Compounds with Vanadium–Nitrogen and Vanadium–Oxygen Multiple Bonds†

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Vanadium nitrido complexes are generally not accessible by routes successful in rhenium and molybdenum chemistry. The vanadium–nitrogen triple bond is reactive, and easily forms phosphiniminato complexes, two of which $[V(NPMe_2Ph)Cl_3(PMe_2Ph)_2]$ and $[V(NPMe_2Ph)Cl_3(PMe_2Ph)_2]\cdot H_2O$, have been structurally characterised. The compound $[V(NMe)Cl_3(py)_2]$ (py = pyridine) and related alkylimido species have been synthesised. They can apparently be converted by base to alkylideneamido complexes, but the only material unequivocally and structurally characterised from such systems was $[VOCl_2(py)_2]$, formed by hydrolysis.

Recent isolation of nitrogenases based upon vanadium[1] has led us to explore whether the chemistry of vanadium–nitrogen systems parallels that of molybdenum–nitrogen systems or whether it is totally distinct. The few dinitrogen complexes of vanadium[2,3] do seen to be rather similar to those of molybdenum, although more heavily reduced (for example, V^{-I} compared to Mo^0 for the isoelectronic terminal end-bound dinitrogen complexes[3]) and less easily accessible.

In this paper we report on studies of species which have analogues that have already been identified on the reaction pathway between co-ordinated dinitrogen on tungsten or molybdenum, and ammonia, namely, nitrido-, imido-, and, parenthetically, hydrazido(2−)-complexes of vanadium. It should be noted that throughout these studies ^1H NMR spectroscopy was not very informative because many of the compounds are paramagnetic, and even with diamagnetic compounds there is line broadening due to the nuclear spin of ^{51}V.

Results and Discussion

Nitrido Complexes.—Nitrido complexes of vanadium have become well established only recently. There are considerably fewer of these than nitrido complexes of molybdenum.[4] One, $[\{VNCl_2(py)_2\}_\infty]$, (py = pyridine)[5,6] contains chains of alternating vanadium and nitrogen atoms and another, $[VNCl_2(qncd)_2]$, (qncd = quinuclidine),[5] consists of distinct non-interacting mononuclear species in the crystal. There are also a few examples of vanadium nitrides bridging through nitrogen to metals such as platinum and rhenium,[7] or vanadium in oxidation states other than V.[8]

We attempted a series of rational syntheses of vanadium nitrido complexes based upon the established chemistry of molybdenum[9] and rhenium,[10] such as $[ReO_4]^- \longrightarrow [ReOCl_3(PMe_2Ph)_2] \longrightarrow [ReO(OEt)Cl_2(PMe_2Ph)_2] \longrightarrow [ReNCl_2(PMe_2Ph)_2]$. However, the reaction of sodium or ammonium trioxovanadate(V) with $N_2H_4\cdot 2HCl$ in ethanol in the presence of phosphines such as PMe_2Ph gave only intractable oils containing less than 2% carbon. The adducts $[VOCl_3(bipy)]$ (bipy = 2,2′-bipyridine),[11] $[VOCl_3(py)_2]$[10] and $[VOCl_3(dmbipy)]$ (dmbipy = 4,4′-dimethyl-2,2′-bipyridine) all show $\nu(V{=}O)$ at 980 cm^{-1}, but none of these gave the desired product upon reaction with $N_2H_4\cdot 2HCl$ in alcohols. However, we did obtain new, relatively insoluble orange materials analysing for $VO(OR)Cl_2\cdot 2L$ (R = Me or Et). These all show $\nu(V{=}O)$ around 970 cm^{-1}.

The products of the reactions of $[VOCl_3]$ with tertiary phosphines, PR_3 (R = alkyl or aryl), were always of the form $[VCl_3(PR_3)_2]$, rather than the expected $[VOCl_3(PR_3)_2]$. Complexes of the former kind are accessible from VCl_3 itself.[12] Henderson *et al.*[13] obtained $[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$, characterised by X-ray crystallography, from $[VOCl_3]$ and PMe_2Ph (5 molar equivalents). The product obtained seems to depend on each of solvent, temperature and stoichiometry.

Sodium azide and $[ReCl_3(PR_3)_3]$ react to generate $[ReNCl_2(PR_3)_3]$,[10] and a bridging nitrido complex has been obtained from $[VBr_2(dmpe)_2]$ [dmpe = 1,2-bis(dimethylphosphino)ethane] and trimethylsilyl azide.[8] However, $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) and $[VCl_3(PMePh_2)_2]$[12] give only ill defined azido species upon reaction with Me_3SiN_3, and $[VCl_3(PMePh_2)_2]$[12] and $[VCl_3(PMe_2Ph)_2(thf)]$ (a new compound) do not react with NaN_3.

The new quinuclidine (qncd) adducts $[VOCl_3(qncd)]$ and $[VOCl_3(qncd)_2]$, and the $[VOCl_3]$ adducts mentioned above, do not produce nitrido complexes by reaction with $(Me_3Si)_2NH$ although the silazane has been used previously for this purpose.[14]

The reaction of $[VOCl_3]$ with $(Me_3Si)_2NH$ in the presence of 2 equivalents of PMe_2Ph produced a crystalline complex $[VNCl_2(PMe_2Ph)_2]$, our only fully characterised new nitrido complex. Its elemental analysis and IR and ^1H NMR spectra, and its high solubility in common organic solvents are all consistent with this formulation. It can be recrystallised from acetonitrile without becoming six-co-ordinate. The ^{31}P-$\{^1H\}$ NMR spectrum is a singlet, not diagnostic of structure, but by analogy with literature data on analogous species,[15] it is almost certainly square pyramidal with apical nitrogen and *trans*-phosphines. Homologous but insoluble complexes were obtained using bipy and dmbipy. Other phosphines (PEt_2Ph, PPh_3, $PMePh_2$, dmpe, $Ph_2PCH_2CH_2PPh_2$ or $Et_2PCH_2CH_2PEt_2$) produced oily (monophosphines) or insoluble (diphosphines) materials with a band assignable to $\nu(V{\equiv}N)$ at 1125–1130 cm^{-1}.

Although formally five-co-ordinate and unsaturated, the strong *trans* influence of the nitride in $[VNCl_2(PMe_2Ph)_2]$ prevents easy addition of a further ligand. We did succeed in producing an 'adduct' with PMe_2Ph, and also less well characterised 'adducts' with bipy and with dmbipy. An X-ray crystal-structure analysis of $VNCl_3(PMe_2Ph)_3$ showed it to be

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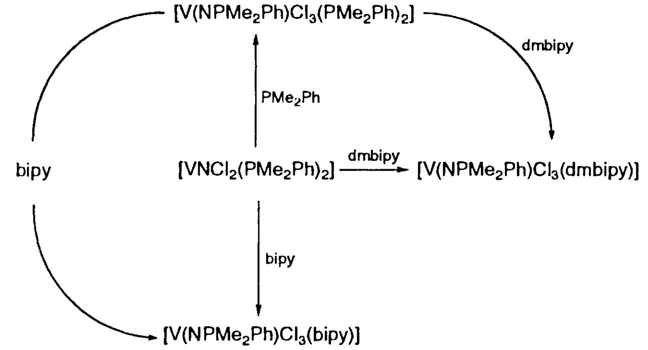
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: mmHg ≈ 133 Pa.

a phosphiniminato complex, [V(NPMe$_2$Ph)Cl$_3$(PMe$_2$Ph)$_2$], and so, presumably, are the other adducts (see Scheme 1).

