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Synthesis and Properties of Complexes of Vanadium(V) Oxide Trichloride with Nitrogen- and Oxygen-Donor Ligands

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Intensely coloured, extremely moisture sensitive complexes [$VOCl_3$(L)] (L = pyridine, quinoline, Ph_3PO, Ph_3AsO, pyridine *N*-oxide), [$VOCl_3(L)_2$] (L = pyridine, Me_3PO, pyridine *N*-oxide), [$VOCl_3$(L–L)] [L–L = 2,2′-bipyridyl, 1,10-phenanthroline, $Ph_2P(O)CH_2P(O)Ph_2$, $MeOCH_2CH_2OMe$, 15-crown-5 or $Me_2NCH_2CH_2NMe_2$] and [$Cl_3OV(\mu\text{-L–L})VOCl_3$] [L–L =18-crown-6 or $Ph_2P(O)CH_2P(O)Ph_2$] have been prepared from $VOCl_3$ and the appropriate ligands in dichloromethane solution. These constitute the first extended series of complexes of vanadium(V) with neutral donor ligands. They have been fully characterised by analysis, IR, UV/Visible and multinuclear (^{1}H, ^{31}P, ^{51}V) NMR spectroscopy, and their solution behaviour probed as a function of temperature using ^{51}V NMR spectroscopy. Reducing ligands including phosphanes, arsanes, thio- and selenoethers immediately reduce $VOCl_3$ to give V^{IV} or V^{III} species. Oxygen atom transfer reactions of some of the complexes with Ph_3P, Ph_3As, Me_2Se and Bu_2S, leading to the corresponding ligand oxides are also described.

Introduction

The chemistry of vanadium(V) is dominated by oxido species including V_2O_5, iso- and hetero-polyvanadates and alkoxides.[1] The only binary halide is VF_5; early claims for the existence of VCl_5 having been shown to be erroneous,[2] and there are three oxide trihalides VOX_3 (X = F, Cl or Br).[1] Adducts of $VOCl_3$ with a variety of neutral ligands have been explored by in situ ^{51}V NMR studies,[3–5] but structurally characterised examples are limited to the nitriles, [$VOCl_3(PhCN)_2$] (octahedral, but with Cl/O disorder) and [$VOCl_3$(RCN)] (R = Me, Ph, $PhCH_2$),[6–8] the surprisingly robust carbene [$VOCl_3\{(mes)N^aCH_2CH_2N(mes)\text{-}C^a(N^a\text{–}C^a)\}$],[9] and [$VOCl_3$(adamantan-2,2′-homoadamantan-3-one)],[10] all of which approximate to square pyramids with the V=O apical. In the six-coordinate [$VOCl_3$\{(2-nitrophenyl)pyridine-2-carboxamide\}] the chlorines are *mer* and the V=O *trans* to the amide oxygen.[11] The isolation of other complexes has been reported from time to time,[12–17] but the data are very limited and frequently inconsistent. The problems arise both from the extreme moisture sensitivity of $VOCl_3$ and many of its complexes, and from the ease with which the vanadium is reduced to V^{IV} or V^{III}. In passing, we note that $VOBr_3$ is reported to be reduced by all *neutral* ligands examined.[18,19] We are currently exploring the use of molecular high-valent vanadium complexes as single source CVD precursors, and to provide comparator compounds for that work we have investigated complexes of $VOCl_3$ with a range of neutral group 15 and 16 donor ligands. We have also explored the solution chemistry using ^{51}V NMR spectroscopy and investigated some oxygen atom transfer reactions of the resulting complexes. The chemistry of high-valent vanadium species is also of relevance to vanadium in biological systems such as the vanadate-dependent haloperoxidases most of which occur in marine organisms.[20]

Results and Discussion

$VOCl_3$ is extremely easily hydrolysed, and all reactions were carried out in rigorously dried glassware using freshly dried ligands and solvents. Many of the complexes are also photochemically unstable and typically were stored in foil-wrapped containers in a dry-box. Even with these precautions, many of the solid samples deteriorate over a few days, hence all measurements were made on freshly prepared samples. Decomposition in solution is faster and, despite many attempts, X-ray quality crystals of the complexes have not proved to be obtainable. The two commonest products of hydrolysis are the dark red $[VOCl_4]^-$ and yellow $[VO_2Cl_2]^-$ anions,[21,22] which are readily detected by ^{51}V NMR spectroscopy [^{51}V:[23] 99.76%, I = 7/2, Ξ = 26.29 MHz, $Q = -5.2 \cdot 10^{-30}$ m^2, D_c (receptivity relative to ^{13}C) = 2150], (Table 1). The ^{51}V chemical shift of the former is slightly solvent-dependent and lies in the range δ = +45 to +50 ppm, which is to high frequency of the resonances of

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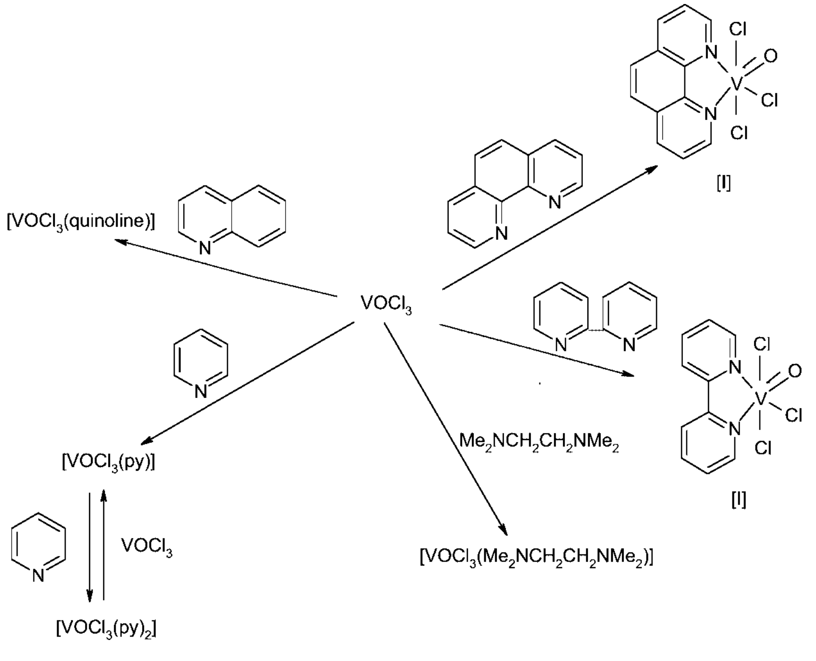
Table 1. Selected spectroscopic data.

