EPR and Crystallographic Studies of Some Reaction Products of VCl_4, $NbCl_4$, and $TaCl_4$ with Trialkyl- and Triarylphosphines

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Solutions containing, or at least made from, the MCl_4 (M = V, Nb, Ta) compounds and alkyl phosphines have been studied. It is concluded that no $VCl_4(PR_3)_2$ species survive, the main reactions being to give various V^{III} species, such as $[VCl_4(PR_3)_2]^-$ accompanied by varying amounts of $VOCl_2(PR_3)_2$ species which are responsible for the observed EPR spectra. When the *trans*-$MCl_4(PEt_3)_2$ molecules are introduced and the solutions are scrupulously protected from laboratory air, little or no EPR intensity can be recorded. The complexes $VOCl_2(PPh_3)_2$ and $[HPMe_2Ph][VCl_4(PMe_2Ph)(OPMe_2Ph)]$ have been structurally characterized: $VOCl_2(PPh_3)_2$ forms monoclinic crystals in space group *C*2/*c* (No. 15) with $a = 24.691(4)$ Å, $b = 9.518(1)$ Å, $c = 15.690(2)$ Å, $\beta = 117.19(1)°$, $V = 3280(1)$ Å^3, $Z = 4$ and $[HPMe_2Ph][VCl_4(PMe_2Ph)(OPMe_2Ph)]$ forms orthorhombic crystals in space group *Pbca* (No. 61) with $a = 17.262(11)$ Å, $b = 28.967(8)$ Å, $c = 12.056(7)$ Å, $V = 6028(5)$ Å^3, $Z = 8$.

Introduction

The study of phosphine complexes of transition metal halides is a large and important area and includes a diversity of products depending on the oxidation state of the metal and its position in the periodic table. Toward the right side, and increasingly so with lower oxidation state, there is considerable π-character to the P−M bonds as a result of back-donation from metal $d\pi$ orbitals to the $p\pi$ orbitals of the phosphorus atom. At the extreme left side (i.e., in groups 4 and 5) and with oxidation states of III and IV, the P → M bonds tend to be relatively long, weak, and labile, and they have little if any π character. Nevertheless, phosphine adducts of the halides of the early transition metals are quite numerous and have been extensively studied.

The chemistry and structures of these phosphine compounds of the early transition metals are often much more complicated than might be expected, owing to two characteristic properties of the early transition metal atoms: (1) a tendency to have coordination numbers greater than 6, and (2) their oxophilicity. In this report, we focus on some of the consequences of the second characteristic property, namely, the tendency of these elements, especially vanadium, to form M^{IV}=O species, which have one unpaired electron and give readily observable EPR (electron paramagnetic resonance) spectra.

The EPR technique has already been employed as a tool in obtaining structural and electronic structural information about compounds with the formula MCl_4L_2 (M = V, Nb, Ta),[1−5] with the ligands, L, being not only phosphines but others. In most cases, axial spectra were observed and the structures were therefore postulated to be of trans geometry.

Adducts of VCl_4 with oxygen-, nitrogen-, phosphorus-, and arsenic-donor ligands have been thoroughly studied by the EPR method by Samuel and his co-workers.[1−3] All the EPR spectra were observed both at room temperature and at low temperatures. They displayed both axial symmetry and well-resolved superhyperfine splitting caused by the phosphine or arsine ligands. This led to the conclusion that those compounds have the general formula of *trans*-VCl_4L_2, that is, they have octahedral geometry with the donor ligands in axial trans positions. The unpaired electron was assumed to reside in a nondegenerate d_{xy} orbital in order to account for the appearance of the spectra at room temperature. The possibility of the degenerate d_{xz}, d_{yz} orbitals being the lowest orbitals was evidently excluded since that would be expected to cause such short relaxation times that the signals would not have been seen at room temperature. Table 1 lists the neutral ligand adducts of VCl_4 that were previously studied by EPR.

EPR studies of $NbCl_4$ and $TaCl_4$ with phosphines and other neutral ligands have also been carried out by Samuel and co-workers[1,2] and by Bereman and co-workers.[4,5] Again, as in the VCl_4 cases, all the compounds with oxygen- and nitrogen-donor ligands ($NbCl_4$) and with phosphorus-donor ligands ($NbCl_4$ and $TaCl_4$) showed axial EPR signals, and in all cases room temperature spectra were obtained. The same conclusion was drawn, namely, that all the compounds have the formula of MCl_4L_2 with the two L ligands trans to each other, and again the unpaired electron was assigned to the nondegenerate d_{xy} orbital. Scheme 1 illustrates the proposed structure and the assumed d-orbital arrangement for these compounds.

