2$	71	339 (339)	198	15.11 (15.02)	21.38 (21.43)		38.93 (38.96)	6.84 (6.84)
$\text{Cp}'\text{VCl}_2(\text{PMe}_3)_2$	84	<i>c</i>	113	14.55 (14.43)	20.25 (20.08)		41.49 (40.82)	7.29 (7.14)
$\text{CpVBr}_2(\text{PMe}_3)_2$	63	<i>c</i>	<i>c</i>	12.00 (11.90)		37.41 (37.34)	30.87 (30.87)	5.44 (5.42)
$\text{CpVCl}_2(\text{PEt}_3)_2$	88	398 (423)	92	12.12 (12.04)	16.79 (16.75)		48.60 (48.24)	8.34 (8.36)
$\text{Cp}'\text{VCl}_2(\text{PEt}_3)_2$	82	<i>c</i>	67	12.03 (11.64)	<i>c</i>		49.32 (49.44)	8.48 (8.53)
$\text{CpVBr}_2(\text{PEt}_3)_2$	57	<i>c</i>	115	9.93 (9.95)		31.28 (31.20)	39.70 (39.87)	6.75 (6.89)
$\text{Cp}'\text{VBr}_2(\text{PEt}_3)_2$	58	<i>c</i>	69	9.68 (10.00)		30.48 (30.37)	40.92 (41.91)	7.11 (7.09)

^a Cryoscopically in benzene. ^b Determined by DTA. ^c Not determined.

Characterization

All complexes $\text{CpVX}_2(\text{PR}_3)_2$ have a characteristic blue colour. Quantitative data for the absorption spectra of $\text{CpVCl}_2(\text{PMe}_3)_2$ and $\text{CpVCl}_2(\text{PEt}_3)_2$ are given in Table 2. The spectra are virtually solvent independent, illustrating the absence of interaction with polar solvent molecules and also showing their stability in chlorinated solvents.

The solubility of the compounds in nonpolar solvents strongly depends on X and PR_3 . For instance $\text{CpVCl}_2(\text{PMe}_3)_2$ is much less soluble in pentane than $\text{CpVCl}_2(\text{PEt}_3)_2$, in accordance with the generally observed increase in solubility when phosphine ligands contain longer alkyl groups. As expected, a methyl group in the Cp ring also results in a marked solubility increase. A similar effect is observed when Cl is substituted by Br.

The compounds are thermally surprisingly stable. DTA data (Table 1) show one reversible endothermic effect due to melting. No further effects (endothermic or exothermic) are observed up to 250°C. Introduction of a methyl group in the Cp

TABLE 2

VISIBLE SPECTRAL DATA FOR $\text{CpVCl}_2(\text{PR}_3)_2$ ^a

	THF		Toluene		CH_2Cl_2	
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
$\text{CpVCl}_2(\text{PMe}_3)_2$	526	63	528	60	527	67
	665	59	662	57	668	61
$\text{CpVCl}_2(\text{PEt}_3)_2$	580	80	583	82	585	80
	695	85	697	86	696	84

^a λ_{max} in nm and ϵ_{max} in $\text{mol}^{-1} \text{cm}^{-1}$.

ring gives the expected decrease in melting point, but the thermal stability is unaffected.

Molecular weight measurements (benzene) show that the compounds are monomers in solution. Magnetic susceptibility measurements show that they are magnetically dilute d_2 compounds. As an example, $\text{CpVCl}_2(\text{PEt}_3)_2$ follows the Curie law in the temperature range measured (80–300 K); μ_{eff} 2.81 BM corresponds to two unpaired electrons per vanadium atom (spin only value: 2.83 BM) as expected for a monomeric d^2 complex.