Complex	υ(V=O)[a] [cm^{-1}]	υ(VCl) [cm^{-1}]	δ(^{51}V)[b]	E_{max}[c] [cm^{-1}]
[VOCl$_3$(2,2′-bipy)]	978	381, 358, 348	–103 (370)	17200 (sh),19120 (sh), 21370, 32260
[VOCl$_3$(1,10-phen)]	973	386, 347, 319	–108 (560)	18000 (sh), 22220, 32895
[VOCl$_3$(py)]	1020	419, 383, 344	–36 (800)[d]	16024 (sh), 20900, 33000
[VOCl$_3$(py)$_2$]	978	393, 372, 347	–58 (300)[d]	20240 (vb), 27940
[VOCl$_3$(quinoline)]	1022	409, 375, 330	–39 (2500)	16600 (sh), 19250, 20800, 3200
[VOCl$_3$(Ph$_3$PO)]	1020	403, 372, 336	–83 (700)	15900 (sh), 19400, 21900 (sh), 32000
[VOCl$_3$(Me$_3$PO)$_2$]	952	381, 367 (br)	–92 (740)	17240 (sh), 19840 (sh), 21930, 28100
[VOCl$_3$(Ph$_3$AsO)]	1016	393, 365, 347	–141 (400)	15500 (sh), 19840, 21750, 29760
[VOCl$_3${Ph$_2$P(O)CH$_2$P(O)Ph$_2$}]	970	395, 337, 320	–81 (2500)	17600 (sh), 22320, 29070
"[{VOCl$_3$}$_2$[Ph$_2$P(O)CH$_2$P(O)Ph$_2$]]"[e]	1023	390, 371, 360	see text	18800 (sh), 20800, 25000
[{VOCl$_3$}$_2$(18-crown-6)]	993	408 (sh), 359 (vbr)	–6 (2000)	ca. 16000 (sh), 21000 (vbr)
[VOCl$_3$(15-crown-5)]	983	395, 351 (br)	–21 (350)	16000 (sh), 20620
[VOCl$_3$(MeOCH$_2$CH$_2$OMe)]	983	359, 348 (br)	–32 (150)	16050 (sh), 20830, 24750, 33800
[VOCl$_3$(pyNO)]	1006	393, 371, 330	see text	16000 (sh), 19700, 22000, 31700
[VOCl$_3$(pyNO)$_2$]	976	373, 348, 325	–67 (800)	18000 (br), 27200
[VOCl$_3$(Me$_2$NCH$_2$CH$_2$NMe$_2$)]	993	360 (sh), 343, 290 (sh)	[f]	16000 (sh), 21000, 30100
[Ph$_4$As][VOCl$_4$]	1025	394, 373	+48 (300)	19840, 25000, 30490
[Ph$_4$As][VO$_2$Cl$_2$]	967, 957	431	–362 (160)	24630, 33000

[a] Nujol mull. [b] ^{51}V Chemical shift in CH$_2$Cl$_2$ solution at 298 K relative to neat VOCl$_3$, $w_{1/2}$ (Hz) in parenthesis. [c] Diffuse reflectance UV/Vis spectra. [d] See text. [e] Not obtained analytically pure, see text. [f] Insufficiently soluble.

the neutral complexes prepared in this study. The [VO$_2$Cl$_2$]$^-$ anion is relatively resistant to further hydrolysis and the ^{51}V chemical shift ($\delta \approx$ –362 ppm) is less solvent-dependent. It seems probable that resonances at ca. δ = –360 to –370 ppm originally ascribed to oligomeric {VOCl$_3$L}$_n$ adducts in in situ studies,[4] are in fact due to hydrolysis to [VO$_2$Cl$_2$]$^-$. Reduction of VOCl$_3$ to blue-green [VOCl$_2$L$_n$] species is also common in the presence of reducing ligands, but the VO^{2+} species are easily identified by the presence of a strong, broad feature at ca. 12000–15000 cm^{-1} in their UV/Visible spectra.[24]

N-Donor Ligands (Scheme 1): The reaction of VOCl$_3$ with 2,2′-bipyridyl or 1,10-phenanthroline (L–L), in anhydrous CH$_2$Cl$_2$ or toluene produced [VOCl$_3$(L–L)] in good yield, as diamagnetic, very dark red-brown powders. These two complexes are amongst the more stable simple adducts of VOCl$_3$, although even these solids decompose in a few weeks at room temperature, hydrolyse rapidly in air, and decompose quite rapidly in solution. The solids show strong υ(VO) bands at 978 and 973 cm^{-1}, respectively, and three strong features in the region 300–400 cm^{-1} assigned as υ(VCl) (Table 1). In VOCl$_3$ complexes υ(VO) ranges from ca. 950–1040 cm^{-1} and, comparing data only on structurally characterised compounds, the value falls from the four-coordinate VOCl$_3$ (1035 cm^{-1}), to five-coordinate [VOCl$_3$(RCN)], [VOCl$_4$]$^-$, [VOCl$_3${(mes)N^{a}CH$_2$CH$_2$N(mes)-C^a(N^a–C^a)}] (1025–1016 cm^{-1}), to six-coordinate [VOCl$_3$(RCN)$_2$] (below ca. 1000 cm^{-1}).[6–9,25,26] This is



Scheme 1.

clearly consistent with the two diimine complexes containing six-coordinate vanadium. In solution the ^{1}H NMR spectra show significant high-frequency shifts of the ring protons and the complex pattern (see Exp. Sect.) shows that the isomer present is the unsymmetrical I (see Scheme 1), rather than the isomer with both N atoms *trans* to Cl which would have given a maximum of four resonances of equal intensity for each complex. The ^{51}V NMR resonances are relatively sharp lines some 100 ppm to low frequency from $VOCl_3$ (Table 1). The UV/Visible spectra in anhydrous CH_2Cl_2 solution consist of strong broad features at ca. 21000 cm^{-1} which are assigned as $\pi(Cl) \rightarrow V$ charge transfer, with several strong overlapping features at higher energy. The diffuse reflectance spectra are similar although the bands are broader and the first bands have weak shoulders to lower energy. Several attempts to produce crystals of the deep red 2,2′-bipy complex reproducibly formed a few very small orange crystals identified as the oxido-bridged dimeric hydrolysis product. The structure (Figure 1) consists of two six-coordinate V atoms linked through a bridging oxido group. The V–O2 distances favour an oxido rather than hydroxo bridge [compare the V–O(H) distance in $[VOCl_3(OH)]^-$ 2.033(4) Å[22]] leading to V^V and on each V the two Cl atoms are in *trans* position. There are two molecules in the asymmetric unit which are very similar.[27] Several X-ray data sets were obtained from crystals grown both in Strathclyde and Southampton, and all showed the same rather poor crystal quality. The origin of this is probably related to the similarity of the triclinic cell to a monoclinic C-lattice cell and the occurrence of twinning, which was particularly marked for one data set.

