Inorg. Chem. **1985**, *24*, 3003-3006

Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Synthesis and Characterization of $VCl_3(PMePh_2)_2$

RICK L. BANSEMER, JOHN C. HUFFMAN, and KENNETH G. CAULTON*

Received December 6, 1984

The synthesis of $VCl_3(PMePh_2)_2$ proceeds in good yield from $VCl_3(THF)_3$ and the phosphine upon reflux in benzene. The crystalline solid, which contains two independent but nearly identical molecules, is shown by X-ray diffraction to be comprised of trigonal-bipyramidal molecules with axial phosphines. The electronic spectrum is consistent with retention of the trigonal-bipyramidal structure in toluene solution with ligand field transitions arising from a $^3A_2'$ ground state. Solution NMR observations (^1H and ^{31}P) are also consistent with two unpaired electrons, as measured by a solution magnetic susceptibility determination. Crystal data (−160 °C): $a = 13.175$ (6) Å, $b = 17.643$ (10), $c = 11.871$ (6), $\alpha = 91.00$ (3)°, $\beta = 91.78$ (3), $\gamma = 74.00$ (2), $Z = 4$, space group $P\bar{1}$.

Introduction

In contrast to the six-coordination found for V(III) in $VCl_3(THF)_3$,[1] $VCl_2(THF)_4^+$,[2] and probably $VCl_3(Me_2PC_2H_4PMe_2)$-THF,[3] the ligands NMe_3[4] and PR_3 (R = Me, Et, *n*-Pr)[5] have been shown to yield only five-coordinate VCl_3L_2 complexes. The compounds $VCl_3(PR_3)_2$ (R = Me, Et) have been shown to be the reagents of choice for preparation of $CpVCl_2(PR_3)_2$, which in turn lead to $[CpVCl(PR_3)]_2$.[3] At the same time, it has been reported that bulkier phosphines (e.g. $PMePh_2$) do *not* yield adducts upon reaction with $VCl_3(THF)_3$ in THF solvent.[3] Our interest in preparing polyhydride complexes of 3d transition metals[6] has led to the study of the interaction of $VCl_3(THF)_3$ with $PMePh_2$, which is reported here. The resulting $VCl_3(PMePh_2)_2$ should serve as a starting material of general utility.

Experimental Section

General Procedures and Materials. All manipulations were carried out under an atmosphere of prepurified (BASF R-311 for O_2 removal) N_2 or argon gas, with use of solvents vacuum transferred from liquid NaK alloy. Anhydrous VCl_3 was commercial material. Magnetic susceptibility was measured at 22 °C in solution and was corrected for ligand diamagnetism.

Synthesis of $VCl_3(PMePh_2)_2$. To $VCl_3(THF)_3$ (1.50 g, 4.00 mmol) suspended in 15.0 mL of toluene at room temperature is added 3.00 mL (16.0 mmol) of PPh_2Me. Stirring the mixture for 15 min yields a red-purple solution containing an orange solid. This mixture is then refluxed for 3–4 h, whereupon all the orange solid dissolves. This red-purple solution is then filtered hot, and the volume of solvent is reduced to half; 35 mL of dry pentane is added dropwise to yield a red-purple precipitate. This red-purple solid is collected by filtration, washed twice with 5-mL portions of pentane, and recrystallized from 5 mL of toluene by slow addition of 35 mL of pentane. The resulting red-purple, crystalline solid is collected by filtration, washed twice with 5-mL portions of *n*-pentane, and vacuum dried for 3 h. Yield: 1.90 g (85%). Anal. Calcd for $C_{26}H_{26}Cl_3P_2VO{\cdot}4C_5H_{12}$: C, 57.31; H, 5.25; Cl, 18.16; V, 8.70. Found: C, 57.02; H, 5.01; Cl, 17.20; V, 7.70. ^1H NMR (360 MHz, 25 °C, C_6D_6): δ 9.8 (ortho H, $\Delta\nu_{1/2} = 800$ Hz), 8.7 (para H, $\Delta\nu_{1/2} = 60$ Hz), 6.7 (meta H, $\Delta\nu_{1/2} = 110$ Hz), −15.8 (methyl H, $\Delta\nu_{1/2} = 1000$ Hz). UV-vis (toluene) λ_{max}, nm (ϵ): 502 (97), 1360 (24), 1900 (50). IR (Nujol): ν_{V-Cl} 417 cm^{-1}.