The IR spectra (Nujol, 4000–400 cm^{-1}) show characteristic Cp or Cp' and coordinated phosphine absorptions. The main Cp absorptions are found in the ranges 807–810vs, 1006–1013w, 1014–1018m, 1121–1122w and 3075–3085m cm^{-1} and Cp' absorptions in the ranges 800–803vs, 863–877m, 1051–1053w, 1072–1074w, 1495–1499w and 3075–3085m. The very strong CH out of plane deformation of the Cp(Cp') group at 800–810 cm^{-1} seems to be characteristic for complexes of trivalent vanadium [9]. The PMe_3 complexes have P–C stretching modes at 669–671m and 730–736s cm^{-1} , CH_3 rocking at 942–949vs cm^{-1} , symmetric CH_3 bending at 1274–1276m, 1281–1283m and 1296–1298w cm^{-1} and asymmetric CH_3 bending at 1419–1421m cm^{-1} [10]. The PEt_3 ligand absorptions are observed at 608–613w 661–664m, 680–686m and 724–727s cm^{-1} , (P–C stretching) at 747–750m and 762–765s cm^{-1} (CH_2 rocking), at 1034–1039s cm^{-1} (CH_3 rocking), at 1246–1250m,br and 1251–1258m,br cm^{-1} (CH_2 wagging), and at 1411–1416m cm^{-1} (CH_2 symm. deform) [11].

^1H NMR spectra of the paramagnetic complexes were recorded at 200 MHz in toluene- d_8 at 20 and 100°C in the range 800 downfield to 500 ppm upfield from TMS. No Cp resonances were detected in this range at 20 nor at 100°C, probably due to unfavorable electron spin relaxation rates. The phosphine resonances are easily observed, and even for paramagnetic compounds, they all show large line widths relative to their rather small isotropic shifts. Data for isotropic (paramagnetic shifts (δ^{para}) and half widths ($\Delta\nu_{1/2}$) at 20°C are given in Table 3. The methyl protons in PMe_3 and the methylene protons in PEt_3 , which are both in β position relative to vanadium, are shifted upfield with a δ^{para} of about +18 ppm (20°C). The methyl protons of PEt_3 (γ relative to vanadium) show a small downfield shift of about –1.5 ppm. These results are in agreement with a strong polarization effect in the alkyl chain, comparable to the observed rapid attenuation of alternating isotropic shifts down the alkyl chain in Cp_2V alkyl [12,13]. Resonances for methyl protons of the Cp' ring were not directly observed for the PEt_3 complexes. However, in $\text{Cp}'\text{VCl}_2(\text{PMe}_3)_2$ a clear additional resonance was found at 8.7 (5.2) ppm upfield from TMS at 20°C (100°C), which is probably due to the methyl protons of the Cp'. The area ratio of 1/6 to the PMe_3 resonance is in agreement with this assignment. A closer examination of the intensity ratio of the methylene resonance relative to the methyl resonance in PEt_3 of the Cp and Cp' complexes at 100°C (both resonances are well separated at this temperature) gives an indication for the presence of an additional peak in the Cp' complexes, coinciding with the methylene resonances, which is possibly due to Me in Cp'. The observed small upfield shifts for Me in Cp' seem to be rather unusual for vanadium complexes [12,16].

Substitution of Cp by Cp' does not give a clear trend in the isotropic shifts of the phosphine protons. The protons of PMe_3 shift upfield, while the methylene protons in PEt_3 shift downfield. Substitution of Cl by Br in the PEt_3 complexes give rise to

TABLE 3

ISOTROPIC SHIFTS^a OF PHOSPHINE PROTONS IN $\text{Cp}^{\vee}\text{X}_2(\text{PR}_3)_2$ AND $\text{Cp}^{\vee}\text{X}_2(\text{PR}_3)_2$ IN TOLUENE- d_8 AT 20°C (Half widths ($\Delta\nu_{1/2}$) in Hz are given between parentheses)

Compound	$\text{P}(\text{CH}_3)_3$	$\text{P}(\text{CH}_2\text{CH}_3)_3$	
		CH_2	CH_3
$\text{Cp}^{\vee}\text{VCl}_2(\text{PMe}_3)_2$	+17.6 (1085)		
$\text{Cp}^{\vee}\text{VCl}_2(\text{PMe}_3)_2$	+18.2 (1160)		
$\text{Cp}^{\vee}\text{VCl}_2(\text{PEt}_3)_2$		+18.8 (2280)	-1.49 (310)
$\text{Cp}^{\vee}\text{VCl}_2(\text{PEt}_3)_2$		+17.8 (2650)	-1.72 (340)
$\text{Cp}^{\vee}\text{VBr}_2(\text{PEt}_3)_2$		+19.9 (1640)	-1.49 (250)
$\text{Cp}^{\vee}\text{VBr}_2(\text{PEt}_3)_2$		+19.0 (1850)	-1.45 (240)