We attempted to obtain suitable crystals of the monomeric nitrido complex for X-ray crystal-structure analysis. After several recrystallisations we finally obtained good crystals, but these were shown to be of [V(NPMe$_2$Ph)Cl$_3$(PMePh)$_2$]·H$_2$O, the water being adventitious, and emphasising the great sensitivity of many of these compounds to moisture.

Structures of [V(NPMe$_2$Ph)Cl$_3$(PMe$_2$Ph)$_2$] **1** *and* [V(NPMe$_2$Ph)Cl$_3$(PMe$_2$Ph)$_2$]·H$_2$O **2**.—Tables 1 and 2 list atomic coordinates for **1** and **2**, and Table 3 selected bond lengths and angles. Figs. 1 and 2 give views of the molecular structures. Both molecules are formally octahedral and six-co-ordinate with *trans* phosphines and meridional chlorides. At first sight the basic units are virtually superimposable. However, the water molecule in the solvate hydrogen bonds between chlorine atoms of adjacent molecules [Fig. 2 and Table 3(*d*)], between the central chlorine of a meridional set on vanadium and an external chlorine of the set on a vanadium neighbour. This produces a zigzag chain of phosphiniminato complexes, all of which have one 'free' chlorine. The three chlorines on any given vanadium are thus inequivalent, whereas in the non-solvated system the three are present as an equivalent pair plus a unique chlorine. In fact complex **1** possesses a crystallographically imposed mirror plane containing the chlorine atoms and the phosphiniminato ligand. The absence of this in complex **2** does not seem to be due to any obvious distortions, but only to the presence and packing of the water molecule.

In both molecules the central chlorine of the meridional three is more distant from vanadium (*ca.* 2.45 Å) than are the other



Scheme 1

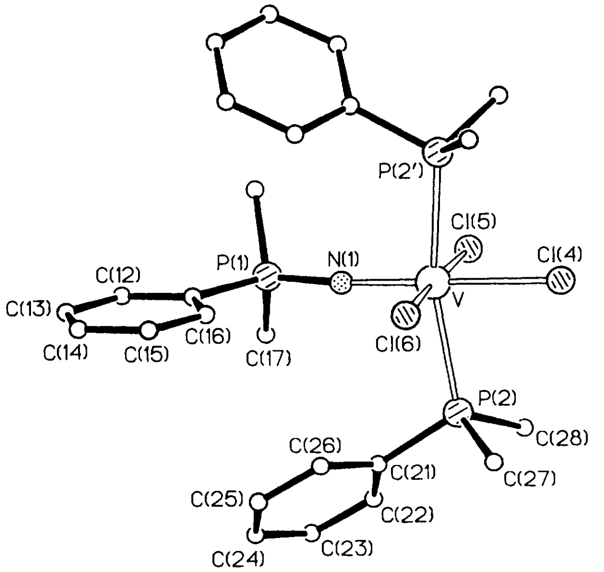


Fig. 1 View of a molecule of [V(NPMe$_2$Ph)Cl$_3$(PMe$_2$Ph)$_2$] **1**

Table 1 Final atomic coordinates (fractional × 10^4) for [V(NPMe$_2$Ph)Cl$_3$(PMe$_2$Ph)$_2$] **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
V	0	1719.2(8)	4568*
N(1)	0	2592(4)	6153(6)
P(1)	0	3043(1)	7835(2)
C(11)	0	4582(5)	7825(7)
C(12)	0	5182(6)	9150(7)
C(13)	0	6371(7)	9103(9)
C(14)	0	6953(6)	7779(10)
C(15)	0	6355(6)	6469(9)
C(16)	0	5177(6)	6480(8)
C(17)	1024(4)	2540(5)	8847(6)
P(2)	1840.2(9)	1612.3(9)	4278(2)
C(21)	2532(3)	2496(4)	5571(5)
C(22)	3214(3)	2044(5)	6560(7)
C(23)	3677(4)	2731(6)	7573(7)
C(24)	3489(5)	3876(6)	7585(9)
C(25)	2839(5)	4356(5)	6608(9)
C(26)	2351(4)	3654(4)	5595(7)
C(27)	2292(4)	2089(5)	2484(6)
C(28)	2346(5)	189(4)	4464(8)
Cl(4)	0	490(2)	2396(2)
Cl(5)	0	42(2)	6057(3)
Cl(6)	0	3331(1)	2929(2)

* The *z* coordinate of the vanadium atom was fixed at this value to define the cell *z* origin.

Table 2 Final atomic coordinates (fractional × 10^4) for [V(NPMe$_2$Ph)Cl$_3$(PMe$_2$Ph)$_2$]·H$_2$O **2** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
V	2500*	2191(4)	909(2)
N(1)	933(25)	2245(16)	1303(8)
P(1)	−762(11)	2279(6)	1576(3)
C(11)	−662(36)	2268(22)	2325(10)
C(12)	−1974(40)	2322(24)	2656(13)
C(13)	−1924(38)	2302(22)	3240(12)
C(14)	−575(40)	2193(22)	3498(12)
C(15)	754(43)	2116(22)	3199(13)
C(16)	716(38)	2140(22)	2595(12)
C(17)	−1873(32)	1270(16)	1310(11)
C(18)	−1782(38)	3353(18)	1361(13)
P(2)	2833(12)	383(5)	869(3)
C(21)	1493(37)	−314(20)	1287(12)
C(22)	428(34)	−901(19)	1009(12)
C(23)	−736(45)	−1325(22)	1359(12)
C(24)	−715(43)	−1194(21)	1932(12)
C(25)	377(40)	−643(24)	2199(13)
C(26)	1471(42)	−134(21)	1861(12)
C(27)	4640(29)	−43(23)	1161(12)
C(28)	2768(42)	−166(20)	150(9)
P(3)	2774(13)	3974(5)	772(3)
C(31)	1556(36)	4700(19)	1224(11)
C(32)	655(45)	5393(26)	1037(16)
C(33)	−239(46)	5930(26)	1388(13)
C(34)	−61(43)	5763(25)	1957(14)
C(35)	835(45)	5079(24)	2179(14)
C(36)	1684(43)	4563(20)	1800(12)
C(37)	4618(27)	4466(22)	939(12)
C(38)	2334(39)	4413(21)	52(9)
Cl(4)	4742(10)	2160(6)	289(3)
Cl(5)	1056(12)	2075(7)	55(3)
Cl(6)	4199(10)	2268(6)	1696(3)
O(7)	7897(46)	3144(23)	−109(14)

* The *x* coordinate of the vanadium atom was fixed at this value to define the cell *x* origin.