Structural Study of $VCl_3(PMePh_2)_2$. A crystal of irregular morphology was selected and transferred to a standard Picker goniostat by using standard inert-atmosphere handling techniques.[7] The diffractometer, of local construction, has been described.[7] The crystal is thermochromic upon cooling to −160 °C.

Table I. Crystal Data for $VCl_3(PMePh_2)_2$

empirical formula	$C_{26}H_{26}Cl_3P_2V$
color	yellow-orange
cryst dimens, mm	0.23 × 0.22 × 0.25
space group	$P\bar{1}$
cell dimens (−160 °C; 30 reflcns)	
a	13.175 (6) Å
b	17.643 (10) Å
c	11.871 (6) Å
α	91.00 (3)°
β	91.78 (3)°
γ	74.00 (2)°
molecules/cell	4
vol, Å^3	2651.13
calcd density, g/cm^3	1.397
wavelength, Å	0.71069
mol wt	557.74
linear abs coeff, cm^{-1}	7.99
no. of unique intensities	6957
no. of unique intensities with $F > 3.00\sigma(F)$	5727
final residuals	
$R(F)$	0.0454
$R_w(F)$	0.0490
goodness of fit for the last cycle	1.016
max Δ/σ for last cycle	0.05

A reciprocal-lattice search revealed no systematic absences or symmetry, indicating a triclinic lattice. Characteristics of the data collected ($6° \leq 2\theta \leq 45°$), with use of graphite-monochromated radiation at −160 °C, are shown in Table I. Tests on the crystal used indicated that no absorption correction was required. The structure was solved (with data where $F > 3\sigma(F)$) by a combination of direct methods (MULTAN78) and Fourier techniques. Statistical tests indicated that the structure is centrosymmetric. All atoms, including hydrogens, were located and refined (isotropic for H; anisotropic for all others). A final difference Fourier was featureless, the largest peak being 0.42 e/Å^3. The data were examined for the effects of extinction, but such a correction was found to be unnecessary.

The results of the structural study are shown in Tables II and III and Figures 1 and 2. Additional data are available as supplementary material. Carbon–hydrogen distances range from 0.81 (5) Å to 1.03 (5) Å.

Powder patterns were recorded with Cu Kα radiation on a Philips Norelco powder camera at 25 °C. Comparison of the powder pattern of bulk material from the synthesis with intensities calculated from the single-crystal study showed no discrepancies up to $2\theta = 30°$.

Results

The reaction of $VCl_3(THF)_3$ with $PMePh_2$ (mole ratio 1:4) in toluene furnishes a high-yield synthesis of a compound of stoichiometry $VCl_3(PMePh_2)_2$. The compound is soluble in aromatic solvents to give deep red-purple solutions that show no detectable ^{31}P NMR signal but that show broadened and isotropically shifted ^1H NMR signals for all hydrogens. Line widths increase systematically for nuclei that are closer to the metal (i.e. Me > ortho > meta > para), and the methyl resonance is dramatically upfield (δ −15.8). The electron-impact mass spectrum shows a very weak peak at *m/e* 553, $(M - 3H)^+$; the strongest peak above mass 380 is a protonated product of coupling of two phosphines, $P_2Ph_3MeC_6H_5^+$, at mass 385. The electronic spectrum in toluene shows three absorptions between 400 and 2000 nm with molar

---

(1) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377.

(2) Folting, K.; Huffman, J. C.; Bansemer, R. L.; Caulton, K. G.; Martin, J. D.; Smith, P. D. *Inorg. Chem.* **1984**, *23*, 4589.

(3) Nieman, J.; Teuben, J. H.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *255*, 193.

(4) Greene, P. T.; Orioli, P. L. *J. Chem. Soc. A* **1969**, 1621.