^a Values in ppm with negative shifts to low field. Isotropic shifts are determined relative to the free phosphine ligands [14,15].

upfield shifts of about 1 ppm for the methylene protons. The line widths of the PEt_3 resonances in the bromide complexes are considerably smaller (~30%) than in the corresponding chloride complexes.

Chemical properties

The chemical properties of the extremely air-sensitive $\text{Cp}^{\vee}\text{X}_2(\text{PR}_3)_2$ complexes will be briefly discussed here. Reduction of $\text{Cp}^{\vee}\text{X}_2(\text{PR}_3)_2$ under N_2 with metals with formation of dinuclear halide bridged V^{II} species, and also the substitution of

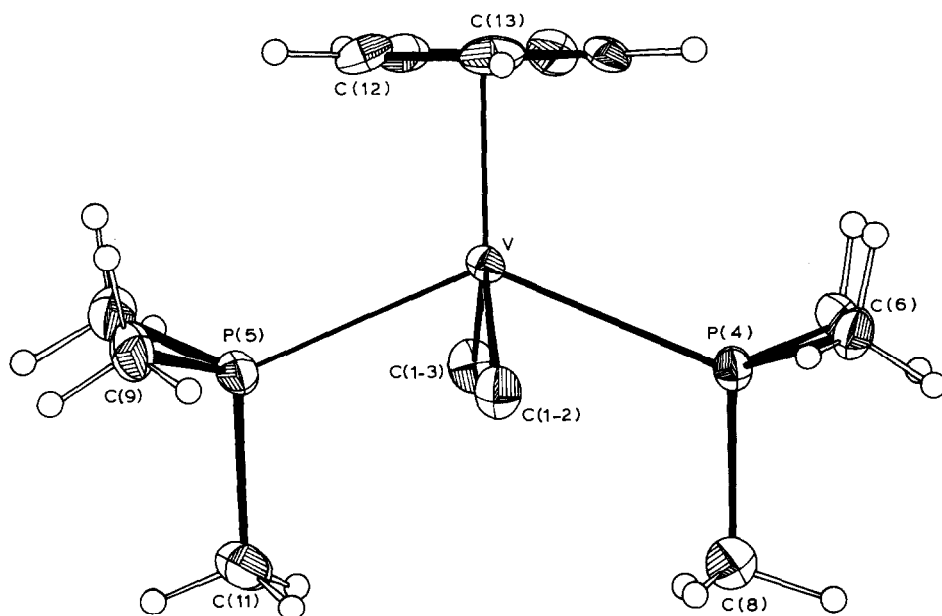


Fig. 1. ORTEP view of $(\eta^5\text{-C}_5\text{H}_5)\text{VCl}_2(\text{PMe}_3)_2$ showing atom labeling. Unlabelled carbons follow the sequence of the labels given.

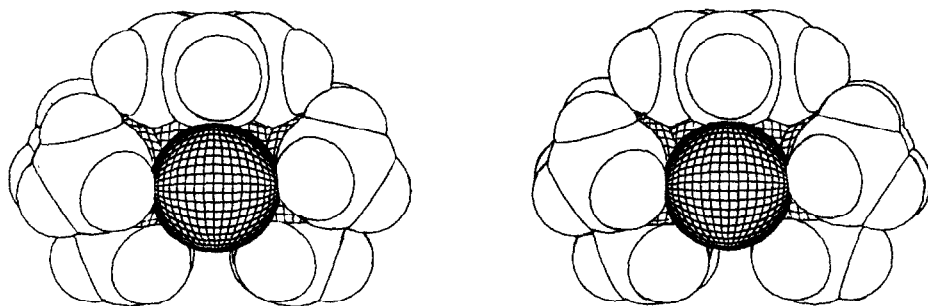


Fig. 2. Stereo space-filling drawing of $\text{CpVCl}_2(\text{PMe}_3)_2$ in the same orientation as Fig. 1.

halide ligands in $\text{CpVX}_2(\text{PR}_3)_2$ using Grignard or lithium reagents will be reported elsewhere [17].