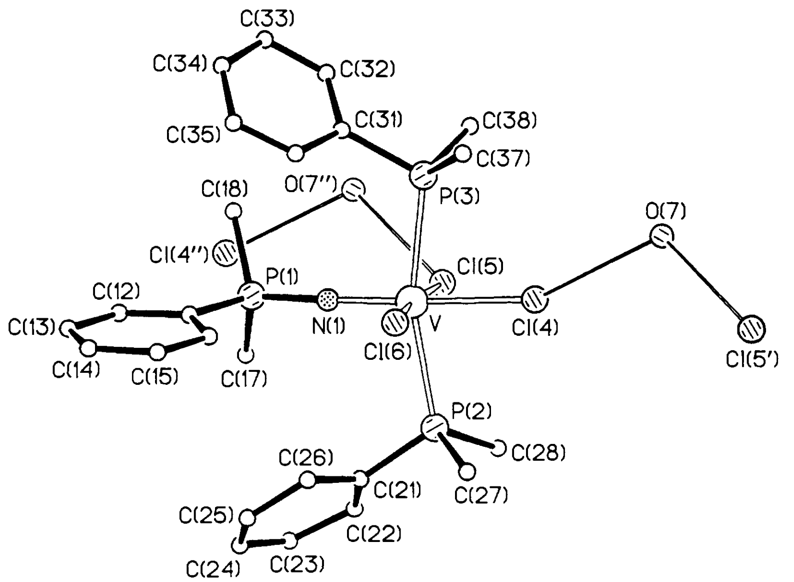


Fig. 2 View of a molecule of $[V(NPMe_2Ph)Cl_3(PMe_2Ph)_2]\cdot H_2O$ **2** with solvate water molecules linking molecules of **2** through hydrogen bonds

two (*ca.* 2.38 Å). We can ascribe this to the *trans* influence of the phosphiniminate. However, the vanadium–nitrogen distances, although not unreasonable for vanadium–nitrogen double bonds at *ca.* 1.7 Å, are significantly different. It is not at all clear why. The nitrogen–phosphorus bonds are much more nearly equal. Since the geometries and distances about the phosphiniminato-phosphorus atoms are reasonable similar, the effects of the secondary co-ordination of water would appear to be localised in the V–N bond. The reason is not obvious. The V–N stretching frequencies in both compounds are at 1100 cm^{-1}.

The only other phosphiniminato complex of vanadium in the literature is $[V(NPMePh_2)Cl_4(NCMe)]\cdot MeCN$.[16] Whatever formalism is adopted for the phosphiniminato ligand, this clearly has vanadium in an oxidation state one unit more positive than do our compounds. Our V–N separations [1.754(7) and 1.675(20) Å] are marginally longer than those in the two independent molecules [1.653(3) and 1.656(3) Å] in the reported species,[16] the P–N separations are much the same [1.604(5) and 1.64(2) compared to reported values of 1.660(3) and 1.667(3) Å], whereas our V–Cl separations, where comparable, are about 0.1 Å longer. All these are compatible with the lower oxidation state in our compounds.

Phosphiniminate can be regarded as bonding to a metal in limiting forms, such as $M{=}\overset{+}{N}{=}PR_3$ and $\overset{-}{M}{\equiv}\overset{+}{N}\longleftarrow \overset{+}{P}R_3$. Schomber, Ziller and Doherty[16] regard the vanadium–nitrogen bond as triple, although the V–N separation is slightly longer than in unequivocal vanadium nitrido-complexes.[5] On the other hand, the V–N stretching frequency in the phosphiniminato complexes is more than 100 cm^{-1} to higher wavenumbers than in the nitrido complexes. These data are, at first sight, incompatible, and will be discussed further below.

Alkylimido complexes.—Alkylimido complexes of vanadium are reasonably well documented. The silylimido complexes $[V(=NSiMe_3)\{N(SiMe_3)_2\}(OSiMe_3)]$ and $[V(=NSiMe_3)(OSiMe_3)]$ have played a central role, both as the first examples of vanadium imido complexes and as a source of further imido complexes.[17–20] The complexes $[V(NBu^t)Cl_3]$,[21] $[V(NMe)Cl_3]$[22] and $[V(NPh)Cl_3]$[22] have been known for some time, and were prepared by more or less complicated routes. Recently, Maata and co-workers[23] have used the reaction of $[VOCl_3]$ and aryl isocyanates to extend the range of arylimido-complexes, but they omitted to report on any reactions of PhNCO, presumably because $[V(NPh)Cl_3]$ has already been claimed.[22] The isocyanate reaction has been used successfully in rhenium and tungsten chemistry.[24] We report here some additional findings on imido complexes, obtained primarily by the isocyanate route, as well as the structure of a hydrolysis product, $[VOCl_2(py)_2]$.[25]

We investigated the reactions of $[VOCl_3]$ and RNCO (R = Me, Et, Bu^t or Ph) in refluxing benzene or toluene. The reaction of Bu^{t}NCO gives rise to the known green $[V(NBu^t)Cl_3]$ [ν(V=N) 1205 cm^{-1}].[21] The signal in the ^{1}H NMR spectrum assignable to the butyl group is observed at δ 1.61 in solution in CD_2Cl_2. The moisture-sensitive solid does not form adducts with PPh_3 or thf, but it does form one (1 : 1) with bipy. The green solid dissolves in benzene to give red solutions. This was observed by Preuss and Towae,[21] and a similar phenomenon has been reported for compounds $[V(NR)Cl_3]$ (R = aryl).[23] The complex $[V(NBu^t)Br_3]$ is monomeric in solution but the molecular weight of $[V(NBu^t)Cl_3]$ in solution in benzene is 1570 (229 required for the monomer). Simple polymerisation in solution may not be the complete explanation.

The compound [VO(salen)] [H$_2$salen = *N,N'*-ethylenebis(salicylideneimine)] does not react with Bu^{t}NCO, and $[VOCl_3(py)_2]$ yields new, green $[VCl_3(py)_2]$ (as it also does with EtNCO). The reaction of VCl_3 or $[VOCl_3]$ and py leads to $[VCl_3(py)_3]$.[26]

Reaction of $[VOCl_3]$ and PhNCO yields sublimable purple $[V(NPh)Cl_3]$, with properties very similar to those of the 4-tolyl homologues of Maata and co-workers.[23] However, the original claim[21] for $[V(NPh)Cl_3]$ described it as insoluble in all usual inert solvents, and it was never obtained pure. We doubt that it was ever obtained at all.

Reaction of $[VOCl_3]$ with MeNCO in toluene at reflux gave an orange solid which was clearly not $[V(NMe)Cl_3]$ on the basis of elemental analysis. The ^{1}H NMR spectrum (CD_3CN) showed a singlet at δ 3.33, and the $^{13}C-\{^1H\}$ NMR spectrum gave rise to two singlets at δ 30 and 50. On removing proton decoupling, the singlet at δ 30 became a quartet. Elemental analysis and the molecular weight are consistent with a formulation $(VNCMe_2)_2$, but this remains to be fully established.

The complex $[V(NMe)Cl_3]$, obtained from $[VOCl_3]$ and $(Me_3Si)_2NMe$, is a benzene-soluble brown crystalline material, with reasonable elemental analysis figures but two strong bands in the region characteristic of ν(V=N), at 985 and 920 cm^{-1}. The identity of this material is not absolutely confirmed. However, $[VOCl_3(py)_2]$ and $(Me_3Si)_2NMe$ gives a relatively insoluble green material which analyses for $[V(NMe)Cl_3(py)_2]$. The compound $[V(NMe)Cl_3(dmbipy)]$, also insoluble, was obtained analogously. These compounds display bands at 980 and 1120 cm^{-1}, respectively, which may be due to ν(V=N).