(5) Issleib, K.; Bohn, G. *Z. Anorg. Allg. Chem.* **1959**, *301*, 188.

(6) Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 6163.

(7) For general sample handling and data collection and processing methods, see: (a) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755. (b) Chisholm, M. H. C.; Folting, K.; Huffman, J. C.; Kirkpatric, C. C. *Inorg. Chem.***1984**, *23*, 1021. The program library includes modification of those of A. C. Larsen and of J. A. Ibers.

0020-1669/85/1324-3003$01.50/0

Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for $VCl_3(PMePh_2)_2$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2		10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
V	3040 (1)	4432.0 (4)	2425 (1)	18	VA	7319 (1)	394.5 (4)	2002 (1)	18
Cl(2)	1514 (1)	5362 (1)	2695 (1)	25	Cl(2)A	7606 (1)	−494 (1)	3398 (1)	23
Cl(3)	4094 (1)	3719 (1)	3781 (1)	26	Cl(3)A	8573 (1)	910 (1)	1356 (1)	29
Cl(4)	3527 (1)	4271 (1)	687 (1)	50	Cl(4)A	5730 (1)	822 (1)	1265 (1)	40
P(5)	2111 (1)	3343 (1)	2446 (1)	17	P(5)A	6935 (1)	1515 (1)	3401 (1)	18
C(6)	2976 (4)	2364 (3)	2173 (4)	23	C(6)A	6419 (4)	2455 (3)	2701 (4)	25
C(7)	949 (3)	3400 (3)	1540 (4)	19	C(7)A	5979 (3)	1522 (2)	4488 (4)	18
C(8)	290 (4)	2920 (3)	1697 (4)	24	C(8)A	5970 (4)	1955 (3)	5471 (4)	25
C(9)	−558 (4)	2945 (3)	982 (4)	27	C(9)A	5241 (4)	1957 (3)	6289 (4)	25
C(10)	−767 (4)	3459 (3)	90 (4)	29	C(10)A	4529 (4)	1521 (3)	6120 (4)	23
C(11)	−124 (4)	3941 (3)	−79 (5)	30	C(11)A	4531 (4)	1093 (3)	5150 (4)	25
C(12)	731 (4)	3914 (3)	645 (4)	24	C(12)A	5253 (3)	1087 (3)	4325 (4)	21
C(13)	1624 (3)	3311 (2)	3854 (3)	17	C(13)A	8099 (3)	1604 (3)	4195 (4)	19
C(14)	2156 (4)	2771 (3)	4652 (4)	23	C(14)A	8540 (4)	2219 (3)	4054 (4)	30
C(15)	1792 (4)	2810 (3)	5752 (4)	25	C(15)A	9442 (5)	2246 (3)	4665 (5)	39
C(16)	909 (4)	3397 (3)	6048 (4)	26	C(16)A	9912 (4)	1660 (3)	5410 (5)	33
C(17)	371 (4)	3940 (3)	5264 (4)	26	C(17)A	9499 (4)	1040 (3)	5540 (5)	31
C(18)	724 (4)	3903 (3)	4173 (4)	22	C(18)A	8595 (4)	1014 (3)	4942 (4)	28
P(19)	3925 (1)	5502 (1)	2898 (1)	20	P(19)A	7978 (1)	−750 (1)	660 (1)	18
C(20)	3694 (4)	5789 (3)	4372 (4)	27	C(20)A	9377 (4)	−1179 (3)	933 (4)	27
C(21)	5351 (4)	5259 (3)	2756 (4)	23	C(21)A	7825 (4)	−555 (3)	−850 (4)	20
C(22)	5866 (4)	4616 (3)	2113 (5)	39	C(22)A	6825 (4)	−197 (3)	−1298 (4)	27
C(23)	6943 (5)	4422 (4)	1993 (6)	47	C(23)A	6669 (4)	−67 (3)	−2443 (4)	34
C(24)	7521 (5)	4856 (4)	2533 (6)	47	C(24)A	7506 (5)	−286 (4)	−3154 (5)	40
C(25)	7031 (4)	5497 (4)	3180 (5)	39	C(25)A	8488 (5)	−623 (4)	−2719 (5)	41
C(26)	5957 (4)	5701 (3)	3286 (5)	30	C(26)A	8667 (4)	−763 (3)	−1574 (4)	30
C(27)	3449 (4)	6428 (3)	2127 (4)	24	C(27)A	7362 (4)	−1543 (3)	850 (3)	21
C(28)	2630 (4)	7042 (3)	2525 (5)	33	C(28)A	7931 (4)	−2318 (3)	1064 (4)	26
C(29)	2300 (5)	7743 (4)	1925 (6)	47	C(29)A	7417 (5)	−2893 (3)	1222 (4)	33
C(30)	2765 (6)	7820 (4)	946 (6)	52	C(30)A	6341 (5)	−2697 (3)	1164 (4)	33
C(31)	3562 (6)	7206 (4)	531 (5)	48	C(31)A	5758 (4)	−1941 (3)	952 (4)	32
C(32)	3902 (5)	6513 (4)	1115 (4)	34	C(32)A	6271 (4)	−1365 (3)	815 (4)	26