The complexes $\text{CpVX}_2(\text{PR}_3)_2$ show no reactivity towards H_2 or alkenes under ambient conditions; isomerization or hydrogenation of alkenes is not observed. Also with CO no reaction was found under the moderate conditions applied (20°C , 1 bar). However, reduction with Al or Zn under CO (20°C , 1 bar) offers a simple and inexpensive method for the preparation of mono-cyclopentadienyl vanadium carbonyl complexes. NMR experiments in $\text{THF-}d_8$ show nearly quantitative formation of $\text{CpV}(\text{CO})_3(\text{PEt}_3)$ within one day. $\text{CpV}(\text{CO})_4$ and $\text{CpV}(\text{CO})_2(\text{PEt}_3)_2$ are present only in traces ($< 0.5\%$; ^1H NMR, IR). $\text{CpV}(\text{CO})_3(\text{PEt}_3)$ can be obtained analytically pure by crystallization from pentane.

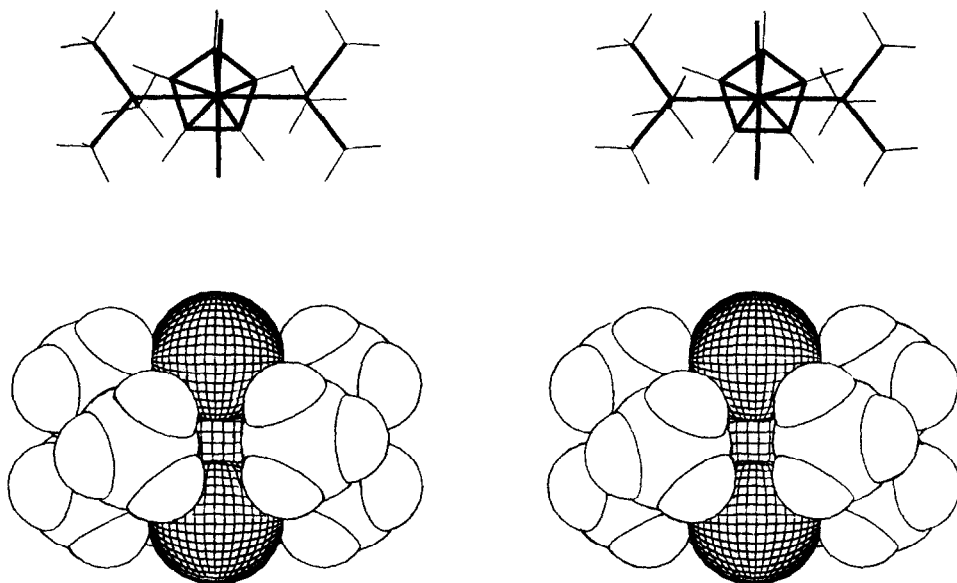


Fig. 3. Stereo stick-figure and space-filling drawings of $\text{CpVCl}_2(\text{PMe}_3)_2$ viewed from below the basal Cl_2P_2 unit. Vanadium appears at the center of the lower figure, widely hatched.

TABLE 4
CRYSTAL DATA FOR $(C_5H_5)VCl_2[P(CH_3)_3]_2$

Empirical formula	$C_{11}H_{23}Cl_2P_2V$
Color	blue
Crystal dimensions (mm)	$0.15 \times 0.15 \times 0.17$
Space group	$P2_1/a$
Cell dimensions (at $-163^\circ C$; 24 reflections)	
<i>a</i>	12.326(4) Å
<i>b</i>	10.148(3) Å
<i>c</i>	13.056(4) Å
β	94.15(2)°
Molecules/cell	4
Volume (Å ³)	1628.8
Calculated density (g/cm ³)	1.383
wavelength	0.71069
Molecular weight	339.10
Linear absorption coefficient (cm ⁻¹)	10.9
Total number of reflections collected	2381
Number of unique intensities	2134
Number with $F > 0.0$	2029
Number with $F > \sigma(F)$	1972
Number with $F > 2.33\sigma(F)$	1888
Final residuals	
$R(F)$	0.0256
$R_w(F)$	0.0300
Goodness of fit for the last cycle	0.925
Maximum Δ/σ for last cycle	0.05