Compounds of this type have also been studied by other methods, such as IR, UV−vis, and magnetic susceptibility measurements as well as by X-ray crystallography. The structural conclusion drawn from the EPR experiments is in accord with the crystal structures of *trans*-$NbCl_4(PEt_3)_2$ and *trans*-$TaCl_4(PEt_3)_2$.[6,7] In other cases, however, the conclusions drawn from EPR do not agree with the proposed structures based on IR results. Moreover, X-ray structure determinations provided evidence for a cis arrangement of ligands in *cis*-$TaCl_4(PMe_2Ph)_2$,[7] *cis*-$NbBr_4(MeCN)_2$·MeCN,[8] and *cis*-$NbCl_4$-

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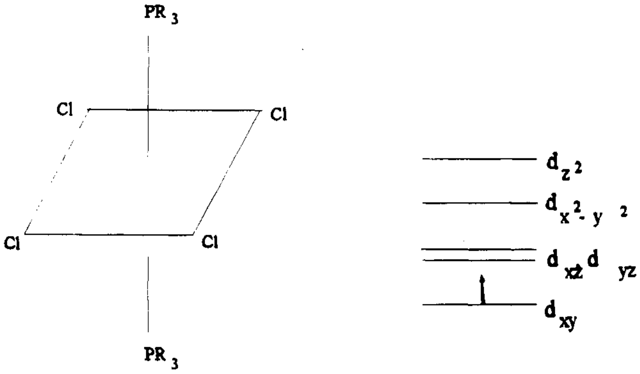
Table 1. "$VCl_4 \cdot 2L$" Compounds Studied by EPR

ligands (L)	comments	ref
PR_3 (R_3 = Me_3, Et_3, $MePh_2$, $EtPh_2$, Ph_3, Pr_3, Bu_3, Cy_3, $Ph(OEt)_2$)	trans geometry, well resolved phosphorus triplet superhyperfine	1, 3
$P(OEt)_3$, PBu_2Cl	trans geometry, superhyperfine not resolved	3
$AsMe_3$	trans isomer, resolved arsenic superhyperfine	3
py, 3-Etpy, 4-Bupy, NMe_3	trans isomer, no nitrogen superhyperfine	3
THF, Diox, PhCOPh	trans isomer	3

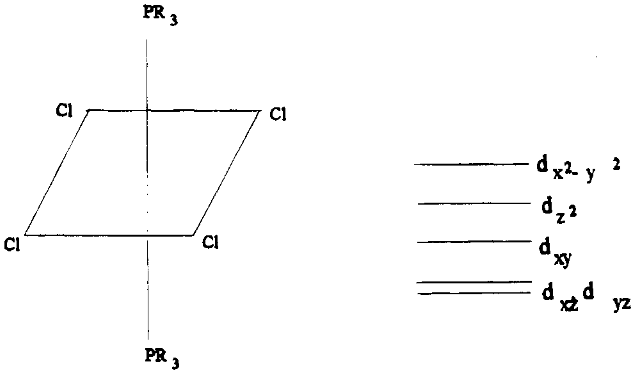
Table 2. Adducts of $NbCl_4$ and $TaCl_4$ Studied by EPR and Other Methods

compounds	comments	ref
$NbCl_4(PR_3)_2$ (R_3 = Et_3, n-Bu_3, i-Bu_3, $EtPh_2$)	trans symmetry, EPR data and X-ray structure	1, 6
	trans, EPR data	2
	trans, X-ray structure	6
$Nb_2Cl_8(PR_3)_4$ (R_3 = Me_3, Me_2Ph)	dimer, X-ray structure	6, 10
$TaCl_4(PEt_3)_2$	trans, EPR data and X-ray structure	1, 7
$TaCl_4(PMe_3)_3$	seven-coordinate, X-ray structure	7
$NbF_4(py)_2$	trans, IR and Raman	11
$NbCl_4(py)_2$	EPR data (trans), IR (uncertain)	5, 12
$NbCl_4(Rpy)_2$ (R = Me, Et, NH_2, Br, Ph)	trans, EPR data	5
$NbCl_4(CH_3CN)_2$	cis, IR and X-ray structure	9, 12
$NbCl_4L_2$ (L = THF, DIO, DFM, DME, HMPA, DMA, DEF)	EPR data (trans), IR (cis)	4,12
	EPR data (trans)	4

Scheme 1



Scheme 2



$(MeCN)_2$[9] and for seven coordination in $TaCl_4(PMe_3)_3$.[7] Table 2 lists the adducts of $NbCl_4$ and $TaCl_4$ studied by EPR and other methods.

Besides the disagreement on some geometries of MCl_4L_2 as determined by EPR and other methods, there also exists a conflict concerning the oxidation state for the phosphine adducts of VCl_4 as detected by EPR and by magnetic susceptibility measurements. Early research on some complexes of VCl_4 had revealed that reduction occurs when VCl_4 is reacted with sulfur, phosphorus, and arsenic ligands, with V(III) compounds being formed.[13] This raises a question as to the identity of the species giving the EPR signals in the vanadium case.

Still another issue, and perhaps the most intriguing one, is the electronic structure of these compounds. According to the proposed explanation of the EPR results, the nondegenerate d_{xy} orbital is the lowest in energy in this distorted octahedral geometry and the unpaired electron therefore resides in this orbital. However, every theoretical approach from simple ligand field theory, or Huckel theory,[14] to fairly rigorous MO theory,[15] leads to the conclusion that this elongated octahedral type complex should have the d_{xz}, d_{yz} orbitals lower in energy than the d_{xy} orbital. The electron should therefore occupy the degenerate E_g (d_{xz}, d_{yz}) orbitals, as shown in Scheme 2. But this energy ordering cannot explain why room temperature spectra are seen. Since the orbital degeneracy would cause a very quick relaxation at room temperature, the spectrum would be too broad to observe according to the Uncertainty Principle $\Delta t\Delta\nu \sim {}^{1}/_{2\pi}$ which requires that the spectrum width be inversely proportional to relaxation time.