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

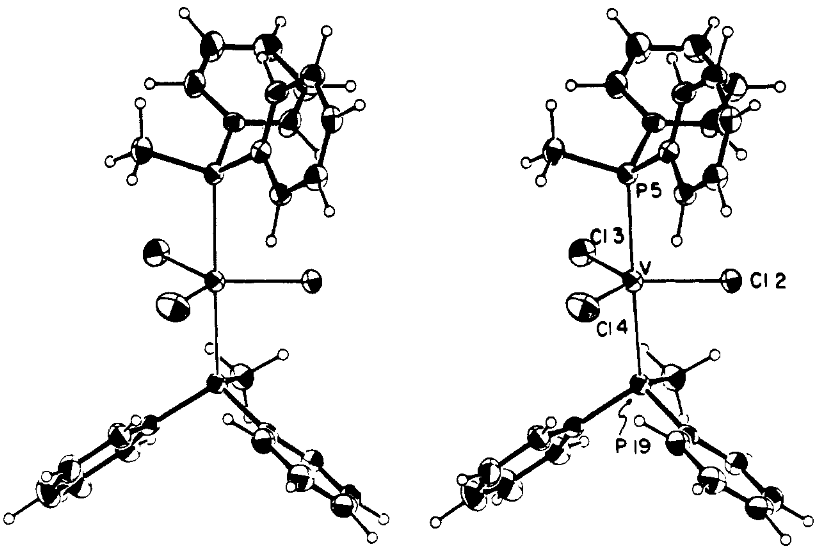


Figure 1. Stereo ORTEP drawing of $VCl_3(PMePh_2)_2$ (molecule A; see tables), showing atom labeling.

absorptivities characteristic of d-to-d transitions. These transitions may be interpreted in terms of the ligand field diagram for high-spin D_{3h} VCl_3L_2 species.[8] The magnetic moment of a 0.0404 M solution in benzene (Evans method) is 2.78 μ_B consistent with two unpaired electrons and retention of the vanadium oxidation state +3 in spite of the presence of excess reducing agent (phosphine) in the synthesis. The infrared spectrum above 500 cm^{-1} shows only intraligand (phosphine) vibrations.

The crystallograhic study shows the unit cell to contain equal amounts of two crystallographically independent $VCl_3(PMePh_2)_2$ molecules. Neither has any rigorous (crystallographic) symmetry element, but the two have essentially identical $VCl_3(PC_3)_2$ frameworks and each approximates a trigonal bipyramid (Figure 1). The similarity of the two independent molecules even extends to the rotational conformation about the V–P bonds: the PC_3 groupings are systematically staggered with respect to the VCl_3 group. Moreover, the relative orientation of the two $PMePh_2$ groups within a given molecule is such that the V–Cl(3) bond is a C_2 symmetry axis for the entire $VCl_3(PC_3)_2$ unit. The four independent V–P distances are within 8σ (difference) of their average value, a scatter we feel is without chemical significance. The VCl_3 units are planar within experimental error, but they *lack* threefold symmetry, the V–Cl(4) distances 2.1753 Å mean value) being 30σ (difference) shorter than the average of the other four (identical) values (2.2505 Å mean value). Note that this asymmetry exists in both independent molecules. Consistent with this distortion is the fact that the Cl–V–Cl angle trans to Cl(4) (av-

---

[8] Wood, J. S. *Prog. Inorg. Chem.* **1972**, *16*, 227.