TABLE 5
FRACTIONAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS ^a FOR
 $(C_5H_5)VCl_2(PMe_3)_2$

	10^4x	10^4y	10^4z	$10B_{iso}$
V(1)	1876.5(4)	4659.4(5)	7168.7(3)	11
Cl(2)	3113(1)	5454(1)	8535(1)	16
Cl(3)	-71(1)	4560(1)	7184(1)	17
P(4)	1706(1)	2904(1)	8499(1)	13
P(5)	1426(1)	7072(1)	7132(1)	13
C(6)	2949(3)	2097(4)	9001(3)	20
C(7)	826(3)	1512(3)	8143(3)	22
C(8)	1133(3)	3514(3)	9654(3)	20
C(9)	2541(3)	8249(3)	7104(3)	22
C(10)	502(3)	7617(4)	6063(3)	21
C(11)	739(3)	7571(4)	8252(3)	20
C(12)	2714(3)	5130(3)	5683(2)	21
C(13)	3394(3)	4245(3)	6251(2)	21
C(14)	2831(3)	3066(3)	6345(2)	20
C(15)	1796(3)	3202(3)	5827(2)	20
C(16)	1730(3)	4482(3)	5422(2)	20

^a Isotropic values for those atoms refined anisotropically are calculated using the formula given by W.C. Hamilton, Acta Cryst., 12 (1959) 609.

Crystal structure of $(\eta^5\text{-Cp})\text{VCl}_2(\text{PMe}_3)_2$

The results of the X-ray diffraction study are shown in Tables 4–7 and Figs. 1–3. $(\eta^5\text{-Cp})\text{VCl}_2(\text{PMe}_3)_2$ displays square pyramidal “piano stool” geometry with transoid (“diagonal”) phosphines and transoid chlorines. The planes $\text{VCl}(2)\text{Cl}(3)$ and $\text{VP}(4)\text{P}(5)$ intersect at an angle of 89.7° . The molecule possesses a non-crystallographic mirror plane of symmetry containing V, C(13), Cl(2) and Cl(3). This mirror symmetry extends even to the rotational conformations about the V–P and P–CH₃ bonds. The rotational conformation about the V–P bonds minimizes CH₃–C₅H₅ contacts, which a space-filling model (Figs. 2 and 3) reveals as already short. This conformation also interleaves the Cl and methyl groups to minimize non-bonded repulsions (Fig. 3). This M–P rotational conformation is also adopted in $\text{CpMo}(\text{CO})_2(\text{PMe}_3)_2^+$ [18] and $(\text{C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)_2\text{Cl}(\text{CPh})$ [19]. This figure also makes it clear that coordinatively unsaturated $\text{CpVCl}_2(\text{PMe}_3)_2$ is sterically incapable of binding a third phosphine.

The structure of the complex diagonal- $\text{Cp}^*\text{Ti}(\text{o-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2$ [20] is quite comparable to that of $\text{CpVCl}_2(\text{PMe}_3)_2$; ring centroid–Ti–N and C angles are 118.1 and 114.8° , respectively.

The V–Cl distances in $\text{CpVCl}_2(\text{PMe}_3)_2$ are not significantly different from that (2.390(4) Å) in monomeric Cp_2VCl [21] and also in $(\text{C}_5\text{H}_4\text{Me})_2\text{VCl}_2$ [22] (2.398(2) Å). The distance in VCl_4 [23] (2.138 Å), is dramatically shorter, as is also true of $\text{VCl}_3(\text{NMe}_3)_2$ (2.239(4) Å) [24]. This V–Cl bond shortening correlates roughly with the degree of apparent coordinative unsaturation, presumably being compensated in part by $\text{Cl} \rightarrow \text{V} \pi$ donation [25]. The V–P distances in $\text{CpVCl}_2(\text{PMe}_3)_2$ (2.51 Å), are significantly longer than those in $\text{CpV}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ [26] (2.442 Å) and