Table 3 Selected molecular dimensions in compounds **1** and **2**; bond lengths in Å, angles in °; e.s.d.s in parentheses

1		**2**	Atom labels in **2** if different from those in **1**
(*a*) About the V atom			
V–N(1)	1.754(5)	1.675(20)	
V–P(2)	2.529(1)	2.531(10)	
		2.510(9)	V–P(3)
V–Cl(4)	2.426(2)	2.469(8)	
V–Cl(5)	2.371(2)	2.388(8)	
V–Cl(6)	2.390(2)	2.391(7)	
N(1)–V–P(2)	96.5(*)	99.3(8)	
		96.2(8)	N(1)–V–P(3)
N(1)–V–Cl(4)	179.2(2)	177.1(7)	
N(1)–V–Cl(5)	91.0(2)	91.2(6)	
N(1)–V–Cl(6)	92.7(2)	95.4(7)	
P(2)–V–P(2′)	166.8(*)	164.5(3)	P(2)–V–P(3)
P(2)–V–Cl(4)	83.5(*)	82.3(3)	
P(2)–V–Cl(5)	91.0(*)	88.0(3)	
P(2)–V–Cl(6)	88.6(*)	90.0(3)	
		82.1(3)	P(3)–V–Cl(4)
		90.6(3)	P(3)–V–Cl(5)
		89.7(3)	P(3)–V–Cl(6)
Cl(4)–V–Cl(5)	88.3(1)	86.4(3)	
Cl(4)–V–Cl(6)	88.0(1)	87.0(3)	
Cl(5)–V–Cl(6)	176.3(1)	173.3(4)	
(*) E.s.d.s are less than 0.05°.			
(*b*) In the $NPMe_2Ph$ ligands			
N(1)–P(1)	1.604(5)	1.638(23)	
P(1)–C(11)	1.794(6)	1.764(23)	
P(1)–C(17)	1.770(5)	1.826(17)	
		1.817(18)	P(1)–C(18)
V–N(1)–P(1)	163.7(3)	169.4(13)	
N(1)–P(1)–C(11)	108.9(3)	110.1(13)	
N(1)–P(1)–C(17)	112.2(2)	109.9(12)	
C(11)–P(1)–C(17)	109.5(2)	111.3(13)	
		112.0(13)	N(1)–P(1)–C(18)
		108.1(14)	C(11)–P(1)–C(18)
C(17)–P(1)–C(17′)	104.4(3)	105.4(14)	C(17)–P(1)–C(18)

(*c*) In the PMe_2Ph ligands

	1, n = 2	2, n = 2	2, n = 3
P(n)–C(n1)	1.820(5)	1.824(30)	1.821(30)
P(n)–C(n7)	1.817(5)	1.845(19)	1.820(18)
P(n)–C(n8)	1.805(5)	1.855(18)	1.839(18)
V–P(n)–C(n1)	114.9(2)	115.5(10)	114.4(9)
V–P(n)–C(n7)	114.5(2)	114.0(11)	115.5(11)
C(n1)–P(n)–C(n7)	102.7(2)	101.3(14)	101.6(14)
V–P(n)–C(n8)	114.6(2)	116.0(9)	115.1(10)
C(n1)–P(n)–C(n8)	105.2(2)	104.6(15)	103.1(14)
C(n7)–P(n)–C(n8)	103.5(3)	103.6(15)	105.4(15)

(*d*) In the hydrogen bonds in compound **2**

O(7)···Cl(4)	3.26(4)	Cl(4)···O(7)··Cl(5′)	121.7(10)
O(7)···Cl(5′)	3.20(4)		

Cl(5′) is at 1 + *x*, *y*, *z*.

Finally, we investigated the reaction of [$VOCl_3$] and EtNCO in toluene at reflux. The product is a red, volatile oil, containing ethyl groups (^1H NMR spectroscopy), which may well be [V(NEt)Cl_3].

The green complex [V(NMe)Cl_3(py)$_2$] reacts with an excess of pyridine to form what appears to be [V(N=CH_2)Cl_2(py)$_3$], based upon the rather uninformative ^1H NMR spectrum and elemental analysis. Treatment with HCl regenerates the parent methylimido complex. Similar protonation/deprotonation reactions have already been observed with rhenium and tungsten.[27]

We attempted to obtain crystals of [V(N=CH_2)Cl_2(py)$_3$] suitable for X-ray crystal-structure analysis. Eventually after several recrystallisations we obtained pale blue crystals, which proved to be the known [$VOCl_2$(py)$_2$][25] {Found: C, 40.5; H, 3.80; N, 9.50. [V(NCH_2)Cl_2(py)$_3$] requires C, 49.6; H, 4.40; N, 14.5; [$VOCl_2(py)_2$] requires: C, 40.5; H, 3.40; N, 9.45%}. This was confirmed by the crystal-structure analysis which is described below. Evidently the oxophilic nature of vanadium(IV) caused hydrolysis, even though we took stringent steps to avoid this outcome.

Crystal and Molecular Structure of [$VOCl_2(py)_2$].—The vanadyl complex [$VOCl_2(py)_2$], whose atomic coordinates are in Table 4, is isostructural with the analogous nitride [$VNCl_2(py)_2$].[5,6] The metal atom is five-co-ordinate with a square-pyramidal co-ordination: the oxygen atom is in the apical position, with a V–O distance of 1.581(9) Å and the vanadium atom lies *ca.* 0.43 Å above the mean plane of the Cl_2N_2 base, Fig. 3. Dimensions in our complex (Table 5) are very similar to those reported for the nitride.

As in the nitride, the complex molecules are aligned along the two-fold symmetry axes, with a V=O ··· V=O ··· arrangement. Thus, an oxygen atom of a neighbouring molecule lies in the sixth, pseudo-octahedral co-ordination position on the vanadium atom but, at a distance of 2.588(9) Å, cannot be considered to be bonded to the vanadium atom. It may be that the alignment is simply a consequence of the packing of the pyridines, as already noted for the nitrides.[5,6] The related complex [$VOCl_2(NMe_3)_2$] has very similar bond lengths, although not such obvious V–O–V–O alignments.[28]

Molecules are tightly bound in the crystal, with some quite short intermolecular contacts, *e.g.* H(34) ··· Cl(2) 2.77 Å with an almost linear C–H ··· Cl hydrogen-bond type interaction. As noted for the nitride, a centre of symmetry relates the pyridine ring with another in a parallel overlapping arrangement.

Conclusions

Although vanadium will form nitrido- and alkylimido-complexes, as do molybdenum, tungsten and rhenium, they are, in fact, not as easily obtainable and are considerably more oxophilic. It is doubtful whether they are involved in the protonation/degradation to ammonia of dinitrogen bound to vanadium. We have been unable to discover facile syntheses of vanadium hydrazido(2−) complexes. Even those which are known are rather unusual.[29–31] Hydrazido(2−) complexes are key intermediates in the protonation of dinitrogen co-ordinated to molybdenum or tungsten.[32]

It is perhaps not surprising that vanadium, being a first transition series element, is not able easily to support vanadium–nitrogen triple bonds. In fact, the established vanadium–nitrogen double and triple bonds seem to be remarkably similar. The nitride nitrogen seems to be very basic, and polymerisation of the type V≡N→V is common. The imido-complexes are also often polymeric, and formal V–N double bonds are also very reactive. There are only two simple hydrazide(2−) complexes of vanadium,[29,31] and a further single bridging example.[30] They are also less likely to be involved in protonation reactions of dinitrogen co-ordinated to vanadium than in the parallel reactions involving molybdenum and tungsten.

Two further points are worthy of note. Complexes containing the vanadyl group, V=O, like those containing V≡N, also form chains in the solid state.[33] It seems that ν(V=O) in such chains occurs at *ca.* 880 cm^{-1}, whereas mononuclear five-co-ordinate species give rise to ν(V=O) between 900 and 1035 cm^{-1}.[33] The situation may be paralleled by nitrido complexes. Our complex [$VNCl_2(PMe_2Ph)_2$] has ν(V–N) at 1125 cm^{-1}. The polymeric compound [$VNCl_2(py)_2$] shows ν(V–N) at *ca.* 970 cm^{-1}, although no frequency has been quoted for the mononuclear nitride. Any correlation of frequency and structure needs to be substantiated.