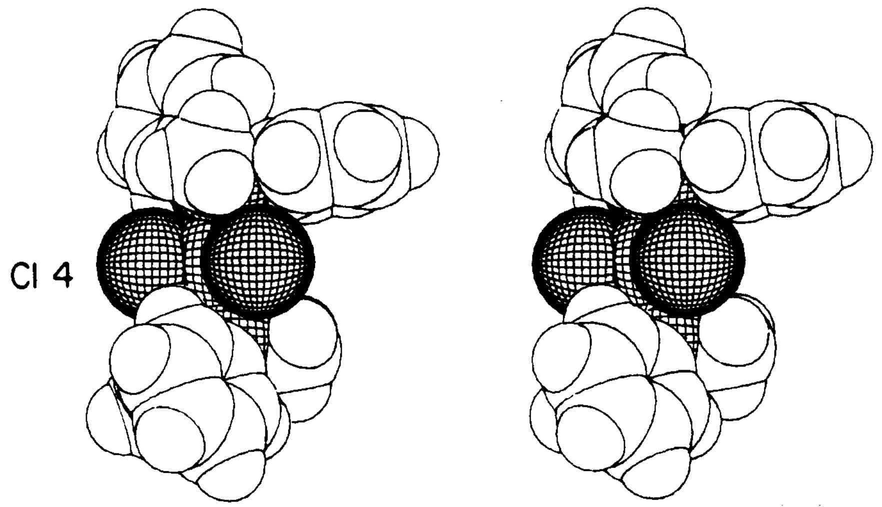


Figure 2. Stereo space-filling drawing, viewed perpendicular to the P–V–P axis, showing the limited space available trans to Cl(4), thus preventing coordination of a third phosphine.

erage value 124.8°) is larger than the angles adjacent to Cl(4) (117.6°). Also consistent with the reality[9] of this distortion is the nature of the P–V–P bending. The P–V–P angles are 166.6° and (molecule A) 171.9°, with the bend tending to move the phosphorus atoms toward the wider Cl(2)–V–Cl(3) angle. Since this distortion of the VCl_3 unit is not symmetric about the V–Cl(3) vector (the molecular C_2 symmetry axis including the phosphine substituents), we conclude that the VCl_3-unit distortion does not originate from the orientation of phenyl and methyl groups (i.e. from intramolecular steric factors). Moreover, since these reductions in symmetry are identical in both independent molecules of $VCl_3(PMePh_2)_2$, we conclude that they do not originate in specific (i.e. single atom) intermolecular packing effects but perhaps are due more generally to forces bending the two large $PMePh_2$ groups slightly off collinearity; the loss of threefold symmetry in the VCl_3 plane is thus viewed as a response to torques working on the $V(PMePh_2)_2$ unit.[10] The occurrence of "unexpected" distortions in trigonal-bipyramidal complexes has been reviewed[11] and seems to correlate with the bulk of the axial ligands. More fundamentally, the soft potential-energy surface in coordination number 5 of course allows distortions at minimal energy expenditure, so even weak packing forces become manifest for five-coordinate species.