TABLE 6
BOND DISTANCES (Å) FOR $\text{CpVCl}_2(\text{PMe}_3)_2$

V(1)–Cl(2)	2.401(1)
V(1)–Cl(3)	2.405(1)
V(1)–P(4)	2.507(1)
V(1)–P(5)	2.510(1)
V(1)–C(12)	2.313(3)
V(1)–C(13)	2.332(3)
V(1)–C(14)	2.310(3)
V(1)–C(15)	2.289(3)
V(1)–C(16)	2.282(3)
P(4)–C(6)	1.817(3)
P(4)–C(7)	1.821(3)
P(4)–C(8)	1.819(3)
P(5)–C(9)	1.823(3)
P(5)–C(10)	1.822(3)
P(5)–C(11)	1.814(3)
C(12)–C(13)	1.403(5)
C(12)–C(16)	1.400(5)
C(13)–C(14)	1.394(5)
C(14)–C(15)	1.407(5)
C(15)–C(16)	1.403(5)
V(1)–M ^a	1.973

^a Center of Cp ring.

TABLE 7
BOND ANGLES FOR $\text{CpVCl}_2(\text{PMe}_3)_2$

Cl(2)-V(1)-Cl(3)	126.1(0)
Cl(2)-V(1)-P(4)	78.7(0)
Cl(2)-V(1)-P(5)	79.3(0)
Cl(3)-V(1)-P(4)	80.3(0)
Cl(3)-V(1)-P(5)	79.7(0)
P(4)-V(1)-P(5)	132.6(0)
M ^a -V(1)-Cl(2)	117.9
M-V(1)-Cl(3)	116.0
M-V(1)-P(4)	113.8
M-V(1)-P(5)	113.6
V(1)-P(4)-C(6)	117.4(1)
V(1)-P(4)-C(7)	116.9(1)
V(1)-P(4)-C(8)	112.9(1)
C(6)-P(4)-C(7)	102.3(2)
C(6)-P(4)-C(8)	102.8(2)
C(7)-P(4)-C(8)	102.4(2)
V(1)-P(5)-C(9)	118.3(1)
V(1)-P(5)-C(10)	115.8(1)
V(1)-P(5)-C(11)	111.9(1)
C(9)-P(5)-C(10)	102.4(2)
C(9)-P(5)-C(11)	103.3(2)
C(10)-P(5)-C(11)	103.3(2)
C(13)-C(12)-C(16)	107.6(3)
C(12)-C(13)-C(14)	108.3(3)
C(13)-C(14)-C(15)	108.3(3)
C(14)-C(15)-C(16)	107.3(3)
C(12)-C(16)-C(15)	108.5(3)

^a Center of Cp ring.

to the diphenylphospino nuclei in $\text{CpVCO}[\text{PPh}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2]$ [27] (2.435 Å). An argument could thus be made for $\text{V} \rightarrow \text{P}$ back bonding in the V^{I} complexes.

Concluding remarks

Complexes CpVCl_2 and CpVBr_2 appear to be unstable, in contrast to CpVI_2 [5]. Disproportionation to Cp_2VX and VX_3 ($\text{X} = \text{Cl}, \text{Br}$) is favored. Stabilization can be achieved with the trialkylphosphine ligands PMe_3 and PEt_3 , but not with THF. The space-filling models of $\text{CpVCl}_2(\text{PMe}_3)_2$ (Figs. 2 and 3) clearly show that stabilization of CpVCl_2 with two sterically more demanding phosphines such as Pcy_3 , PPh_3 or PPh_2Me would probably be difficult, and in fact these complexes were not isolated. Complexes with the bulkier bromide ligands form less readily, as is indicated by the lowered yield relative to the chloride species (Table 1). It is remarkable that a phosphine like PPhMe_2 , with a small cone angle and electronically only slightly different from PMe_3 [28], does not give the desired complex. Also the failure to prepare the lateral complex $\text{CpVCl}_2(\text{DMPE})$ is rather puzzling in view of small steric requirements of the DMPE ligand. It is possible that the intermediate $\text{VCl}_3(\text{DMPE})(\text{THF})$ in some way interferes with the preparation in this case. In this context we mention the successful preparation of the stable mono-halide derivative $\text{CpVCl}(\text{DMPE})$ from reaction of $[\text{CpVCl}(\text{PEt}_3)]_2$ with DMPE [17]. This monomeric

complex could provide an alternate route to the dihalide. The results show that subtle (steric and electronic) effects influence the formation of CpVX_2L_2 .