Quinoline and $VOCl_3$ react in dry CH_2Cl_2 to form dark red $[VOCl_3(quinoline)]$ which has the υ(VO) at 1022 cm^{-1} and υ(VCl) at 409, 375 and 330 cm^{-1}, the higher frequency of υ(VO) is in agreement with five-coordination at the vanadium centre based on the trends described above [if significant V=O···V interactions occur such that a six-coordinate oligomer description is appropriate υ(VO) would be much lower]. At ambient temperature the ^{51}V NMR spectrum is a broad ($w_{1/2}$ = 2500 Hz) line at δ = –39 ppm, which sharpens on cooling the solution, but with little change in the chemical shift. In contrast, the $VOCl_3$–pyridine system is more complicated and initial attempts to isolate reproducible materials from the reaction of $VOCl_3$ with pyridine in either a 1:1 or 1:2 molar ratio in anhydrous CH_2Cl_2 were unsuccessful. Using a 2:1 $VOCl_3$/py ratio led to red-brown $[VOCl_3(py)]$, whilst a 1:4 ratio gave $[VOCl_3(py)_2]$, but with stoichiometric ratios of the reagents only mixtures are produced. In this respect the pyridine systems seem to resemble the nitrile complexes.[6–8] The IR spectra show υ(VO) at 1020 and 978 cm^{-1} for the 1:1 and 1:2 complexes, respectively (Table 1), consistent with assignment as five- and six-coordinate vanadium. The υ(VCl) modes in $[VOCl_3(py)_2]$ have a very similar pattern to those in $[VOCl_3(L–L)]$ (L–L = 2,2′-bipy or 1,10-phenanthroline) and strongly suggest the same isomer is present with *mer* chlorines and one pyridine ligand *trans* to Cl and the second *trans* to O. The diffuse reflectance spectra are similar, although the lowest energy feature in the 1:1 complex is at slightly lower energy than that of the 1:2 complex. It seems that the charge-transfer spectra are not suited to distinguishing reliably five- and six-coordination in these systems. The solution spectroscopic data obtained from either $[VOCl_3(py)]$ or $[VOCl_3(py)_2]$ are similar, consistent with equilibrium mixtures in solution. In particular, the ^{51}V NMR spectra show only single resonances for solutions of either complex, which vary with concentration and temperature. However, at –90 °C CH_2Cl_2 solutions of $[VOCl_3(py)_2]$ containing excess pyridine show a relatively sharp resonance at δ = –58 ppm, which broadens and drifts to higher frequency on warming. This is probably due to the 1:2 complex. Similarly, at –90 °C a CH_2Cl_2 solution of $[VOCl_3(py)]$ containing excess $VOCl_3$ shows two resonances at δ = –6 and –38 ppm, which broaden and then coalesce (–40 °C) on warming. These are tentatively attributed to $VOCl_3$ and $[VOCl_3(py)]$ respectively, although the lines are still broad, indicating that the low temperature limit has not been reached. However, further cooling results in precipitation of the complex. The reaction of $VOCl_3$ with amines was violent and generated considerable heat and decomposition. We were unable to obtain pure complexes with Et_3N or Et_2NH, but adding a CH_2Cl_2 solution of $VOCl_3$ to a solution of $Me_2NCH_2CH_2NMe_2$ in CH_2Cl_2 frozen in liquid nitrogen, and slowly allowing the mixture to thaw, gave dark brown $[VOCl_3(Me_2NCH_2CH_2NMe_2)]$. The complex is very poorly soluble in chlorocarbons, preventing useful solution-phase spectroscopic data being obtained, but the IR and UV/Visible data (Table 1) are consistent with six-coordinate V^V.

Comparison of the data above shows that adducts of $VOCl_3$ with nitrogen heterocycles form readily under anhydrous conditions. For the rigid chelates, 2,2′-bipyridyl and 1,10-phenanthroline, the complexes are six-coordinate, whilst for the bulky monodentate quinoline, five-coordina-

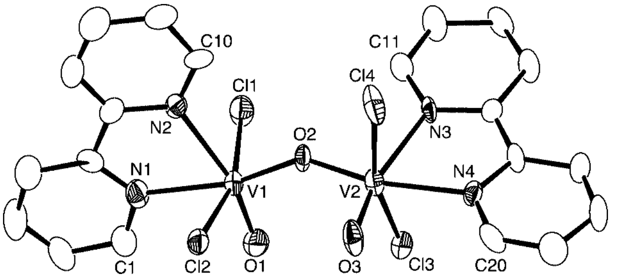
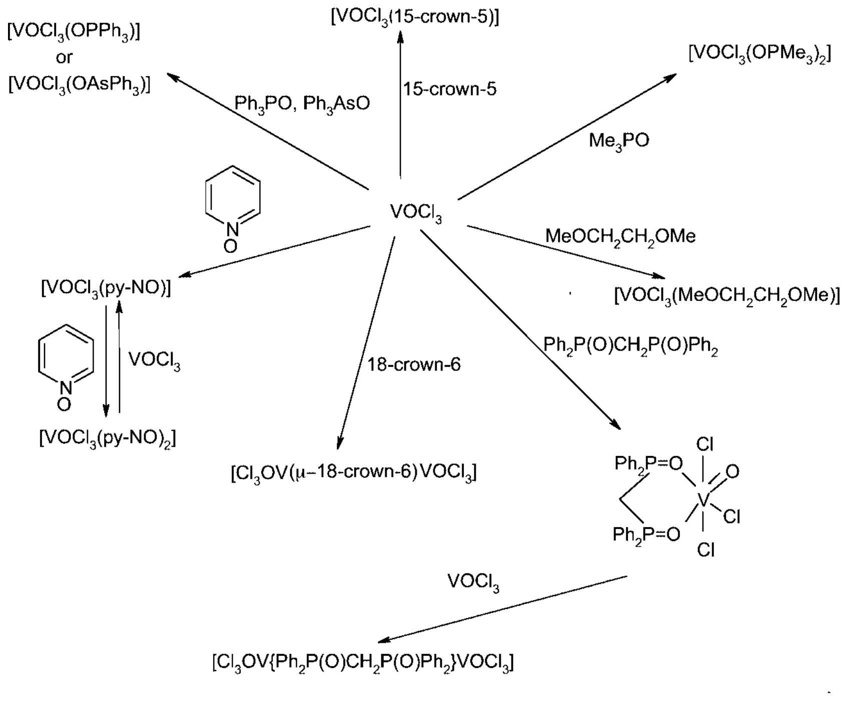