These inconsistencies led us to conduct further investigations of the electronic structure of these systems. From a theoretical point of view,[14] it is important that while a rather thorough ab initio calculation[15] correctly predicted the geometry of the molecule, the g values from this calculation were far from the experimental ones. This lead to the conclusion that the reported EPR signals could not be due to $NbCl_4(PR_3)_2$ complexes. Clearly more experimental work was called for.

In an earlier report,[16] we presented results showing that trialkylphosphines reduce VCl_4 to V^{III} in various forms, a finding in accord with at least one earlier publication.[12] This led us to consider seriously the possibility that earlier reports of VCl_4L_2 EPR spectra might actually be due to hydrolysis products of the type $VOCl_2(PR_3)_2$. While there are no reports of the structures of such species, there are two reports concerning the

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structures of analogous amine complexes, VOCl$_2$(NMe$_3$)$_2$[17] and VOCl$_2$(2-Etpy)$_2$·H$_2$O.[18]

In this paper we report further studies of the vanadium as well as the niobium and tantalum solutions that are obtained by reactions of halides and oxohalides of these elements with phosphines. A principal feature of this work is that EPR spectra were not only recorded (if observable) but quantitated by comparison to an intensity standard. We have also obtained the crystal structures of VOCl$_2$(PPh$_3$)$_2$ and [HPMe$_3$][VCl$_4$(PMe$_2$Ph)(OPMe$_2$Ph)].

Experimental Section

All operations were carried out under an atmosphere of dry argon or dry nitrogen. All of the compounds studied are very sensitive to air and/or moisture. Both vacuum-line and glovebox techniques were used. VOCl$_3$, VCl$_3$(THF)$_3$, phosphines, NbCl$_5$, TaCl$_5$, NbCl$_4$(THF)$_2$, and granular aluminum were purchased from Aldrich Chemical Co. and used as received. [HPEt$_3$][VCl$_4$(PEt$_3$)$_2$], NbCl$_4$(PEt$_3$)$_2$, and TaCl$_4$(PEt$_3$)$_2$ were made by literature methods[6,7,16] and the crystals were checked by unit cell to confirm their identity. NbOCl$_3$ was synthesized according to a literature method[19] and the powder diffraction pattern checked before use. VOCl$_3$ was diluted in toluene to make a 1 M solution.

The EPR system consisted of an X-band Bruker ESP 300 spectrometer, an Oxford instruments ER910A cryostat, an HP5352B frequency counter and a Bruker ER035M NMR gaussmeter. The intensity standard for EPR calibration was a 1 mM Cu-EDTA aqueous solution.

Simulations of EPR spectra ($S = {}^1/_2$ and $S = 1$) for the vanadium system were performed in Dr. Jørgen Glerup's group at the University of Copenhagen.

EPR Experiment on [HPEt$_3$][VCl$_4$(PEt$_3$)$_2$]. The EPR spectra recorded for a solution of this compound in dichloromethane (it will not redissolve in toluene) at both room temperature and 130 K were essentially the same as those reported before for the reaction solution of VCl$_4$ and PEt$_3$ in toluene.[1,3] Calibration at 130 K showed only 1.0% of the vanadium present gave rise to the spectrum.

EPR on Reaction Solutions of VCl$_4$ with PEt$_3$ and PBu$_3$. A literature method[3] was used to react VCl$_4$ with each phosphine in toluene, and EPR spectra were taken on the orange-colored reaction solutions at both room and low temperature (130 K). Calibration showed that in each case less than 5% of the total vanadium contributed to the signals.

EPR on Reaction Solution of VOCl$_2$(OPPh$_3$)$_2$ and PEt$_3$. While VOCl$_2$(OPPh$_3$)$_2$ is a known compound,[19] it was prepared differently from the literature[20] method. A mixture of 1.0 g of VCl$_3$(THF)$_3$ and 1.32 g PPh$_3$ was placed in a 100 mL flask and 30 mL of CH$_2$Cl$_2$ was added. The mixture was stirred overnight to yield a purple solution. Air was bubbled in for 2 h with no observable change, but a few drops of water changed the color of the solution to green immediately. Approximately 5 mL of water was added, and a bluish green suspension was formed. The reaction mixture was pumped dry and the solid extracted with 30 mL of CH$_2$Cl$_2$. Solvent was removed from the filtered CH$_2$Cl$_2$ solution under vacuum, and the residue was recrystallized from CH$_2$Cl$_2$. A unit cell check proved the product to be VOCl$_2$(OPPh$_3$)$_2$. It was treated with PEt$_3$ in toluene, and EPR spectra were taken at both room temperature and at 130 K. Essentially all the vanadium contributed to the intensity in the spectra.

EPR on Reaction Solution of PEt$_3$ with NbCl$_4$(THF)$_2$. A commercial sample of NbCl$_4$(THF)$_2$ was reacted with PEt$_3$ in toluene to give a deep yellow-brown solution. EPR signals like those reported[1] were present both at room temperature and at 130 K. The solution was allowed to stay overnight in the flask, and the color changed to deep blue.

EPR on Solutions of NbCl$_4$(PEt$_3$)$_2$ and TaCl$_4$(PEt$_3$)$_2$. Deep red crystals of NbCl$_4$(PEt$_3$)$_2$ and TaCl$_4$(PEt$_3$)$_2$ were dissolved in toluene to give yellow and greenish-yellow solutions, respectively. Spectra were recorded at both room and low temperature. The NbCl$_4$(PEt$_3$)$_2$ solution showed spectra like those reported[1] but calibrations revealed that only 0.5−2.2% of the metal contributed to the spectra. The spectra of TaCl$_4$(PEt$_3$)$_2$ solutions were featureless.