Experimental

General remarks

All experiments were carried out under nitrogen by using Schlenk or glove box techniques. Solvents (except CH_2Cl_2) were distilled from sodium-potassium melts under nitrogen. $\text{VX}_3(\text{THF})_3$ was prepared from commercially available VCl_3 (Merck) and VBr_3 (Alfa) by continuous extraction with boiling THF. Elemental analyses were performed at the Analytical Department of the Chemical Laboratories of this University. Molecular weights were determined by cryoscopy in benzene. Melting points were determined using a low temperature DTA apparatus; heating rate $2\text{--}3^\circ\text{C}/\text{min}$. Absorption spectra were recorded on a Perkin-Elmer EPS-3T spectrophotometer. IR-spectra were measured on a Jasco-IRA-2 spectrophotometer using Nujol mulls between KBr discs. 200-MHz ^1H NMR spectra were measured by Drs. R.J. Bouma on a Nicolet NT 200 spectrometer equipped with a Nicolet model 1180 data system. Due to the lack of ^1H NMR data on chemical shifts in isostructural diamagnetic complexes, we used the chemical shifts of the free phosphine ligands to determine the isotropic shifts of the phosphine protons in $\text{CpVX}_2(\text{PR}_3)_2$ (Table 3).

Preparation of $\text{VCl}_3(\text{PEt}_3)_2$

To a solution of 7.78 g (20.8 mmol) of $\text{VCl}_3(\text{THF})_3$ in 150 ml of THF, 6.20 ml (42.1 mmol) of PEt_3 was added at room temperature. A dark solution formed rapidly. After stirring for 3 h, the solution was slowly cooled to -80°C . Dark crystals separated and 6.86 g (81% based on vanadium) of crude $\text{VCl}_3(\text{PEt}_3)_2$ was obtained. After recrystallization from pentane dark red crystals of analytically pure $\text{VCl}_3(\text{PEt}_3)_2$ were isolated. Elemental analyses, found (calcd. $\text{C}_{12}\text{H}_{30}\text{Cl}_3\text{P}_2\text{V}$): V, 12.94 (12.94); Cl, 26.94 (27.02); C, 37.08 (36.61); H, 7.73% (7.68%).

Preparation of $\text{VCl}_3(\text{DMPE})(\text{THF})$

DMPE (1.38 g, 9.17 mmol) was added dropwise to a stirred solution of 3.31 g (8.86 mmol) of $\text{VCl}_3(\text{THF})_3$ in 100 ml of THF at room temperature over a 15 min period. The mixture turned green. After stirring for 1 h, the solution was filtered and concentrated to 20 ml. Pentane (100 ml) was slowly added and a green precipitate formed. The solvent was decanted and after three pentane washings, 8.3 mmol (93%) of $\text{VCl}_3(\text{DMPE})(\text{THF})$ was isolated. Elemental analyses, found (calcd. $\text{C}_{10}\text{H}_{24}\text{Cl}_3\text{OP}_2\text{V}$): V, 13.48 (13.42); Cl, 27.86 (28.02); C, 31.82 (31.65); H, 6.42% (6.37%). IR (KBr-Nujol): THF at 1026s and 870vs cm^{-1} ; DMPE at 1410s, 1298m, 1284m, 946vs, 934sh, 745s and 711s cm^{-1} .

Upon reaction of $\text{VCl}_3(\text{DMPE})(\text{THF})$ with half a mole of Cp_2Mg at -78°C in THF and warming to room temperature, a purple solution formed. After removal of the solvent a greenish dark solid was obtained, which was insoluble in pentane. The IR spectrum showed the presence of $\text{VCl}_3(\text{DMPE})(\text{THF})$.