Figure 1. Structure of one of the two vanadium-containing molecules in the asymmetric unit of $[V_2Cl_4O_3(2,2'\text{-bipy})_2]\cdot 1.75CH_2Cl_2$. Displacement ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: V1–Cl1 2.308(4); V1–Cl2 2.330(3); V1–O1 1.578(8); V1–N1 2.164(10); V1–N2 2.258(10); V1–O2 1.783(7); V2–Cl3 2.309(4); V2–Cl4 2.290(4); V2–O3 1.595(8); V2–N3 2.228(9); V2–N4 2.167(9); V2–O2 1.785(8); Cl1–V1–Cl2 163.6(2); N1–V1–N2 72.1(4); N1–V1–O2 163.0(4); N2–V1–O1 164.3(4); V1–O2–V2 145.8(5); Cl3–V2–Cl4 163.2(2); N3–V2–N4 72.7(4); N4–V2–O2 164.1(3); N3–V2–O3 164.8(4). The second molecule involving V3 and V4 has very similar bond lengths and angles.

tion is preferred. The formation of both 1:1 and 1:2 complexes with the smaller pyridine suggests that electronically the stability of the five- and six-coordinate complexes are similar. Paul et al.[16] reported dark brown [$VOCl_3(L)_3$] (L = py, 1-, 2-, or 3-picoline, or quinoline), described as hygroscopic and insoluble in common solvents. We have been unable to reproduce these results, and the coordination of seven monodentate ligands to the small V^V centre seems highly unlikely. The only examples of "seven-coordinate" V^V are with small-angle chelates such as [$VO(NO_3)_3$] or [$VO(S_2CNR_2)_3$], or in "side-on" peroxido complexes.[1] The complexes described above are easily soluble in organic solvents, although some insoluble decomposition or hydrolysis products we have obtained include dark brown or sometimes green solids, which often show evidence of protonation of the heterocycle in the IR spectra.

O-Donor Ligands (Scheme 2): Reaction of excess $VOCl_3$ with 15-crown-5 and 18-crown-6 in CH_2Cl_2 under rigorously anhydrous conditions gave dark red-brown solutions from which removal of the solvent and excess $VOCl_3$ in vacuo, left very moisture sensitive, red-brown powders. The products were identified as [$VOCl_3$(15-crown-5)] and [$(VOCl_3)_2$(18-crown-6)] by analysis. Repeated attempts to obtain a pure complex with 12-crown-4 were unsuccessful. The presence of V^V was confirmed by their diamagnetism, and by broad features in the UV/Visible spectra of both the solids and CH_2Cl_2 solution at ca. 21000 cm^{-1} assigned as $(\pi)Cl \rightarrow V^V$ charge transfer, the absence of features to lower energy ruling out lower oxidation states of vanadium.[24] The IR spectra show broad, intense features in the regions between ca. 1100 and ca. 800 cm^{-1} attributable to $(COC)_{asym}$ and $(COC)_{sym}$ vibrations, respectively, of the crowns. ν(VO) is assigned as the broad medium intensity features at 983 cm^{-1} (15-crown-5) or 993 cm^{-1} (18-crown-6) and ν(VCl) as overlapping bands at ca. 360–430 cm^{-1}. The compounds are extremely moisture sensitive and labile in solution. In rigorously dry CD_2Cl_2 the ^1H NMR spectra show singlet methylene resonances over the range +25 to –95 °C, indicating reversible ligand dissociation or "ring whizzing". The ^{51}V NMR spectrum of [$VOCl_3$(15-crown-5)] shows a single line at $\delta = -21$ ppm and that of [$(VOCl_3)_2$-(18-crown-6)] a broad feature at $\delta = -6$ ppm, both of which drift upfield on cooling the solutions, the effects reversing on warming to ambient temperatures. This is consistent with reversible dissociation on the vanadium NMR timescale, and from mixtures with added $VOCl_3$ we were unable to observe separate resonances for the complex and $VOCl_3$ even at –90 °C. The data are consistent with six-coordinate vanadium centres, with the $VOCl_3$ coordinated to two crown ether oxygen atoms. The behaviour of these complexes is reminiscent of the [$TiCl_4$(crown)] systems,[28] although in these the exchange processes were slowed sufficiently at low temperatures for the different methylene environments to be observed in the ^1H NMR spectra, consistent with the stronger Lewis acidity of $TiCl_4$ compared with $VOCl_3$. Hydrolysis of the V^V complexes with traces of water in chlorocarbon solvents produce $[VO_2Cl_2]^-$ $\delta(^{51}V) = -363$ ppm, and the ^{51}V resonance of a CH_2Cl_2 solution of [Ph_4As][VO_2Cl_2] is unshifted on adding 18-crown-6 showing no interaction with the crown in solution.

The acyclic ether, 1,2-bis(methoxy)ethane (dme) gave a dark red complex [$VOCl_3$(dme)], which was also very labile in solution and deliquescent in the solid state. The very similar IR and ^{51}V NMR spectra of this complex (Table 1) to those of the two crown ethers is strong evidence for the κ^2-coordination of the crown proposed above.



Scheme 2.

The reaction of $VOCl_3$ with Ph_3PO and Me_3PO gave $[VOCl_3(Ph_3PO)]$ and $[VOCl_3(Me_3PO)_2]$ irrespective of the V/L ratio used. The former is a dark brown solid which exhibits υ(PO) at 1050 cm^{-1} and υ(VO) at 1020 cm^{-1}, whilst the latter is dark red-brown and has υ(PO) at 1085 cm^{-1} and υ(VO) at 952 cm^{-1}, the differences in υ(VO) suggesting these are five- and six-coordinate species, respectively. The dry solids are relatively resistant to hydrolysis and may be handled briefly in air, although in solution hydrolysis to chlorido-oxidovanadates occurs readily (^{51}V NMR evidence). In solution the complexes exhibit large high-frequency coordination shifts in the $^{31}P\{^1H\}$ NMR spectra, consistent with coordination to a high-valent metal centre, and have $\delta(^{51}V)$ at –83 and –92 ppm, respectively. The observation of single ^1H and ^{31}P NMR resonances for $[VOCl_3(Me_3PO)_2]$ even at low temperatures, suggests a single isomer with equivalent phosphane oxides is present, and the single υ(PO) vibration tentatively suggests the R_3PO groups are mutually *trans*. The corresponding reaction of $VOCl_3$ with Ph_3AsO in CH_2Cl_2 produced an extremely moisture-sensitive dark red solid $[VOCl_3(Ph_3AsO)]$, which from its spectroscopic signature [υ(VO) at 1016 cm^{-1}, υ(AsO) at 803 cm^{-1}, $\delta(^{51}V) = -141$ ppm] appears to be analogous to the $OPPh_3$ complex.