EPR on Reaction Solution of NbOCl$_3$ with PEt$_3$ and Na/Hg. To a suspension of 0.201 g of NbOCl$_3$ in 20 mL of toluene, 0.35 mL of PEt$_3$ was added. After being stirred for about half an hour, the solution was clear and light yellow in color. Then 0.8 mL of 1 M sodium in mercury was transferred to this solution. Under prolonged stirring, the color of the solution changed to yellow-brown and finally to deep blue. The EPR spectrum of the fresh solution showed very strong signals and the pattern was the same as those reported for "NbCl$_4$(PEt$_3$)$_2$" at both room and low temperature.

Reaction of VOCl$_3$ with PEt$_3$. A mixture of 10 mL of toluene and 5 mL of hexanes was added as a layer on top of a VOCl$_3$ solution (1 mL, 1 M in toluene) in a Schlenk tube. Another 15 mL of hexanes was then added carefully. Finally, 0.29 mL (2 mmol) of PEt$_3$ was layered on the very top. In about a week, orange crystals of [HPEt$_3$][VCl$_4$(PEt$_3$)$_2$] formed on the wall and bottom of the tube. The formation of a small amount of white precipitate was also observed. The unit cell of an orange crystal was identical to the one reported.[16]

Reaction of VOCl$_3$ with PMe$_2$Ph. The literature method[21] was used. Toluene (40 mL) was added to a 100 mL flask that contained 2 mL of a 1 M solution of VOCl$_3$ in toluene. The flask was put in an ice bath before 0.6 mL of PMe$_2$Ph was added with stirring. The solution became light orange but no green color was observed, contrary to what was reported.[21] Continued addition of 0.4 mL of PMe$_2$Ph resulted in a pale orange precipitate. The product was dried under vacuum after filtration. Upon recrystallization from dichloromethane and hexanes, an abundant crop of orange thin plate crystals of [HPMe$_2$Ph][VCl$_4$(PMe$_2$Ph)(OPMe$_2$Ph)] was obtained.

Reaction of NbOCl$_3$ with PEt$_3$. Toluene (20 mL) was added to a 100 mL flask containing 0.12 g of NbOCl$_3$, and 0.45 mL of PEt$_3$ was added subsequently. After vigorous stirring for an hour, the solution was clear yellow and was then reduced to about 5 mL and stored in a freezer at −20 °C overnight. Nicely formed yellow block crystals were obtained the next day. A structure determination showed this compound to be [HPEt$_3$][NbOCl$_4$(PEt$_3$)],[22] but because of poor refinement, the detailed dimensions will not be reported.

Preparation of VOCl$_2$(PPh$_3$)$_2$. A mixture of 0.4 g of VCl$_3$(THF)$_3$ and 0.65 g of PPh$_3$ was placed in a 100 mL flask together, and 25 mL of CH$_2$Cl$_2$ was then added. After 24 h of stirring, the flask contained a purple-red solution and was set aside capped with a rubber septum in which holes had been punched. After about a month, green block crystals of VOCl$_2$(PPh$_3$)$_2$ were harvested. The EPR spectrum obtained on a dichloromethane solution of VOCl$_2$(PPh$_3$)$_2$ showed the same pattern as those reported.[1−3] A similar procedure was tried with PEt$_3$ in the hope of obtaining VOCl$_2$(PEt$_3$)$_2$, but it was not successful.

X-ray Crystallography

[HPMe$_2$Ph][VCl$_4$(OPMe$_2$Ph)(PMe$_2$Ph)]. An orange plate-shaped crystal was carefully put in a 0.3 mm Lindemann capillary with mother liquor and set on an AFC5R Rigaku diffractometer at room temperature. A total of 18 reflections found in the range (2θ) 34−40° yielded an orthorhombic cell and later the Laue class *mmm* was established by axial photos. Intensity data were collected in the 2θ range 4−120° by the $2\theta-\omega$ scan method. The space group was uniquely defined to be *Pbca* (No. 61) from systematic absences. Owing to the shape of the crystal, substantial absorption corrections (1.00−0.18) were required.

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(22) Crystal data for [HPEt$_3$][NbOCl$_4$(PEt$_3$)]: NbCl$_4$P$_2$OC$_{12}$H$_{31}$, M = 488.02, orthorhombic, space group $Pca2_1$, a = 13.589(2) Å, b = 14.424(3) Å, c = 22.140(2) Å, V = 4340(2) Å^3, μ(Mo Kα) = 11.89 cm^{-1}, Z = 4, D_c = 1.494 g/cm^3. There are two molecules in each asymmetric unit. Data were collected at −60 °C on a FAST area detecter made by Enraf-Nonius. Refinement was conducted with SHELX-93 and converged at R = 0.098 and wR^2 = 0.239 for all data.