Table III. Selected Bond Distances (Å) and Angles (deg) for $VCl_3(PMePh_2)_2$

V–Cl(2)	2.2448 (18)	2.2515 (18)[a]
V–Cl(3)	2.2524 (18)	2.2534 (16)[a]
V–Cl(4)	2.1700 (21)	2.1806 (19)[a]
V–P(5)	2.5470 (18)	2.5113 (19)[a]
V–P(19)	2.5248 (18)	2.5250 (19)[a]
Cl(2)–V–Cl(3)	125.92 (6)	123.66 (6)[a]
Cl(2)–V–Cl(4)	114.81 (8)	118.88 (7)[a]
Cl(2)–V–P(5)	91.47 (6)	91.22 (7)[a]
Cl(2)–V–P(19)	85.83 (7)	87.44 (7)[a]
Cl(3)–V–Cl(4)	119.23 (8)	117.42 (7)[a]
Cl(3)–V–P(5)	84.39 (6)	86.31 (6)[a]
Cl(3)–V–P(19)	86.54 (6)	87.76 (6)[a]
Cl(4)–V–P(5)	97.11 (6)	90.48 (6)[a]
Cl(4)–V–P(19)	95.97 (6)	97.20 (6)[a]
P(5)–V–P(19)	166.56 (5)	171.86 (5)[a]

[a] Molecule "A".

Numerous attempts on several preparations failed to give analytical data for V, C, H, or Cl that agree satisfactorily with the composition $VCl_3(PMePh_2)_2$ found in the unit cell. Carbon and hydrogen were consistently observed high, while V and Cl were low. When it was recognized that ^1H NMR spectra displayed resonances of *n*-pentane, we evaluated the influence of lattice inclusion of this molecule in solid samples. Samples subjected to vacuum at 25 °C for 12 h gave satisfactory analytical compliance to the average composition $VCl_3(PMePh_2)_2 0.4 C_5H_{12}$. Apparently the crystal selected for the single-crsytal X-ray work contained a negligible amount of this volatile lattice guest. To confirm the homogeneity of the bulk sample of $VCl_3(PMePh_2)_2$ produced, we have recorded its X-ray powder pattern and established that the single-crystal lattice and positional parameters account for all lines in the powder pattern. The small and nonstoichiometric amount of included *n*-pentane thus confuses the analytical data, but the powder data ensure that the single-crystal study was indeed carried out on material representative of the bulk sample.

Discussion

$VCl_3(PMePh_2)_2$ is a molecule that appears (by electronic spectroscopy) to retain its trigonal-bipyramidal structure when dissolved in aromatic solvents. This exemplifies the typical difference between coordination number for 3d vs. 4d or 5d analogues: the PMe_2Ph complex of $NbCl_3$ is the diamagnetic dimer $[NbCl_3(PMe_2Ph)_2]_2$.[12] However, on dissolution in THF, the color of $VCl_3(PMePh_2)_2$ is not the deep red-purple observed in toluene but orange; the visible–UV spectrum of the latter solution resembles that of *mer*-$VCl_3(THF)_3$. This therefore explains the previous negative results for the reaction of $VCl_3(THF)_3$ with $PMePh_2$ in THF. While no ^{31}P NMR spectrum is detectable for a toluene solution of $VCl_3(PMePh_2)_2$ (short ^{31}P relaxation times due to paramagnetic V(III)), the observation of a sharp ^{31}P signal

---

(9) Cl(4) in both molecules has significantly larger equivalent isotropic thermal parameters (4.0–5.0 $Å^2$) than do Cl(2) and Cl(3) (2.3–2.9 $Å^2$). Given this indication of *possible* inadequacy of the refinement model chosen, we want to emphasize other features of the structure (e.g. Cl(2)–V–Cl(3) and P–V–P angles) that are consistent with the idea that the V–Cl(4) distance is *in reality* shorter than the other two V–Cl distances.