Table 4 Final atomic coordinates (fractional × 10^4) for [$VOCl_2(py)_2$] with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
V	2500	2500	38(3)
O(1)	2500	2500	−1858(11)
Cl(2)	4014(2)	3669(1)	577(3)
N(3)	4352(7)	1697(5)	375(9)
C(31)	5498(9)	1813(6)	−535(12)
C(32)	6763(11)	1353(7)	−406(14)
C(33)	6829(11)	715(7)	716(15)
C(34)	5656(11)	576(6)	1698(13)
C(35)	4430(9)	1068(5)	1482(12)

Table 5 Molecular dimensions in [$VOCl_2(py)_2$]; bond lengths in Å, angles in °; e.s.d.s in parentheses

(*a*) About the V atom			
V–O(1)	1.581(9)	V–Cl(2)	2.329(2)
V–O(1′)	2.588(9)	V–N(3)	2.131(7)
O(1)–V–Cl(2)	101.1(1)	Cl(2)–V–N(3)	86.9(2)
O(1)–V–N(3)	97.6(2)	Cl(2)–V–N(3″)	90.2(2)
Cl(2)–V–Cl(2″)	157.8(1)	N(3)–V–N(3″)	164.9(3)
(*b*) In the py ligand			
N(3)–C(31)	1.314(10)	C(32)–C(33)	1.362(16)
N(3)–C(35)	1.343(11)	C(33)–C(34)	1.373(14)
C(31)–C(32)	1.370(13)	C(34)–C(35)	1.376(12)
V–N(3)–C(31)	119.3(6)	C(31)–C(32)–C(33)	117.9(10)
V–N(3)–C(35)	123.7(6)	C(32)–C(33)–C(34)	119.2(10)
C(31)–N(3)–C(35)	116.9(8)	C(33)–C(34)–C(35)	118.9(10)
N(3)–C(31)–C(32)	124.7(9)	N(3)–C(35)–C(34)	122.3(10)

Symmetry-related positions: (′) 0.5 − *x*, *y*, 0.5 + *z*; (″) 0.5 − *x*, 0.5 − *y*, *z*.

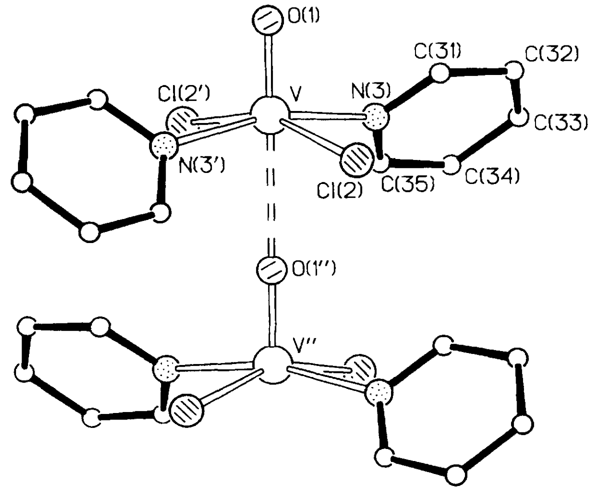


Fig. 3 Two molecules of [$VOCl_2(py)_2$] showing the V=O ··· V=O ··· alignment along a two-fold symmetry axis

Finally, the data reported here suggest that ν(V–N) may not be diagnostic for the formal vanadium–nitrogen bond type, V=N or V≡N. Some workers represent and speak of the vanadium–nitrogen bond as if it were triple, and V≡N may indeed define the system accurately.[16] It was observed some time ago that ν(Re≡N) in complexes such as [$ReNCl_2(PEt_2Ph)_2$] is at *ca.* 1030 cm^{-1}, at lower frequency than in imido complexes such as [$Re(NMe)Cl_3(PEtPh_2)_3$] (*ca.* 1100 cm^{-1}).[10] A similar phenomenon may exist in osmium–nitrogen chemistry.[34] Our phosphiniminato complexes seem to exhibit unexpectedly high values for ν(V=N). Formal vanadium–nitrogen double bonds are longer than vanadium–nitrogen triple bonds. This is also true in rhenium chemistry. Since vanadium is apparently loath to support simple vanadium–nitrogen triple bonds, it seems unwise to regard all these bonds as triple bonds or to expect a correlation of bond length and stretching frequency. The situation is obviously more complex.

Experimental

All manipulations were carried out using the Schlenk-tube technique under dry dinitrogen. The NMR spectra were obtained using a JEOL GSX-270 spectrometer. Magnetic moments were measured in solution in $CDCl_3$ by Evans' method.[35] Microanalyses were by Mr. C. J. Macdonald with a Perkin Elmer 2400 analyser. Molecular weights were determined by use of a Mechrolab vapour pressure osmometer.

(2,2'-Bipyridine)trichlorooxovanadium(v),[11] trichlorooxobis(pyridine)vanadium(v),[11] trichlorobis(methyldiphenylphosphine)vanadium(III),[12] and trichlorotris(tetrahydrofuran)vanadium(III)[36] were synthesised by literature methods.

Ammonium metavanadate, trichlorooxovanadium(v), 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, trimethylsilyl azide and quinuclidine were obtained commercially.

Preparation and Reactions.—Trichloro(4,4'-*dimethyl*-2,2'-*bipyridine*)*oxovanadium*(v). 4,4'-Dimethyl-2,2'-bipyridine (0.99 g, 5.32 mmol) was added to a solution of $[VOCl_3]$ (0.5 cm^3, 5.31 mmol) in CH_2Cl_2 (20 cm^3). The solution was stirred overnight at room temperature, and the solvent removed under vacuum. The product was isolated as a dark purple solid. Yield 62% Found: C, 39.5; H, 3.6; N, 7.9. $C_{12}H_{14}Cl_3N_2OV$ requires C, 40.0; H, 3.9; N, 7.8%. IR: ν(V=O) 980 cm^{-1}.

(2,2'-*Bipyridine*)*dichloro*(*ethoxo*)*oxovanadium*(v). The compound $[VOCl_3(bipy)]$ (1.15 g, 3.49 mmol) was stirred in ethanol (30 cm^3) for 1 h at room temperature. An orange solid resulted which was collected by filtration and dried under vacuum. Yield 46%. The filtrate was taken to dryness to obtain an oil which we were not able to solidify. Found: C, 42.1; H, 3.8; N, 7.4. $C_{12}H_{13}Cl_2N_2O_2V$ requires C, 42.5; H, 3.8; N, 8.2%. IR: ν(V=O) 970, ν(C–O) 1020, 1340 cm^{-1}. Due to the insolubility of this compound no NMR data could be obtained.

Dichloro(*ethoxo*)*oxobis*(*pyridine*)*vanadium*(v). The compound $[VOCl_3(py)_2]$ (0.51 g, 1.54 mmol) was stirred in ethanol (20 cm^3) for 1 h at room temperature. The product, an orange solid, was filtered off and dried under vacuum. Yield 60%. After removal of the solvent under vacuum the filtrate gave an oil which we were unable to solidify. Found: C, 42.3; H, 3.9; N, 7.6. $C_{12}H_{15}Cl_2N_2O_2V$ requires C, 42.2; H, 4.3; N, 8.2%. IR: ν(V=O) 970, ν(C–O) 1020, 1340 cm^{-1}. This compound is extremely insoluble and no NMR data could be obtained.

Dichloro(4,4'-*dimethyl*-2,2'-*bipyridine*)(*ethoxo*)*oxovanadium*(v). The compound $[VOCl_3(dmbipy)]$ (0.30 g, 1.61 mmol) was stirred in ethanol (20 cm^3) for 1 h at room temperature. The resulting orange solid was collected by filtration and dried under vacuum. Yield 74%. The filtrate was taken to dryness to yield an intractable oil. Found: C, 45.5; H, 5.1; N, 7.3. $C_{14}H_{19}Cl_2N_2O_2V$ requires C, 45.5; H, 5.1; N, 7.6%. IR: ν(V=O) 970, ν(C–O) 1030, 1340 cm^{-1}. No NMR data could be obtained due to solubility problems.