Table 3. Crystal Data for [$HPMe_2Ph$][$VCl_4(PMe_2Ph)(OPMe_2Ph)$] and $VOCl_2(PPh_3)_2$

formula	$VCl_4P_3OC_{24}H_{34}$	$VCl_2P_2C_{36}H_{30}O$
fw	624.21	662.38
space group	*Pbca* (No. 61)	*C2/c* (No. 15)
a, Å	17.262(11)	24.691(4)
b, Å	28.967(8)	9.518(1)
c, Å	12.056(7)	15.690(2)
α, deg	90	90
β, deg	90	117.186(7)
γ, deg	90	90
V, Å^3	6028(5)	3280(1)
Z	8	4
d_{calc}, g/cm^3	1.375	1.341
μ(Cu Kα), cm^{-1}	78.039	51.59
transm factors: max, min	1.00, 0.18	1.00, 0.65
R^a	0.062	0.062
R_w (wR^2)	$0.088^{b,c}$	$(0.183)^{d,e}$
quality (goodness) of-fit indicator	$2.147^{f,c}$	$(1.516)^{g,e}$

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $w = 1/\sigma^2(|F_o|)$. [d] $wR^2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$. [e] $w = [\sigma^2(F_o^2) + (0.0318(\max(F_o^2,0) + 2F_c^2)/3)^2 + 4.938(\max(F_o^2,0) + 2F_c^2)/3]^{-1}$. [f] quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observed} - N_{parameters})]^{1/2}$. [g] goodness-of-fit $= [\sum w(|F_o^2| - |F_c^2|)^2/(N_{observed} - N_{parameters})]^{1/2}$.

The atoms were located by direct methods and difference Fourier maps. The refinement was done with the SDP package.

$VOCl_2(PPh_3)_2$. A green block crystal with dimensions 0.32 × 0.28 × 0.44 was covered with epoxy glue and carefully mounted on the tip of a glass fiber. The crystal was centered on an AFC5R Rigaku diffractometer using monochromated Cu Kα radiation. The monoclinic cell was determined on 25 reflections centered in the range of 48° ≤ 2θ ≤ 60° and confirmed by axial photos. The scan method used was $2\theta-\omega$ and the intensity loss during the data collection was 7.9%.

The space group was selected to be *C2/c* (rather than *Cc*). Direct methods were used to locate vanadium, chlorine and phosphorus atoms. Carbon atoms were found from difference Fourier maps. The refinement was done with SHELX-93 software.[23]

The crystallographic data for both compounds are summarized in Table 3.

Results and Discussion

Reaction Chemistry. The reactivities of VCl_4 and $VOCl_3$ toward phosphines are quite different from those of $NbCl_4$ and $NbOCl_3$. Phosphines reduce VCl_4 to V(III) species such as [$HPEt_3$][$VCl_4(PEt_3)_2$] and $V_2Cl_6(PMe_3)_4$,[16] while they serve simply as coordinating ligands to $NbCl_4$ as in $Nb_2Cl_8(PMe_3)_4$ and $NbCl_4(PEt_3)_2$.[6] Trialkylphosphines remove the oxygen from $VOCl_3$ to form the phosphine oxides and reduce $VOCl_3$ to V(III). In the case of PMe_2Ph, the phosphine oxide reappears as a ligand in the final product. On the other hand, the Nb=O bond in $NbOCl_3$ was not affected by phosphines,[24,25] and the reactions lead to products such as $NbOCl_3(PMe_3)_3$[24] and [$HPEt_3$][$NbOCl_4(PEt_3)$].

Compounds containing the $V{=}O^{2+}$ unit are stable under ordinary conditions,[26] and formation of $VOCl_2{\cdot}2L$ compounds has been widely reported before.[27,28] Unlike VCl_4 and $VOCl_3$, $VOCl_2$ reacts with phosphines with retention of the VO^{2+} core.[27] The stability of oxovanadium(IV) compounds is also revealed in that if water or air took part in the reaction containing VCl_4 or $VCl_3(THF)_3$, the product would generally be a $VOCl_2$ adduct.[18,29] The formation of aquadichlorobis(ethylpyridine)oxovanadium starting from VCl_4 is a good example to show the sensitivity of VCl_4 *and* its pronounced tendency to form oxovanadium compounds.[18]

Table 4. Selected Bond Distances (Å) and Angles (deg) for [$HPMe_2Ph$][$VCl_4(PMe_2Ph)(OPMe_2Ph)$][a]

	Bond Distances		
V–Cl(1)	2.362(2)	V–P(2)	2.585(2)
V–Cl(2)	2.388(2)	V–O(1)	1.983(5)
V–Cl(3)	2.377(2)	P(1)–O(1)	1.502(5)
V–Cl(4)	2.370(2)		
	Bond Angles		
Cl(1)–V–Cl(2)	91.22(8)	Cl(2)–V–O(1)	91.0(2)
Cl(1)–V–Cl(3)	173.4(1)	Cl(3)–V–Cl(4)	88.29(8)
Cl(1)–V–Cl(4)	93.53(8)	Cl(3)–V–P(2)	89.39(8)
Cl(1)–V–P(2)	84.54(8)	Cl(3)–V–O(1)	88.5(1)
Cl(1)–V–O(1)	89.1(1)	Cl(4)–V–P(2)	83.87(8)
Cl(2)–V–Cl(3)	94.93(9)	Cl(4)–V–O(1)	174.0(2)
Cl(2)–V–Cl(4)	94.37(8)	P(2)–V–O(1)	91.0(2)
Cl(2)–V–P(2)	175.29(9)	V–O(1)–P(1)	142.4(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $VOCl_2(PPh_3)_2$[a]

V(1)–O	1.572(4)	P(1)–C(10)	1.820(4)
V(1)–Cl	2.2809(10)	P(1)–C(20)	1.820(4)
V(1)–P(1)	2.6217(11)	P(1)–C(30)	1.824(4)
O–V(1)–Cl	112.03(4)	Cl′–V(1)–P(1)	86.85(4)
O–V(1)–Cl′	112.03(4)	O–V(1)–P(1)′	99.44(3)
Cl–V(1)–Cl′	135.94(7)	Cl–V(1)–P(1)′	86.85(4)
O–V(1)–P(1)	99.44(3)	Cl′–V(1)–P(1)′	86.10(3)
Cl–V(1)–P(1)	86.10(3)	P(1)–V(1)–P(1)′	161.12(6)

[a] Numbers in parentheses are estimated standard deviations.