The diphosphane dioxide $Ph_2P(O)CH_2P(O)Ph_2$, reacts with 1 equiv. of $VOCl_3$ to form dark brown $[VOCl_3\{Ph_2P(O)CH_2P(O)Ph_2\}]$. In the solid state the complex exhibits bands at 1164 and 1080 cm^{-1} assigned as υ(PO) and 970 υ(VO), suggesting a six-coordinate vanadium centre. In CH_2Cl_2 solution the complex is labile and exhibits a ^{31}P NMR resonance only on cooling, and at –70 °C the spectrum reveals doublets of equal intensity at δ = 48.2 and 34.5 ppm (^2J = 12 Hz) ["free" $Ph_2P(O)CH_2P(O)Ph_2$ has $\delta(^{31}P)$ = 25 ppm]. The ^{51}V (δ = –81 ppm) resonance is broad ($w_{1/2}$ ca. 2500 Hz) at room temperature, and sharpens on cooling, although the chemical shift varies only slightly with temperature. The large difference in υ(PO) in the IR spectrum and the inequivalence of the phosphorus centres in solution strongly suggest the structure of this complex has the phosphinoyl groups *trans* to VO and VCl, respectively, and hence has *mer*-Cl atoms. Evaporation of a CH_2Cl_2 solution of $[VOCl_3\{Ph_2P(O)CH_2P(O)Ph_2\}]$ with excess $VOCl_3$ and pumping to dryness in vacuo, gave a second complex which was not obtained analytically pure, but which appears to be $[(VOCl_3)_2\{\mu\text{-}Ph_2P(O)CH_2P(O)Ph_2\}]$ with υ(PO) at 1094 cm^{-1} and υ(VO) at 1023 cm^{-1}, and which from NMR studies was undergoing ligand exchange in solution even down to very low temperatures. The data show that like the pyridine systems above, the balance between five- and six-coordination in the phosphane oxide systems is subtle. In the case of the $Ph_2P(O)CH_2P(O)Ph_2/VOCl_3$ system the relative mismatch of the small vanadium centre and the large chelate bite in the six-membered ring is probably responsible for the dynamic behaviour in solution. Attempts to isolate a complex of $VOCl_3$ with the diphosphane dioxide $o\text{-}C_6H_4\{P(O)Ph_2\}_2$, which is both more rigid and sterically larger, were unsuccessful.

Pyridine *N*-oxide afforded two complexes, red $[VOCl_3(pyNO)]$ and darker red-black $[VOCl_3(pyNO)_2]$, depending upon the experimental conditions. The υ(VO) at 976 cm^{-1} in the latter is within the range of other six-coordinate complexes, whilst for the former the υ(VO) at 1006 cm^{-1} is at the lowest frequency observed for an (assumed) five-coordinate vanadium centre. The complexes also show strong υ(NO) at 1195 and 1200 cm^{-1}, lowered from the value of 1228 cm^{-1} in pyridine *N*-oxide.[29] The ^{51}V NMR spectrum of $[VOCl_3(pyNO)_2]$ in anhydrous CH_2Cl_2 solution at ambient temperatures is a very broad resonance at δ = –67 ppm ($w_{1/2}$ = 800 Hz) which on cooling the solution sharpens and shows a small low-field shift. In the presence of added pyNO the limiting chemical shift is δ = –72 ppm ($w_{1/2}$ = 1000 Hz) at –70 °C, which probably corresponds to the 1:2 complex. In contrast, a CH_2Cl_2 solution of $[VOCl_3(pyNO)]$ only shows a ^{51}V NMR resonance below ca. –30 °C as a very broad feature at ca. δ = –25 ppm, which does not sharpen appreciably on cooling the solution, although as expected, addition of excess pyNO replicates the behaviour observed from $[VOCl_3(pyNO)_2]$. Overall, the data suggest that neutral O-donor ligand complexes of $VOCl_3$ are less stable, particularly in solution, than the N-donor adducts, and with the exception of the phosphane oxides, the lability precludes using solution NMR spectroscopic data to identify the isomer present in the six-coordinate complexes. Again examples of both five- and six-coordination are found, the coordination number presumably largely driven by steric factors.

S-, Se-, P- and As-Donor Ligands: The reaction of $VOCl_3$ with R_2S (R = Me, Et or Bu) in chlorocarbons or hydrocarbons even at low temperatures gave dark solutions, which became blue-green in seconds. The UV/Visible spectrum of the latter (E_{max} = 13500 cm^{-1}) showing reduction to a vanadyl VO^{2+} species, as reported by Baker et al.[15] Similar reduction occurred with Ph_2S and $PhSCH_2CH_2SPh$. The reaction of Me_2Se, $MeSeCH_2CH_2SeMe$, Ph_3P, $Ph_2PCH_2CH_2PPh_2$, or $o\text{-}C_6H_4(AsMe_2)_2$ with $VOCl_3$ even at –78 °C caused instant reduction to V^{IV} or V^{III} (identified by in situ UV/Visible spectroscopy).

Oxygen Atom Transfer Reactions: The results above clearly show that the V^V complexes are extremely reactive and unstable towards reduction. Hence we have investigated their possible utility as O-atom transfer reagents towards R_3E (E = P or As) and R_2E' (E′ = S or Se). Many high valent metal oxido complexes have been shown to behave as O-atom transfer reagents to organic molecules.[30] The addition of 1 equiv. of Ph_3P to CH_2Cl_2 solutions of $[VOCl_3(2,2'\text{-bipy})]$, $[VOCl_3(py)_2]$ or $[VOCl_3(quinoline)]$ resulted in instant loss of the dark red V^V complexes, leaving pale pink solutions, and in situ ^{31}P NMR studies showed clean conversion to Ph_3PO (δ = +28 ppm). The corresponding reactions with Me_3As and Ph_3As with $[VOCl_3(quinoline)]$ also resulted in rapid discharge of the colour, and after hydrolysis with aqueous ammonia, a mixture of the corresponding R_3AsO and quinoline were isolated from the organic extracts, and identified by comparison of their IR and ^1H NMR spectra with literature data.[31] The reaction of [$VOCl_3$(quinoline)] with Me_2Se was also rapid, and in this case the product was identified as Me_2SeO by its ^{77}Se NMR [δ(CH_2Cl_2 solution) = +825 ppm; ref.[32] +812 ppm (in H_2O)] which, given the solvent-dependence of selenium chemical shifts, is good agreement. In contrast, the reactions of [$VOCl_3$(quinoline)] with thioethers, including $n$$Bu_2S$ and Ph_2S, were slow, taking several hours to discharge the deep red colour (contrast the rapid reduction of $VOCl_3$ by these ligands described above). In these cases, after hydrolysis with aqueous ammonia and extraction with CH_2Cl_2, evaporation of the organic solvents left the corresponding[33] colourless liquid sulfoxides, R_2SO.