(2,2'-*Bipyridine*)*dichloro*(*methoxo*)*oxovanadium*(v) This compound was obtained by the reaction of $[VOCl_3(bipy)]$ and methanol in a similar procedure to that described above. Yield 65% Found: C, 40.5; H, 3.4; N, 8.1. $C_{11}H_{11}Cl_2N_2O_2V$ requires C, 40.6; H, 3.4; N, 8.6%. IR: ν(V=O) 970, ν(C–O) 1150, 1380 cm^{-1}.

Dichloro(*methoxo*)*oxobis*(*pyridine*)*vanadium*(v). This compound was prepared by reaction of $[VOCl_3(py)_2]$ with methanol in the same way as the analogous complexes above. Yield 66%. Found: C, 40.1; H, 3.8; N, 8.3. $C_{11}H_{13}Cl_2N_2O_2V$ requires C, 40.4; H, 4.0; N, 8.6%. IR: ν(V=O) 970, ν(C–O) 1150, 1380 cm^{-1}.

Dichloro(4,4'-*dimethyl*-2,2'-*bipyridine*)(*methoxo*)*oxovanadium*(v). This compound was prepared by reaction of $[VOCl_3(dmbipy)]$ with methanol using the procedure described above. Yield 53%. Found: C, 43.9; H, 4.75; N, 7.6. $C_{13}H_{17}Cl_2N_2O_2V$ requires C, 43.95; H, 4.8; N, 7.9%. IR: ν(V=O) 970, ν(C–O) 1150, 1380 cm^{-1}. No NMR data could be obtained for the last three compounds due to solubility problems.

Trichlorobis(*dimethylphenylphosphine*)(*tetrahydrofuran*)*vanadium*(III). The compound $[VCl_3(thf)_3]$ (2 g, 5.35 mmol) was dissolved in CH_2Cl_2 (30 cm^3) and PMe_2Ph (2.28 cm^3, 16.05 mmol) added. The mixture was stirred overnight at room temperature, and the solvent then removed under vacuum. The residue was solidified with diethyl ether and a brown precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*. The product was recrystallised from CH_2Cl_2–Et_2O–hexane as orange crystals. Found: C, 47.1; H, 5.8. $C_{20}H_{30}Cl_3OP_2V$ requires: C, 47.5; H, 5.9. The ^1H NMR spectrum in CD_2Cl_2 consists of broad signals at δ 2.15 (CH_3) and 7.23, 7.60 (C_6H_5). The thf molecule gives rise to resonances at δ 1.7 and 3.8.

Trichlorobis(*triphenylphosphine*)*vanadium*(III)–*dichloromethane* (1/1). A solution of $[VOCl_3]$ (0.5 cm^3, 5.3 mmol) in CH_2Cl_2 was treated with 2 equivalents of triphenylphosphine and the reaction mixture stirred at room temperature overnight. The solution was taken to dryness and the residue solidified with diethyl ether. The solids obtained were recrystallised from CH_2Cl_2–Et_2O–hexane. Yield 22%. Found: C, 58.1; H, 4.5. $C_{19}H_{17}Cl_5P_2V$ requires C, 57.9; H, 4.2%. The ^{31}P-{^1H} NMR spectrum in CD_2Cl_2 shows a singlet at δ − 40.69. The ^1H NMR spectrum in CD_2Cl_2 has broad peaks in the region of the phenyl groups (δ 7.83, 7.95). The ^1H NMR spectrum in CD_3CN, apart from the peaks due to the phenyl groups, has a peak at δ 5.32 which is assigned to CH_2Cl_2. However, an accurate integration could not be obtained because the signals are rather broad.

Trichlorobis(*dimethylphenylphosphine*)*vanadium*(III)–*dichloromethane* (1/1). This compound was prepared similarly and on the same scale to that described above. Yield 38%. Found: C, 39.4; H, 5.45. $C_{17}H_{24}Cl_5P_2V$ requires: C, 39.35; H, 4.6%. The ^1H NMR spectrum in CD_2Cl_2 has broad peaks at δ 2 (CH_3) and 7.41, 7.67 (C_6H_5). The presence of CH_2Cl_2 was confirmed by a peak at δ 5.3 in the ^1H NMR spectrum of this compound in CD_3CN. Again, no accurate integration was obtained.

Trichlorooxo(*quinuclidine*)- *and trichlorooxobis*(*quinuclidine*)-*vanadium*(v). Quinuclidine (1.2 g, 10.8 mmol) was added to a solution of $[VOCl_3]$ (0.5 cm^3, 5.31 mmol) in CH_2Cl_2 (30 cm^3). The solution was stirred overnight at room temperature. A brown solid was filtered off, washed with CH_2Cl_2 and dried under vacuum. Yield 35%. Found: C, 29.85; H, 4.6; N, 4.8. $C_7H_{13}Cl_3NOV$ requires: C, 29.55; H, 4.6; N, 4.9%. IR: ν(V=O) 980 cm^{-1}. This is the mono(quinuclidine) adduct. The filtrate was taken to dryness, and the residue taken up with CH_2Cl_2 and layered with diethyl ether–hexane. From this solution a pale pink solid was obtained which was filtered off, washed with Et_2O and then hexane, and dried under vacuum. Yield 30%. Found: C, 42.1; H, 6.9; N, 6.3. $C_{14}H_{26}Cl_3N_2OV$ requires C, 42.5; H, 6.6; N, 7.1%. IR: ν(V=O) 980 cm^{-1}. This corresponds to the bis(quinuclidine) adduct.

Dichlorobis(*dimethylphenylphosphine*)*nitridovanadium*(v). A solution of $[VOCl_3]$ (0.5 cm^3, 5.31 mmol) in thf (20 cm^3) was treated with $(Me_3Si)_2NH$ (1.11 cm^3) in the presence of PMe_2Ph (1.52 cm^3). The mixture was stirred at room temperature overnight. A yellow solid was filtered off, washed with thf and then Et_2O, and dried under vacuum. The product was dissolved in MeCN at reflux temperature, and the solution left to cool slowly to room temperature to obtain the nitride as yellow needles. Yield 78%. Found: C, 46.9; H, 5.9; N, 3.3. $C_{16}H_{22}Cl_2NP_2V$ requires C, 46.60; H, 5.4; N, 3.35%. This compound has a band at 1125 cm^{-1} in the IR spectrum assignable to ν(V–N). The ^1H NMR spectrum consists of broad peaks in the region of methyl groups (δ 2.18) and the phenyl groups (δ 7.14 and 7.60). The ^{31}P-{^1H} NMR spectrum consists of a sharp singlet at δ −99.50 with respect to $P(OMe)_3$.

$[V(NPMe_2Ph)Cl_3(PMe_2Ph)_2]$. The compound $[VNCl_2(PMe_2Ph)_2]$ (0.54 g, 1.31 mmol) in CH_2Cl_2 (20 cm^3) was treated with PMe_2Ph (0.17 cm^3) and the reaction mixture stirred at reflux temperature for 4 h. The solvent was removed under vacuum and the product obtained as an orange-brown solid. The product was dissolved in CH_2Cl_2 at reflux temperature, left to cool slowly to room temperature, and held at −20 °C for one week. Orange-brown crystals were obtained. Yield 42%. Found: C, 49.0; H, 5.35; N, 2.25. $C_{24}H_{33}Cl_3NP_3V$ requires C, 49.2; H, 5.65; N, 2.4%. The phosphiniminato group has a band at *ca.* 1100 cm^{-1} in the IR spectrum.