While oxoniobium(IV) and oxotantalum(IV) compounds have not been so thoroughly studied, it is known that $NbCl_4$ and $TaCl_4$ can also be easily hydrolyzed to oxo species,[30,31] and, of course, $NbOCl_2$ and $TaOCl_2$ are very well-known.

New Molecular Structures. Important interatomic distances and angles of [$HPMe_2Ph$][$VCl_4(PMe_2Ph)(OPMe_2Ph)$] and $VOCl_2(PPh_3)_2$ are presented in Tables 4 and 5. ORTEP drawings of these molecules are shown in Figures 1 and 2.

[$HPMe_2Ph$][$VCl_4(PMe_2Ph)(OPMe_2Ph)$] is another product from the reaction of $VOCl_3$ with PMe_2Ph, in addition to $VCl_3(PMe_2Ph)_2(OPMe_2Ph)$.[16] They bear the similarity that PMe_2Ph and $OPMe_2Ph$ are cis to each other. The bond distances and angles are also similar, although the V–P bond (2.585(2) Å) is longer than those in $VCl_3(PMe_2Ph)_2(OPMe_2Ph)$ (2.540(3) Å), probably because of the stronger trans effect of chlorine compared to that of phosphorus.

The vanadium atom in $VOCl_2(PPh_3)_2$ is in a distorted trigonal bipyramidal environment, very reminiscent of those in $VOCl_2(3\text{-}Etpy)_2$ and [$VOCl_2(THF)$]$_2$(dppm).[29] The 2-fold axis goes through the V=O bond and only half of the remaining atoms are unique. The bond distances and angles between V, O, and Cl are close to those in [$VOCl_2(THF)$]$_2$(dppm) although the V–P distance (2.622(1) Å) is longer, perhaps due to the steric effect of the PPh_3 ligand.

EPR Spectra of Phosphine Adducts of VCl_4. The EPR spectra taken on the reaction solutions of PEt_3 or PBu_3 with VCl_4 or the EPR spectra of [$HPEt_3$][$VCl_4(PEt_3)_2$] in CH_2Cl_2,

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(23) See, for example: *Acta Crystallogr.* **1990**, *A46*, 467. Sheldrick, G. M. *J. Appl. Cryst.*, in press.

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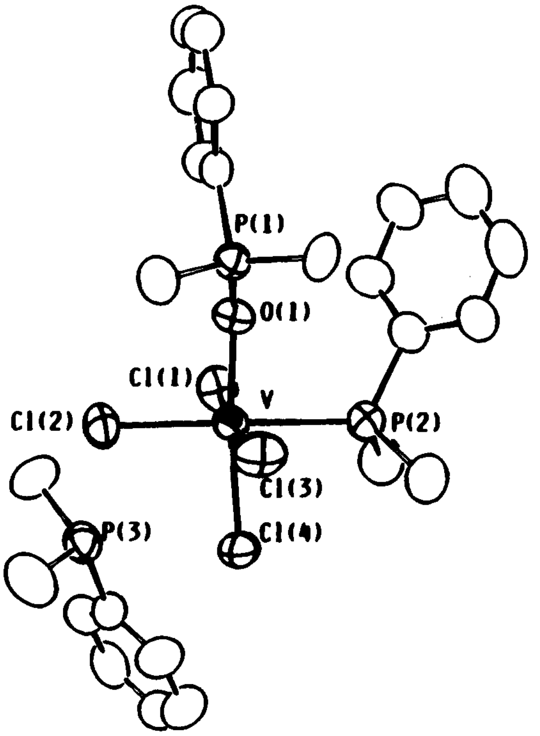

Figure 1. ORTEP drawing of $[HPMe_2Ph][VCl_4(PMe_2Ph)(OPMe_2Ph)]$. All atoms are represented by 50% thermal ellipsoids.

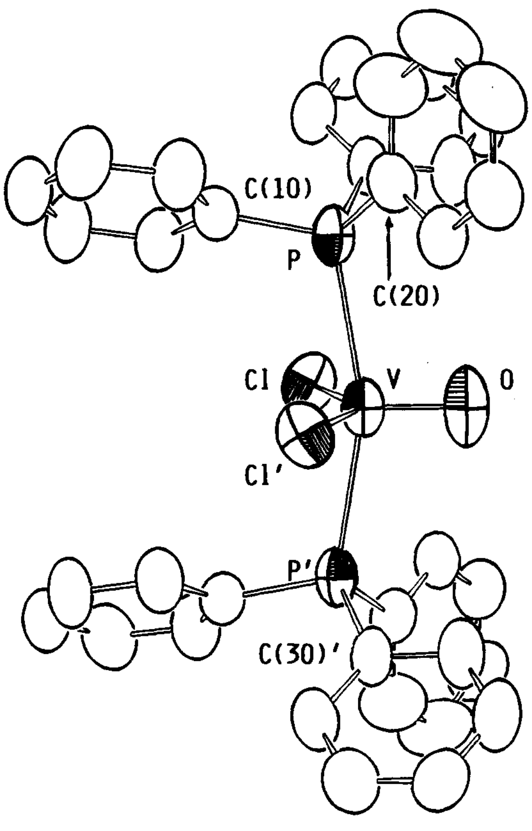

Figure 2. ORTEP drawing of $VOCl_2(PPh_3)_2$. All atoms are represented by 50% thermal ellipsoids.