(10) (a) We have carefully evalauted the possibility that the observed V–Cl bond shortening could originate in an impurity of $VOCl_2(PMePh_2)_2$. An examination of a difference Fourier calculated by deleting Cl(4) and Cl(4)A shows no evidence of elongation of the ligand electron density along the line toward vanadium, as would be anticipated (a typical VO distance would be 1.6 Å). Moreover, the infrared spectrum of the batch of crystals from which the X-ray specimen was selected shows no absorption in the region 900–1100 cm^{-1}, typical of $\nu(VO)$ in $VOCl_2(NMe_3)_2$.[10b] Finally, no $VOCl_2(PMePh_2)_2$ peak is seen in the mass spectrum. It is equally improbable, on the basis of the above mentioned difference Fourier, that V–Cl(4) is artifactually short in consequence of Cl(4) disorder. To account for apparent shortening to 2.17 Å, the disordered chlorine positions would have to be 1.16 Å apart, and nothing resembling this is evident in the difference map. (b) Drake, J. E.; Vekris, J.; Wood, J. S. *J. Chem. Soc. A* **1968**, 1000. This work indicates that $VOCl_2L_2$ compounds should have a band at approximately 14 000 cm^{-1}. This region is a featureless minimum in the spectra recorded for our samples of $VCl_3(PMePh_2)_2$.

(11) Daran, J.-C.; Jeannin, Y.; Martin, L. M. *Inorg. Chem.* **1980**, *19*, 2935.

(12) Hubert-Pfalzgraf, L.; Riess, J. *Inorg. Chim. Acta* **1978**, *29*, L251.

for added $PMePh_2$ suggests that exchange of free and coordinated phosphine is slow on the NMR time scale. This contrasts with the situation for *mer*-$VCl_3(CN\text{-}t\text{-}Bu)_3$[13] exchanging with CN-*t*-Bu. Indeed the finding here (and for $VCl_3(NMe_3)_2$) of five-coordination, while octahedral six-coordination is found for ligands THF and CN-*t*-Bu, indicates that steric factors are dominant in determining both thermodynamics and kinetics of VCl_3L_n complexes (see Figure 2). Note also that PEt_3 gives only a five-coordinate complex.[5] For comparison, the sum of van der Waals radii of P and Cl is 3.7 Å, while $VCl_3(PMePh_2)_2$ has Cl–P separations of 3.4 Å.

The curious adoption of a C_{2v} structure, rather than D_{3h}, by both independent molecules of $VCl_3(PMePh_2)_2$ remains unexplained. $VCl_3(NMe_3)_2$ exhibits neither inequivalent V–Cl bond lengths (2.241 (4) (twice) and 2.236 (5) Å) nor bending of the N–V–N axis (179.0 (5)°).[4] The C_{2v} structure cannot originate in a Jahn–Teller effect, since the ground state of a D_{3h} structure should be nondegenerate ($^3A_2'$). In any event, the good agreement between the electronic spectrum of $VCl_3(PMePh_2)_2$ in toluene and the theoretical model[8] (as well as the observed spectrum of $VCl_3(NMe_3)_2$[8]) suggests that the phosphine complex shows no significant symmetry reduction *in solution*. Moreover, the detection of two unpaired electrons in benzene solutions of $VCl_3(PMePh_2)_2$ confirms that there is no splitting of the $(e'')^2$ electronic configuration sufficient to yield the diamagnetism that would characterize a low-spin C_{2v} molecule.

The V–Cl distances in $VCl_3(PMePh_2)_2$ are 0.15–0.20 Å shorter than those in $CpVCl_2(PMe_3)_2$ and $(CpVClPEt_3)_2$,[3] evidence for chlorine π donation into the half-occupied e″ (d_{xz}, d_{yz}; *z* axis along the P–V–P line) orbitals of the trichloride. The V–P distances are essentially the same in all three compounds.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank the Stauffer Chemical Co. for material support, Scott Horn for skilled technical assistance, and Jan Teuben for assistance with analytical problems.

Supplementary Material Available: Listings of hydrogen positional and isotropic thermal parameters, anisotropic thermal parameters, and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

---

[13] Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 379.