Conclusions

A range of five- and six-coordinate oxido V^V complexes incorporating neutral N- and O-donor ligands has been isolated and characterised spectroscopically and analytically. This represents the first detailed characterisation of an extended series of adducts of $VOCl_3$. The compounds are highly reactive and undergo moderately rapid degradation both in solution and in the solid state even in the dark. They are immediately decomposed by water or alcohols and reduced by ligands containing the heavier groups 15 or 16 donors, and for selected examples we have shown that this decomposition involves oxygen atom transfer to the group 15/16 atom. ^{51}V NMR studies show resonances to low frequency of $VOCl_3$ for all of the complexes reported here. Variable temperature studies have shown that most of the complexes are labile in chlorocarbon solvents. Although for some of the monodentate ligands both 1:1 and 1:2 ligand/metal complexes have been isolated as solids, in solution these are in fast equilibrium.

Experimental Section

All reactions were conducted under anhydrous conditions under dry dinitrogen using standard vacuum line, Schlenk and glove-box techniques. $VOCl_3$ (Aldrich) was used as received. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), Na/benzophenone ketyl (hexane and diethyl ether). 2,2′-Bipyridyl, 1,10-phenanthroline, Ph_3PO, Ph_3AsO and pyridine *N*-oxide were dried by heating in vacuo, Me_3PO was freshly sublimed in vacuo. 18-crown-6, 15-crown-5 and 12-crown-4 were dried by refluxing with excess $SOCl_2$, followed by vacuum drying at 60 °C. 1,2-bis(methoxy)ethane was dried by distillation from Na pellets. Quinoline, pyridine and $Me_2NCH_2CH_2NMe_2$ were refluxed over BaO and freshly distilled. [Ph_4As][$VOCl_4$] and [Ph_4As][VO_2Cl_2] were made by literature methods.[20,21] ^{51}V NMR spectra were recorded in 10-mm o.d. tubes from dry CH_2Cl_2 solutions containing 5% CD_2Cl_2 as lock, with a Bruker DPX400 operating at 105.2 MHz, and referenced to external neat $VOCl_3$ (δ = 0 ppm). Other physical measurements were made as described.[9,28] Analytical data were obtained from the microanalytical laboratory of Strathclyde University.

[$VOCl_3$(2,2′-bipy)]: A solution of $VOCl_3$ (0.23 g, 1.3 mmol) in dry CH_2Cl_2 (5 mL) was added to a solution of 2,2′-bipyridyl (0.2 g, 1.3 mmol) in dry CH_2Cl_2 (10 mL). The dark red solution was concentrated to ca. 5 mL in vacuo, dry hexane (5 mL) added and the red-black solid isolated by filtration, and dried in vacuo. Yield 0.30 g, 70%. $C_{10}H_8Cl_3N_2OV$ (329.5): calcd. C 36.5, H 2.5, N 8.5; found C 37.1, H 2.1, N 8.2. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.6 (m, 2 H), 8.5 (m, 4 H), 9.35 (s, H), 9.70 (s, H) ppm. IR (Nujol): $\tilde{\nu}$ = 1314 (m), 1261 (m), 1157 (w), 1104 (w), 1026 (m), 978 (s), 802 (m), 763 (s), 658 (m), 381 (s), 358 (s), 348 (s) cm^{-1}. UV/Vis: E_{max} [cm^{-1}] (ε_{mol}, cm^{-1} dm^3 mol^{-1}) = 19250 (sh), 21550 (1325), 22730 (1300), 26310 (sh), ca. 33000 (ca. 20000).

[$VOCl_3$(1,10-phen)]: Prepared similarly from $VOCl_3$ (0.29 g, 1.6 mmol) and 1,10-phenanthroline (0.29 g, 1.6 mmol). A dark red-brown solid was isolated. Yield 0.32 g, 55%. $C_{12}H_8Cl_3N_2OV$ (353.2): calcd. C 40.7, H 2.3, N 7.9; found C 39.8, H 2.0, N 7.5. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.0 (m, 4 H), 8.65 (s, 2 H), 9.75 (s, H), 9.95 (s, H) ppm. IR (Nujol): $\tilde{\nu}$ = 1308 (w), 1258 (w), 1171 (m), 1140 (s), 1023 (w), 973 (s), 839 (s), 776 (m), 431 (m), 386 (s), 347 (s), 319 (sh) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] (ε_{mol}, cm^{-1} dm^3 mol^{-1}) = 18200 (sh), 21505 (1680), 22730 (1730), ca. 33000 (ca. 15000).

[$VOCl_3(py)_2$]: A solution of pyridine (0.4 g, 5.0 mmol) in CH_2Cl_2 (5 mL) was added to $VOCl_3$ (0.21 g, 1.2 mmol) in CH_2Cl_2 (5 mL) producing an immediate precipitate. The mixture was stirred briefly, concentrated in vacuo to small volume and hexane (5 mL) added. The red solid was filtered off, rinsed with hexane, and dried in vacuo. Yield 0.23 g, 51%. $C_{10}H_{10}Cl_3N_2OV$ (331.5): Calcd. C 36.2, H 3.0, N 8.5; found C 36.3, H 3.9, N 8.3. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.3–7.5 (m) ppm. IR (Nujol): $\tilde{\nu}$ = 1604 (m), 1375 (m), 1325 (w), 1263 (w), 1161 (w), 1054 (m), 978 (s), 800 (s), 750 (s), 671 (s), 426 (s), 393 (m), 372 (m), 347 (m) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] = 19800 (sh), 21740, 28730.

[$VOCl_3$(py)]: A solution of pyridine (0.2 g, 2.5 mmol) in CH_2Cl_2 (5 mL) was added to $VOCl_3$ (0.84 g, 4.8 mmol) in CH_2Cl_2 (25 mL) producing an immediate precipitate. The solution was stirred for 30 min and then pumped to dryness in vacuo at room temperature. The dark brown powder produced was rinsed with hexane (5 mL), the solid filtered off and dried in vacuo. Yield 0.40 g, 64%. $C_5H_5Cl_3NOV$ (252.4): calcd. C 23.8, H 2.0, N 5.6; found C 23.1, H 2.1, N 5.4. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.5 (s, 2 H), 8.0 (s, H), 8.9 (s, 2 H) ppm. IR (Nujol): $\tilde{\nu}$ = 1604 (w), 1361 (m), 1250 (w), 1236 (w), 1158 (m), 1071 (m), 1020 (s), 964 (w), 869 (m), 757 (s), 734 (s), 687 (s), 642 (m), 419 (s), 385 (s), 344 (s) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] = 21500, 29110.