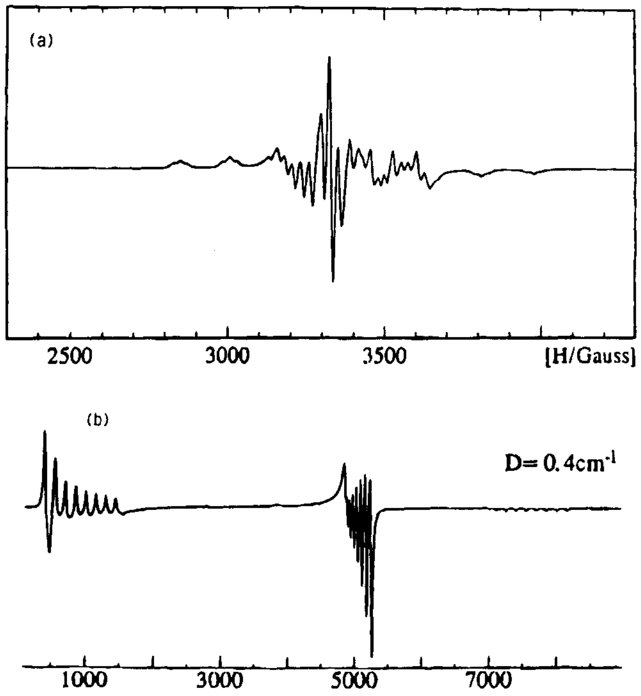

Figure 3. (a) Simulated EPR spectrum of vanadium ($S = {}^1/_2$). (b) Simulated EPR spectrum of vanadium ($S = 1$) with $D = 0.4$ cm^{-1}.

gave signals identical to those reported for "$VCl_4{\cdot}2PEt_3$" at both low and room temperature.[1,3] However, the major reaction product, $[HPEt_3][VCl_4(PEt_3)_2]$, is a V(III) species, a d^2 system, which should be EPR silent due to the large zero-field splitting.[32] Only in a few special cases has V(III) been detected by EPR at low temperature.[33]

In order to further determine the nature of the species responsible for the EPR signal, computer simulations were made on both $S = 1$ and $S = {}^1/_2$ systems. The spin Hamiltonian used for the $S = {}^1/_2$ system was

$$\hat{H} = \mu_B(S\cdot g\cdot H) + S\cdot A\cdot I_V + \sum_{i=1}^{2} S\cdot a_i\cdot I_P$$

and the parameters employed were close to the reported ones on the frozen glass spectrum:[1] $S = {}^1/_2$, $I_V = {}^7/_2$, $I_P = {}^1/_2$, $A_x = A_y = 0.0058$ cm^{-1}, $A_z = 0.0148$ cm^{-1}, $g_x = g_y = 1.985$, $g_z = 1.972$, $a_{1,x} = a_{1,y} = a_{2,y} = 0.0025$ cm^{-1}, and $a_{1,z} = a_{2,z} = 0.0021$ cm^{-1}. The simulated spectrum is illustrated in Figure 3a. It matches with the experimental spectrum almost perfectly.

The simulation for the $S = 1$ (V^{III}) system with different D (zero-field-splitting parameter) values gave spectra totally dissimilar to the one seen in experiment. The Hamiltonian used was

$$\hat{H} = \mu_B(S\cdot g\cdot H) + S\cdot A\cdot I_V + S\cdot D\cdot S$$

with the D value ranging from 0.1 to 0.4 cm^{-1}. The other parameters employed were $S = 1$, $I = {}^7/_2$, $g_x = g_y = g_z = 2$, $A_x = A_y = 0.0051$ cm^{-1}, and $A_z = 0.0140$ cm^{-1}. The nuclear spins on the two phosphorus atoms were ignored to save computing time, but had they been included, each line would be split into three in the simulated spectra. The resulting spectrum with $D = 0.4$ cm^{-1} is presented in Figure 3b.

While these results confirmed that all the spectra observed in the solutions made from VCl_4 were from a V^{IV} compound with two phosphine ligands, this compound could not be the major product of the reaction between VCl_4 and PEt_3 since that is a V^{III} compound. An EPR quantitation done at low temperature on $[HPEt_3][VCl_4(PEt_3)_2]$ revealed that only about

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Table 6. EPR Parameters of "$VCl_4 \cdot 2PEt_3$" and $VOCl_2 \cdot 2PEt_3$

parameter	"$VCl_4 \cdot 2PEt_3$" (at −130 °C)	$VOCl_2 \cdot 2PEt_3$ (at −140 °C)
$g_{\parallel}$	1.972	1.974
$g_{\perp}$	1.985	1.980
g_{iso}	1.981	1.981
$A_{v\parallel}$ (G)	163	159 (440 MHz)
$A_{v\perp}$ (G)	55	56 (154 MHz)
$A_{v,iso}$ (G)	91	90 (250 MHz)
$A_{p\parallel}$ (G)	25.6	28.6 (79 MHz)
$A_{p\perp}$ (G)	27	25.3−28.9 (70−80 MHz)
$A_{p,iso}$ (G)	26.5	26 (72 MHz)

1% of the total vanadium contributed to the signal. Therefore, the EPR signal must be due to a V^{IV} impurity in the reaction solution.