Contribution from the Department of Chemistry,
The University of Michigan, Ann Arbor, Michigan 48109

Molybdenum(IV) Cyclopentadienyl Phosphine Halide Complexes

KNUT STÄRKER and M. DAVID CURTIS*

Received February 4, 1985

Slow addition of a solution of $CpMo(CO)_3Cl$ ($Cp = \eta^5\text{-}C_5H_5$) to $Ph_2PCH_2CH_2PPh_2$ (dppe) in boiling toluene gives CpMo(dppe)(CO)Cl (**2**) as red crystals in 85% yield. Oxidation of **2** with Cl_2 or Br_2 at 0 °C results in the formation of the formally eight-coordinate complexes $CpMo(dppe)X_2Cl$ (X = Cl (**4**), Br (**5**), respectively). The solid-state structure of **4** shows the molecule adopts a pseudooctahedral structure (counting Cp as occupying one coordination site) with *mer*-Cl_3 groups and one P atom trans to the Cp centroid. ^1H and ^{31}P NMR and conductivity studies show that, in solution, this isomer is in equilibrium with the *fac* isomer (**4a**) and with an ionic form, $[CpMo(dppe)Cl_2]Cl$ (**4c**), formed by dissociation of one chloride ligand. The structure of **4** was obtained on a solvate, **4**$\cdot CH_2Cl_2$: triclinic, $P\bar{1}$, $Z = 4$ with cell constants a, b, c (Å) = 12.329 (2), 15.778 (4), 17.448 (4), α, β, γ (deg) = 91.59 (2), 99.89 (2), 101.14 (2), and $V = 3274$ (1) Å^3. The structure was solved by direct methods and Fourier syntheses to agreement indices $R_1 = 0.052$ and $R_2 = 0.059$ on 4963 reflections with $I > 3\sigma(I)$. Some relevant molecular dimensions are as follows: Mo–C(Cp) = 2.32 (6) Å; Mo–Cl = 2.456 (2), 2.481 (3), 2.491 (3) Å; Mo–P(1)(ax) = 2.688 [4] Å; Mo–P(2)(eq) = 2.521 [2] Å; P(1)–Mo–Cl = 70.6 [2]–77.7 [1]°; P(1)–Mo–P(2) = 77.2 [1]°.

Introduction

The trihalides $CpMo(LL)X_3$ are potentially useful starting materials for the synthesis of alkyl and hydride complexes of Mo(IV). These complexes may show unusual behavior. For example, $CpMo(dmpe)H_3$ (dmpe = 1,2-bis(dimethylphosphino)ethane) has been reported to show photoinduced catalysis of H/D exchange with various aliphatic and aromatic hydrocarbons.[1] However, existing syntheses of $CpMo(LL)X_3$ complexes either have inconvenient precursors or suffer from the formation of mixtures and low yields of the desired products (see Discussion).

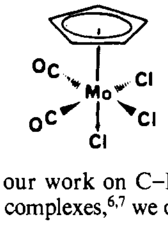
Furthermore, little is known about the stereochemistry and solution behavior of these compounds. Green et al.[2,3] have shown that the trihydrides of the type $CpMo(PP)H_3$ exhibited a 1:2:1 triplet for the ^1H NMR signal, which suggests the compounds undergo a fluxional process in solution wherein the respective magnetic environments of the two phosphorus donors and the three hydrides are equalized.

The dicarbonyl–trihalogeno derivatives $CpMo(CO)_2X_3$ (X = Cl, Br, I), which are available as air-sensitive brown solids from oxidation of $Cp_2Mo_2(CO)_6$ (eq 1) or $CpMo(CO)_3X$ (eq 2), have been described previously:[4,5]

$$[CpMo(CO)_3]_2 + 3X_2 \rightarrow 2CpMo(CO)_2X_3 \qquad (1)$$

$$CpMo(CO)_3X + X_2 \rightarrow CpMo(CO)_2X_3 + CO \qquad (2)$$

A pseudooctahedral structure with the two neutral ligands in the equatorial positions was suggested by Green et al.:[5]



In connection with our work on C–H activation with (organosilyl)transition-metal complexes,[6,7] we desired to investigate some

---

[1] Grebenik, P. D.; Green, M. L. H.; Izquierdo, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1986.

[2] Aviles, T.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1367.

[3] Adams, G. S. B.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1981**, 353.

[4] Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1966**, 1606.

[5] Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. A* **1967**, 686.

[6] Gustavson, W. A.; Epstein, P. S.; Curtis, M. D. *Organometallics* **1982**, *1*, 884.

0020-1669/85/1324-3006$01.50/0