Preparation of $\text{CpVX}_2(\text{PR}_3)_2$ ($X = \text{Cl}, \text{Br}$; $R = \text{Me}, \text{Et}$)

We give here a general procedure for the preparation of $\text{CpVX}_2(\text{PR}_3)_2$ on 100 mmol scale. Reactions on smaller scale are conveniently performed using the same

metal/solvent ratios and reaction conditions. Since isolation of $VX_3(PR_3)_2$ prior to reaction with Cp_2Mg lowers the overall yield of $CpVX_2(PR_3)_2$, due to losses in workup and isolation of the phosphine complex, it is advantageous to use $VX_3(PR_3)_2$ prepared in situ.

Pure PR_3 (200 mmol) was added to a solution of 100 mmol of $VX_3(THF)_3$ in 1200 ml of THF at room temperature. After stirring for 3 h, the resulting dark solution was cooled to $-80^\circ C$ and 50 mmol of Cp_2Mg dissolved in 100 ml of THF was added dropwise in 2 h. On slowly warming the mixture to room temperature a blue solution formed. The mixture was stirred for another two hours at room temperature. The solvent was removed in vacuo. The resulting sticky product was stirred with 200 ml of pentane for 15 min and then evaporated in order to remove all THF. The resulting dry product was carefully powdered and continuously extracted with pentane. The blue pentane extract was slowly cooled to $-25^\circ C$, to crystallize the blue $CpVX_2(PR_3)_2$. For yields and elemental analyses see Table 1.

The Cp' derivatives were prepared by the same procedure as the Cp derivatives by using $Cp'Na$ (dissolved in THF) instead of Cp_2Mg .

Preparation of $CpV(CO)_3(PEt_3)$

A solution of 5.0 mmol of $CpVCl_2(PEt_3)_2$ was stirred with an excess (2.5 g, 38 mmol) of zinc powder in 50 ml of THF under 1 bar of CO for 16 h at room temperature. A yellow solution formed. The solvent was removed in vacuo and the residue extracted with 200 ml of pentane. Crystallization from a concentrated solution yielded 3.5 g (70%) of yellow orange $CpV(CO)_3(PEt_3)$. Analysis, found (calcd. $C_{14}H_{20}O_3PV$): V, 15.75 (16.01); C, 52.98 (52.84) and H, 6.44% (6.33%). IR (KBr-Nujol): $\nu(CO)$ at 1949s, 1870m and 1847vs cm^{-1} . 1H -NMR (benzene- d_6): $\delta(Cp)$ at 4.54 ppm. Alternatively, sublimation can be applied to obtain pure $CpV(CO)_3(PEt_3)$.

Crystallographic study of $CpVCl_2(PMe_3)_2$

Multifaceted deep blue crystals were grown by cooling an ether solution. The highly air-sensitive crystal was mounted at the end of a glass fiber and transferred to the goniostat using inert atmosphere handling techniques [29]. Thereafter, an inert atmosphere was maintained by the gaseous nitrogen cold stream ($-163^\circ C$). A systematic search of a limited hemisphere of reciprocal space revealed diffraction maxima which could be indexed as monoclinic, space group $P2_1/a$. General data collection and reduction methods have been described [29]. Parameters of the data set collected ($6^\circ \leq 2\theta \leq 45^\circ$) are shown in Table 4. The structure was solved by direct methods (MULTAN 78) and Fourier techniques and refined by the full-matrix least-squares method. All hydrogen atoms were located and refined. There is no evidence for disorder in the structure; the final difference Fourier was featureless, the largest peak being 0.31 $e/\text{\AA}^3$. Hydrogen atom coordinates, all anisotropic thermal parameters and structure factors are available [30].

Carbon-hydrogen distances range from 0.85(3) to 1.02(4) Å. Angles H-C-H within methyl groups range from 106 to 115°. Hydrogens of the C_5H_5 ring deviate to both sides of the carbon least-squares plane by less than 0.08 Å.

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