Now, we know that VCl_4 is very hygroscopic and absorbs moisture quite easily to form VO^{2+} compounds[25] which give EPR signals even at room temperature. In fact, it has already been shown that essentially identical spectra were obtained for an adduct of $VOCl_2$ with PEt_3.[34] The quantitation shown there proved that almost 100% of the vanadium was responsible for the signals. Table 6 lists the EPR parameters of $VOCl_2 \cdot 2PEt_3$ and those of "$VCl_4 \cdot 2PEt_3$".[1] These parameters further support the idea that the EPR spectra we obtain as well as those which were reported earlier[1−3] originated from phosphine adducts of $VOCl_2$.

The presence of $VOCl_2$ in the reaction solution of VCl_4 and PEt_3 could be attributed to either an impurity originally present in the purchased VCl_4 (Alfa, 90%) or from the hydrolysis of VCl_4[35] in the course of the preparation or subsequent handling. The reaction solution of $VOCl_2(OPPh_3)_2$ with PEt_3 also showed very intense signals, practically identical to those for "$VCl_4 \cdot 2PEt_3$". Finally, the CH_2Cl_2 solution of $VOCl_2(PPh_3)_2$ showed the same EPR spectrum.

EPR of Solutions of Nb(IV) with Phosphine. A reaction solution prepared from purchased $NbCl_4(THF)_2$ with PEt_3 showed strong EPR signals like those reported[1] for "$NbCl_4 \cdot 2PEt_3$" (Figure 4a) but later we recognized that this purchased $NbCl_4(THF)_2$ had been contaminated (as indicated by its brown color, whereas pure $NbCl_4(THF)_2$ is light yellow). The deep blue color of the solution after prolonged stirring suggested the increased accumulation of niobium oxo species.[36]

Conversely, the EPR of a toluene solution of $NbCl_4(PEt_3)_2$ crystals proved conclusively that EPR signals reported to be from that compound are instead due to impurities. Quantitation on several samples of $NbCl_4(PEt_3)_2$ solution showed that only 0.05−2.2% of the niobium was responsible for the signal intensity. This small portion of impurity may be attributed to contamination by oxygen and/or moisture during reaction or sample preparation since $NbCl_4(PEt_3)_2$ solutions are very sensitive to the laboratory atmosphere.

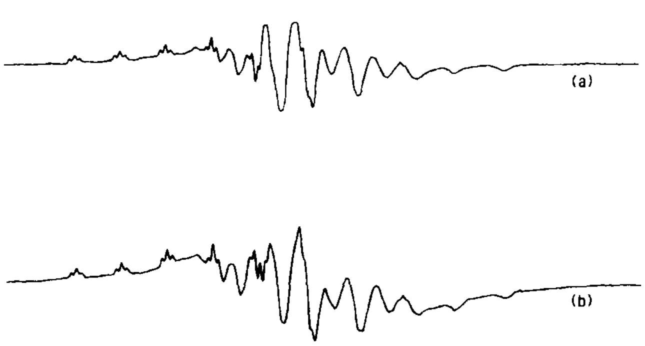

Figure 4. EPR spectra of reaction solution of (a) purchased $NbCl_4(THF)_2$ + PEt_3 in toluene at 130 K and (b) $NbOCl_3$ + PEt_3 + Na/Hg in toluene at 130 K.

The EPR spectrum of a reaction mixture consisting of $NbOCl_3$, PEt_3 and Na/Hg in toluene was recorded and comparison with the spectrum from purchased $NbCl_4(THF)_2$ with PEt_3 is illustrated in Figure 4b. We believe that the following reaction occurred:

$$NbOCl_3 + 2PEt_3 + Na/Hg \rightarrow NbOCl_2(PEt_3)_2$$

and that $NbOCl_2(PEt_3)_2$ is the compound responsible for the EPR signal. The spectrum is essentially identical to that reported,[1] and it is therefore concluded that the reported EPR signals were from an oxo species of niobium(IV). The origin of the oxo compound in the early work was probably from the hydrolysis of $NbCl_4$.[30]

EPR of Solutions of Ta(IV) with Phosphine. The reaction solution of $TaCl_5$ with Na/Hg and PEt_3 showed weak EPR signals with features similar to those reported[1]. Something less than 1% of the total tantalum gave rise to the EPR spectrum at 130 K. When a $TaCl_4(PEt_3)_2$ crystal was dissolved in toluene, it formed a light greenish yellow solution, which showed no EPR signals at either room temperture or 130 K. It would appear that the EPR signals reported previously were from some kind of impurity, the identity of which remains to be determined.

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Supplementary Material Available: Tables of crystallographic data, bond lengths and angles, anisotropic displacement parameters, and positional parameters and an ORTEP drawing of the $[NbOCl_4(PEt_3)]$ anion (29 pages). Ordering information is given on any current masthead page.

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