[$VOCl_3$(quinoline)]: A solution of quinoline (0.26 g, 2.0 mmol) in CH_2Cl_2 (10 mL) was added to $VOCl_3$ (0.52 g, 3.0 mmol) in CH_2Cl_2 (25 mL) producing an immediate red-black precipitate. The solution was stirred for 30 min and then pumped to dryness in vacuo at room temperature. The dark brown powder produced was stirred with hexane (5 mL) for 15 min, the solid filtered off and dried in vacuo. Yield 0.45 g, 74%. $C_9H_7Cl_3NOV$ (302.5): calcd. C 35.7, H 2.3, N 4.6; found C 35.5, H 2.4, N 4.5. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.7 (s, H), 7.9 (s, H), 8.1 (s, 2 H), 8.4 (s, H), 8.7 (s, H), 9.4 (s, H) ppm. IR (Nujol): $\tilde{\nu}$ = 1610 (w), 1354 (m), 1298 (w), 1261 (m), 1091 (m),1022 (s), 798 (s), 771 (m), 710 (s), 634 (w), 596 (m), 496 (s), 458 (m), 409 (sh), 375 (s), 330 (sh) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] = 21600, 27700.

[$VOCl_3(Me_2NCH_2CH_2NMe_2)$]: A solution of $Me_2NCH_2CH_2NMe_2$ (0.12 g, 1.0 mmol) in CH_2Cl_2 (20 mL) was frozen in liquid nitrogen and a solution of $VOCl_3$ (0.17 g, 1.0 mmol) in CH_2Cl_2 (10 mL) syringed in. The mixture was allowed to thaw and then warm slowly to room temperature to produce a dark brown solution. The solution was stirred for 30 min and then concentrated to ca. 10 mL in vacuo. The dark red-brown solid was filtered off and dried in vacuo. Yield 0.25 g, 86%. $C_6H_{16}Cl_3N_2O_3V$ (281.5): calcd. C 24.9, H 5.6, N 9.7; found C 24.3, H 6.0, N 9.5. IR (Nujol): $\tilde{\nu}$ = 1590 (w), 1260 (m), 1161 (w), 1080 (sh), 993 (s), 946 (m), 914 (w), 803 (s), 733 (s), 525 (w), 360 (sh), 343 (s), 290 (sh) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] = 20830, 32100.

[$VOCl_3$(15-crown-5)]: $VOCl_3$ (0.14 g, 0.8 mmol) in dry CH_2Cl_2 (5 mL) was added to 15-crown-5 (0.17 g, 0.77 mmol) in dry CH_2Cl_2 (10 mL) and the solution pumped to dryness under vacuum. The solid was washed with pentane (10 mL), filtered off and dried in vacuo. Yield 0.2 g, 64%. $C_{10}H_{20}Cl_3O_6V$ (393.5): calcd. C 30.5, H 5.2; found C 29.4, H 5.7. IR (Nujol): $\tilde{\nu}$ = 1304 (w), 1261 (m), 1098 (vs), 1022 (s), 983 (m), 940 (m), 802 (s), 610 (w), 428 (m), 395 (m), 351 (m) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] = 22420. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 3.6 (br. s) ppm. ^{51}V NMR (CH_2Cl_2, 223 K): δ = –54 ($w_{1/2}$ = 1000 Hz) ppm.

[$\{VOCl_3\}_2$(18-crown-6)]: Excess $VOCl_3$ (0.42 g, 2.4 mmol) in dry CH_2Cl_2 (5 mL) was added to 18-crown-6 (0.2 g, 0.76 mmol) in dry CH_2Cl_2 (10 mL) and worked up as described for [$VOCl_3$(15-crown-5)]. Red-brown solid. Yield 0.2 g, 30%. $C_{12}H_{24}Cl_6O_8V_2$ (610.9): calcd. C 23.6, H 4.0; found C 24.3, H 4.6. IR (Nujol): $\tilde{\nu}$ = 1300 (w), 1260 (m), 1146 (w), 1098 (vs), 1027 (s), 993 (m), 927 (m), 803 (s), 563 (m), 408 (sh), 359 (s,br), 306 (m) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] = 22320. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 3.66 (s) ppm. ^{51}V NMR (CH_2Cl_2, 203 K): δ = –47 ($w_{1/2}$ = 2000 Hz) ppm.

[$VOCl_3(Ph_3PO)$]: A solution of triphenylphosphane oxide (0.56 g, 2.0 mmol) in CH_2Cl_2 (5 mL) was added to $VOCl_3$ (0.35 g, 2.0 mmol) in CH_2Cl_2 (5 mL), the dark solution stirred briefly and then concentrated in vacuo. The solution was treated with hexane (5 mL) and refrigerated to give a red-brown solid, which was filtered off and dried in vacuo. Yield 0.53 g, 58%. $C_{18}H_{15}Cl_3PO_2V$ (451.6): calcd. C 47.9, H 3.3; found C 48.5, H 3.3. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.4–7.8 (m, Ph) ppm. ^{51}V (CH_2Cl_2, 200 K): δ = –102 ($w_{1/2}$ = 850 Hz) ppm. $^{31}P\{^1H\}$ (CH_2Cl_2, 295 K): δ = 56 ppm. IR (Nujol): $\tilde{\nu}$ = 1312 (w), 1260 (m), 1182 (m), 1119 (s), 1050 (s, PO), 1020 (s), 992 (m), 749 (s), 688 (s), 535 (vs), 432 (m), 403 (m), 372 (m), 336 (m), 311 (m) cm^{-1}. UV/Vis (CH_2Cl_2) E_{max} [cm^{-1}] (ε_{mol}, $cm^{-1}dm^3mol^{-1}$) = 17000 (110), 23250 (500), 31000 (15000).

[$VOCl_3(Me_3PO)_2$]: A solution of trimethylphosphane oxide (0.09 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was added to $VOCl_3$ (0.09 g, 0.5 mmol) in CH_2Cl_2 (5 mL), the dark brown solution which was stirred briefly, filtered, and the solvents evaporated to dryness in vacuo. Yield 0.16 g, 88%. $C_6H_{18}Cl_3O_3P_2V$ (357.5): calcd. C 20.1, H 5.0; found C 20.6, H 5.3. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 2.0 (br., CH_3) ppm. $^{31}P\{^1H\}$ (CH_2Cl_2, 295 K): δ = 74 ppm, essentially unchanged on cooling to 210 K. IR (Nujol): $\tilde{\nu}$ = 1297 (s), 1260 (m), 1085 (vs, PO), 1016 (s), 952 (s), 863 (m), 801 (m), 757 (w), 608 (w), 468 (sh), 431 (m), 381 (sh), 367 (br., m) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] = 17240 sh, 18380, 23580, 33000.