$[V(NPMe_2Ph)Cl_3(bipy)]$. The compound $[VNCl_2(PMe_2Ph)_2]$ (0.86 g, 2.1 mmol) was dissolved in MeCN and bipy (0.33 g, 2.11 mmol) added. The reaction mixture was heated under reflux for 3 h. A yellow solid was obtained which was collected by filtration, washed with Et_2O and dried under vacuum. The filtrate was taken to dryness to obtain an oil which we were not able to solidify. The product is very insoluble in common solvents and it was very difficult to purify. Found: C, 43.5; H, 4.3; N, 9.5. $C_{18}H_{19}Cl_3N_3PV$ requires C, 46.4; H, 4.1; N, 9.0%. By Soxhlet extraction with CH_2Cl_2 we obtained a sample approximately 96% pure which analyses as: C, 44.6; H, 4.5; N, 9.5%. Yield 28%. The phosphiniminato group has a band at *ca.* 1100 cm^{-1} in the IR spectrum.

$[V(NPMe_2Ph)Cl_3(dmbipy)]$. The compound $[VNCl_2(PMe_2Ph)_2]$ (0.53 g, 1.29 mmol) in CH_2Cl_2 (20 cm^3) was treated with dmbipy (0.25 g, 1.34 mmol) and the mixture stirred for 3 h at reflux temperature. The solution was then taken to dryness and a yellow solid obtained. This product was shown to be very air-sensitive and insoluble in common solvents. Dichloromethane (10 cm^3) was added and the suspension stirred at reflux for 1 h. Then it was filtered off and the filtrate layered with hexane and cooled in the freezer. A yellow precipitate was collected by filtration, washed with hexane and dried under vacuum. Yield 66%. Found: C, 47.0; H, 4.6; N, 7.8. $C_{20}H_{25}Cl_3N_3PV$ requires: C, 48.4; H, 5.0; N, 8.5%. The phosphiniminato group shows a band at 1100 cm^{-1} in the IR spectrum.

The last two phosphiniminato complexes were also obtained by reaction of $[V(NPMe_2Ph)Cl_3(PMe_2Ph)_2]$ with bipy and dmbipy. Thus, $[V(NPMe_2Ph)Cl_3(PMe_2Ph)_2]$ (0.45 g, 0.77 mmol) in thf (20 cm^3) was treated with bipy (0.15 g, 0.97 mmol) and the mixture stirred at room temperature for 3 h. The yellow product was filtered off, washed with thf and then Et_2O, and dried under vacuum. Yield 45%. Found: C, 43.3; H, 4.3; N, 7.8. After Soxhlet extraction with CH_2Cl_2: C, 44.4; H, 4.2, N, 8.5. $C_{18}H_{19}Cl_3N_3PV$ requires C, 46.4; H, 4.1; N, 9.0%.

The same procedure was employed to prepare $[V(NPMe_2Ph)Cl_3(dmbipy)]$ from $[V(NPMe_2Ph)Cl_3(PMe_2Ph)_2]$ and dmbipy. Yield 52%. Found: C, 47.2; H, 4.4; N, 7.9. $C_{20}H_{25}Cl_3N_3PV$ requires C, 48.4; H, 5.0; N, 8.5%.

(tert-*Butylimido*)*trichlorovanadium*(V). The compound $[VOCl_3]$ (0.5 cm^3, 5.31 mmol) was treated with Bu^tNCO (0.61 cm^3, 5.34 mmol) in benzene (20 cm^3). The mixture was stirred under reflux for 2 h. The solution was then taken to dryness and a green solid obtained. This solid was collected by filtration, washed with Et_2O and dried under vacuum. Yield 0.82 g. Found: C, 21.5; H, 4.2; N, 5.8. $C_4H_9Cl_3NV$ requires C, 21.0; H, 4.0; N, 6.1%). Proton NMR (CD_2Cl_2): δ 1.61 (s); IR: ν(V=N) 1205 cm^{-1}; *M ca.* 1570.

Trichloro(*phenylimido*)*vanadium*(V). The compound $[VOCl_3]$ (1 cm^3, 10.62 mmol) was treated with PhNCO (1.2 cm^3, 11.04 mmol) in toluene (20 cm^3). The reaction mixture was stirred at reflux temperature for 2 h. The solvent was then removed under vacuum and a purple solid obtained. This solid was filtered off, washed with Et_2O and dried under vacuum. The product was purified by sublimation at 0.01 mmHg and large dark purple crystals were collected. Yield 1.65 g. Found: C, 30.6; H, 2.4; N, 5.5. $C_6H_5Cl_3NV$ requires C, 29.0; H, 2.0; N, 5.6%. Proton NMR (CD_2Cl_2): δ 7.35 (s); IR: ν(V=N) 1170 cm^{-1}; *M* 1580.

Trichloro(*ethylimido*)*vanadium*(V). The compound $[VOCl_3]$ (1 cm^3, 10.62 mmol) was treated with EtNCO (1 cm^3, 12.64 mmol) in benzene (20 cm^3) and the mixture stirred at room temperature for 3 h. The temperature was then raised slowly until reflux temperature and the reaction mixture stirred for a further 2 h. The resulting solution was taken to dryness to obtain an exceedingly air-sensitive, volatile red oil. We were unable to solidify the residue. It was dissolved in CH_2Cl_2 (10 cm^3) for ^1H NMR spectroscopy. The protons from the ethyl group were identified at δ 1.17 (CH_3) and 3.82 (CH_2) as broad singlets. The IR spectrum of the residue has a band at *ca.* 1200 cm^{-1} which can be assigned to ν(V=N).

The solution of $[V(NEt)Cl_3]$ in CH_2Cl_2 was treated with an excess of pyridine (3.4 cm^3) and the mixture stirred at room temperature for 3 h. After that time the solution was filtered through Celite and the filtrate taken to dryness. The residue was taken up with CH_2Cl_2 at reflux temperature, and the resulting solution filtered through Celite. A sample from the filtrate was analysed by ^1H NMR spectroscopy: δ 1.2 (t of d, CH_3), 3.35 (d, CH_2), 3.20 (q, CH_2), 3.92 (q, CH), 3.83 (t, CH).

Reaction of $[VOCl_3]$ *with* MeNCO. The compound $[VOCl_3]$ (0.5 cm^3, 5.31 mmol) in toluene (20 cm^3) was treated with MeNCO (0.32 cm^3, 5.42 mmol). The mixture was heated under reflux for 2 h and then the solvent removed under vacuum. An orange-brown solid was obtained. Yield 0.44 g. Found: C, 31.7; H, 5.1; N, 12.7. CH_3Cl_3NV requires C, 6.4; H, 1.6; N, 7.5%. It was clear that the compound was not $[V(NMe)Cl_3]$. The ^1H NMR spectrum (CD_3CN) shows a singlet at δ 3.33. The $^{13}C-\{^1H\}$ NMR spectrum consists of two singlets at δ 30 and 150. Undecoupling of the ^{13}C NMR splits the singlet at δ 30 into a quartet while the singlet at δ 150 remains unchanged. [*M* ca. 300. $(C_3H_6NV)_n$ requires C, 33.6; H, 5.6; N, 13.1%.]