[$VOCl_3[Ph_2P(O)CH_2P(O)Ph_2]$]: A solution of the diphosphane dioxide (0.27 g, 0.65 mmol) in CH_2Cl_2 (10 mL) was added to $VOCl_3$ (0.11 g, 0.65 mmol) in CH_2Cl_2 (5 mL), and the dark solution stirred briefly. Hexane (5 mL) was added and the dark-brown precipitate filtered off and dried in vacuo. Yield 0.175 g, 46%. $C_{25}H_{22}Cl_3O_3P_2V$ (589.7): calcd. C 50.9, H 3.8; found C 50.9, H 3.5. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.4–7.9 (m, Ph), 3.95 (br. s, CH_2) ppm; no change at 210 K. ^{51}V (CH_2Cl_2, 200 K) δ = –85 ($w_{1/2}$ = 1100 Hz) ppm. $^{31}P\{^1H\}$ (CH_2Cl_2, 223 K): δ = 48 (br., P), 35 (br., P) ppm; (200 K): δ = 48.2 (d, $^2J_{P-P}$ = 12 Hz, P), 34.5 (d, $^2J_{P-P}$ = 12 Hz, P) ppm. IR (Nujol): $\tilde{\nu}$ = 1260 (m), 1164 (s, PO), 1125 (s), 1099 (m), 1080 (m, PO), 1055 (m), 1025 (m), 970 (w), 777 (s), 687 (s), 517 (s), 395 (m), 337 (s), 320 (sh) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] (ε_{mol}, $cm^{-1}dm^3mol^{-1}$) = 17980 (1300), 22730 (3750), 30490 (2200).

[$VOCl_3(Ph_3AsO)$]: Triphenylarsane oxide (0.32 g, 1.0 mmol) was melted in vacuo after 20 min the melt was cooled to room temperature, dissolved in dry CH_2Cl_2 (10 mL) and added to $VOCl_3$ (0.35 g, 2.0 mmol) in CH_2Cl_2 (5 mL). (Unless rigorously anhydrous conditions are used this reaction gives the product as a black oil which appears spectroscopically identical to the solid complex.) The dark solution stirred briefly and then concentrated in vacuo. The solution was treated with hexane (5 mL) to give a red-black solid, which was filtered off and dried in vacuo. Yield 0.40 g, 80%. $C_{18}H_{15}AsCl_3O_2V{\cdot}CH_2Cl_2$ (580.5): calcd. C 39.3, H 3.0; found C 39.6, H 2.7. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.4–7.8 (m, Ph), 5.4 (s, CH_2Cl_2) ppm. ^{51}V (CH_2Cl_2, 298 K): δ = –142 ($w_{1/2}$ = 400 Hz) ppm. IR (Nujol): $\tilde{\nu}$ = 1363 (m), 1260 (m), 1087 (s), 1016 (s), 801 (m, AsO), 735 (s), 684 (m), 530 (w), 461 (m), 393 (m), 365 (m), 347 (sh) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] (ε_{mol}, $cm^{-1}dm^3mol^{-1}$) = 16000 (sh) (ca. 200), 21550 (3100), 30490 (2295).

[$VOCl_3(MeOCH_2CH_2OMe)$]: A solution of dme (0.18 g, 2.0 mmol) in CH_2Cl_2 (10 mL) was added to $VOCl_3$ (0.19 g, 1.0 mmol) in CH_2Cl_2 (25 mL) producing a very dark solution. The solution was stirred for 30 min, and then pumped to dryness in vacuo at room temperature. The dark red-black powder produced was stirred with hexane (5 mL) for 15 min, the solid filtered off and dried in vacuo. Yield 0.35 g, 66%. $C_4H_{10}Cl_3O_3V$ (263.4): calcd. C 18.3, H 3.8; found C 18.7, H 4.2. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 3.8 (br) ppm; (220 K): δ = 4.01 (s, 2 H, CH_2), 4.05 (s, 3 H, CH_3) ppm. IR (Nujol): $\tilde{\nu}$ = 1346 (m), 1278 (w), 1260 (m), 1240 (m), 1190 (m), 1107 (s), 1076 (s), 1026 (s), 999 (s), 983 (s), 864 (m), 820 (m), 770 (m), 421 (m), 359 (s), 348 (vbr), 282 (w) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] = 19840, 26050 (sh), 32000.

[$VOCl_3$(pyNO)]: A solution of pyridine *N*-oxide (0.55 g, 5.8 mmol) in toluene (50 mL) was treated dropwise with $VOCl_3$ (1.0 g, 5.8 mmol). A dark red precipitate was formed immediately and the mixture stirred for 2 h. The supernatant was removed by cannula and the solid residue washed with hexane (15 mL). Filtration yielded a red solid which was dried in vacuo. Yield 0.96 g, 62%. $C_5H_5Cl_3NO_2V$ (268.4): calcd. C 22.4, H 1.9, N 5.2; found C 22.1, H 1.7, N 5.7. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.85 (s, 2 H), 9.20 (s, 1 H), 9.65 (s, 2 H). IR (Nujol): $\tilde{\nu}$ = 1605 (w), 1258 (m), 1197 (s), 1172 (m), 1092 (m), 1006 (s), 979 (m), 836 (m), 768 (s), 727 (m), 690 (m), 393 (m), 371 (s), 330 (s) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] = 16000 (sh), 19700, 22000, 31700.

[$VOCl_3(pyNO)_2$]: A solution of pyridine *N*-oxide (0.55 g, 5.8 mmol) in CH_2Cl_2 (30 mL) was treated with $VOCl_3$ (0.5 g, 2.8 mmol). A very dark red-black solution resulted. After stirring for 1 h. the mixture was taken to dryness in vacuo at room temperature. The resulting dark red solid was suspended in hexane (10 mL) and stirred for 15 min, the solid filtered off and dried in vacuo. Yield 0.86 g, 82%. $C_{10}H_{10}Cl_3N_2O_3V$ (363.5): calcd. C 33.0, H 2.8, N 7.7; found C 32.7, H 2.6, N 7.1 ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.82 (s, 2 H), 9.15 (s, 1 H), 9.60 (s, 2 H). IR (Nujol): $\tilde{\nu}$ = 1605 (w), 1258 (m), 1200 (s), 1175 (m), 1092 (s), 996 (s), 976 (m), 830 (m), 768 (s), 727 (m), 695 (m), 373 (m), 348 (s), 325 (s) cm^{-1}. UV/Vis (CH_2Cl_2): E_{max} [cm^{-1}] = 18000 (br), 27200.

Oxidation Reactions: General method: Ph_3P (0.026 g, 0.1 mmol) was dissolved in CH_2Cl_2 (5 mL) and a solution of the vanadium complex (0.1 mmol) in CH_2Cl_2 (5 mL) added. After 5 min the mixture was pumped to dryness in vacuo, and the residue shaken up with aqueous ammonia (5 mL of 4 $mol{\cdot}dm^{-3}$) and CH_2Cl_2 (5 mL). The organic phase was separated and used for ^{31}P NMR studies. The reactions with Me_3As, Ph_3As, Me_2Se, $n$$Bu_2S$ and Ph_2S were conducted similarly, the products being identified by ^{1}H, ^{77}Se NMR and IR spectroscopy as appropriate.

X-ray Data: CCDC-608276 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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