Trichlorobis(*pyridine*)*vanadium*(III). The compound $[VOCl_3(py)_2]$ (0.89 g, 2.7 mmol) in toluene (30 cm^3) was treated with Bu^tNCO (0.46 cm^3) and the reaction mixture stirred at room temperature for 2 h. Then the temperature was raised slowly to 80 °C. A brown precipitate was filtered off and the filtrate taken to dryness. The residue, an intractable oil, was discarded. The solid was dissolved in CH_2Cl_2 at reflux temperature and the resulting solution filtered. The filtrate was cooled in the freezer overnight. A microcrystalline solid was obtained which was collected by filtration, washed with CH_2Cl_2, then Et_2O, and dried under vacuum. Yield < 15%. Found: C, 37.9; H, 3.4; N, 8.8. $C_{10}H_{10}Cl_3NV$ requires C, 38.0; H, 3.2; N, 8.9%. Proton NMR (CD_2Cl_2): δ 7.19 (m).

Alternatively, $[VOCl_3(py)_2]$ (1.5 g, 4.52 mmol) in toluene (30 cm^3) was treated with EtNCO (0.5 cm^3, 6.32 mmol) and the mixture stirred at room temperature for 2 h. The temperature was then raised slowly to reflux temperature and the mixture stirred for a further 1 h. A green precipitate was filtered off, washed with Et_2O and dried under vacuum. The filtrate was taken to dryness to obtain an oil which we were unable to solidify. Found: C, 37.6; H, 3.5; N, 8.4%. The product was again $[VCl_3(py)_2]$.

Trichloro(*4,4′-dimethyl-2,2′-bipyridine*)(*methylimido*)*vanadium*(V). The compound $[VOCl_3(dmbipy)]$ (0.64 g, 1.8 mmol) in toluene (20 cm^3) was treated with $(Me_3Si)_2NMe$ (0.4 cm^3) and the mixture stirred at reflux temperature for 1 h. A green precipitate was collected by filtration, washed with Et_2O and dried under vacuum. Yield 0.45 g. Found: C, 42.4; H, 4.3; N, 11.0. $C_{13}H_{17}Cl_3N_3V$ requires C, 41.9; H, 4.6; N, 11.3%. This compound is insoluble in common solvents and therefore no NMR data could be obtained.

Trichloro(*methylimido*)*bis*(*pyridine*)*vanadium*(V). The compound $[VOCl_3(py)_2]$ (0.72 g, 2.2 mmol) in toluene (20 cm^3) was treated with $(Me_3Si)_2NMe$ (0.5 cm^3) and the mixture stirred at room temperature for 1 h. A green precipitate was filtered off, washed with diethyl ether and dried under vacuum. Yield 0.32 g. Found: C, 37.6; H, 4.0; N, 10.9. $C_{11}H_{13}Cl_3N_3V$ requires C, 38.3; H, 3.8; N, 12.2%. The filtrate was cooled in the freezer and green crystals were obtained (Found: C, 37.6; H, 3.9; N, 11.2%). The ^1H NMR spectrum in CD_3CN consists of broad peaks at δ 2.32 (s, CH_3) and 7.16 (m, C_5H_5N) due to coupling with vanadium. This compound is relatively insoluble in common solvents, and we were unable to prepare a sample concentrated enough to be

Table 6 Experimental crystallographic details and crystal data

Compound	$[V(NPMe_2Ph)Cl_3(PMe_2Ph)_2]$	$[V(NPMe_2Ph)Cl_3(PMe_2Ph)_2]\cdot H_2O$	$[VOCl_2(py)_2]$
Elemental formula	$C_{24}H_{33}Cl_3NP_3V$	$C_{24}H_{33}Cl_3NP_3V\cdot H_2O$	$C_{10}H_{10}Cl_2N_2OV$
M	585.8	603.8	296.0
Crystal colour, shape	Orange-brown, rectangular prismatic needles	Very fine, pale yellow rectangular prismatic needles	Fine, pale blue needles in rosette formation
Crystal size/mm	0.75 × 0.14 × 0.12	0.20 × 0.07 × 0.07	0.67 × 0.07 × 0.07
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pmn2_1$ (no. 31)	$P2_1cn$ (equiv. to no. 33)	*Pccn* (no. 56)
a/Å	13.653(6)	8.888(1)	9.228(2)
b/Å	11.656(2)	13.893(2)	15.471(9)
c/Å	9.012(2)	23.517(2)	8.338(12)
U/Å	1434.1	2903.9	1190.3
Z	2	4	4
D_c/g cm^{-3}	1.356	1.381	1.652
F(000)	606	1252	596
μ(Mo-Kα)/cm^{-1}	7.9	7.9	12.4
λ(Mo-Kα)/Å	0.710 69	0.710 69	0.710 69
Mounting	Under N_2, on glass fibre coated with epoxy resin	Under N_2, in capillaries	Under N_2, in capillaries
On CAD4 diffractometer:			
No. of reflections centred for cell dimensions	24	25	25
θ Range/°	14–15	5–10*	6–10*
θ_{max} for data collection/°	25	20	22
Corrections on diffraction intensities:			
Lorentz-polarisation	Yes	Yes	Yes
Deterioration	Yes	No	No
Absorption	No	No	Yes
Negative intensities	Yes	Yes	Yes
No. of unique reflections	1409	1470	728
Structure determination	Direct methods in SHELXS for V atom. Then Fourier and Fourier difference syntheses	Automated Patterson (SHELXS) for V co-ordination sphere. Then Fourier difference maps	SHELXS—both automated Patterson and direct methods
Thermal parameters:			
Anisotropic atoms	All non-H atoms	V, P, Cl atoms	All non-H atoms
Isotropic atoms	H atoms	C, N, O, H atoms	H atoms
Hydrogen atoms:			
Positions	Idealised positions, Me groups staggered	Phenyl, idealised positions; Methyl, constrained	Idealised
Thermal parameters	U_{iso} free	Riding U_{iso}	U_{iso} free
Refinement:			
R	0.039	0.068	0.080
R_g	0.039	0.086	0.097
No. of reflections with $I > n\sigma_I$	1409	827	617
n	0	2	1
g in weighting scheme $w = (\sigma_F^2 + gF^2)^{-1}$	0	0.004 71	0.01
Highest peaks in final difference map/e Å^{-3}	*ca.* 0.35, close to V atoms	*ca.* 0.7, close to V atoms	*ca.* 0.7, close to V and O atoms

* These crystals were small, do not diffract strongly and have rather low θ limits of measurable diffraction intensity. Hence the θ angles of reflections selected for the determination of cell parameters were low, and the final *R* factors relatively high, for these two complexes.

analysed by ^{13}C NMR spectroscopy. The IR spectrum shows bands at 980 and 1120 cm^{-1} which can be assigned to ν(V=N).

Crystal-structure analyses.—The structure determination of $[VOCl_2(py)_2]$ is described below. The procedures for the other structure determinations followed this closely and the methods and results are summarised in Table 6 together with the crystal data for the three complexes.

Crystal-structure analysis of $[VOCl_2(py)_2]$ The complex crystallised in rosettes of fine, pale blue needles which were air-sensitive. Several single needles were mounted, under dinitrogen, in glass capillaries for photographic examination which showed all crystals to have streaky diffraction spots. The best crystal was transferred to an Enraf–Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (from the goniometer settings of 25 reflections, θ = 6–10°, each centred in four orientations) and for measurement of diffraction intensities (to θ_{max} 22°).

The intensity data were corrected for Lorentz-polarisation effects, absorption (by semi-empirical Ψ-scan methods) and to eliminate negative net intensity measurements (by Bayesian statistical methods). No deterioration correction was necessary. 728 Unique reflections were read into the SHELX system[37] where the structure was solved by both direct methods and automated Patterson methods in SHELXS.[38] Refinement, by full-matrix least-squares methods, with all non-H atoms allowed anisotropic thermal parameters and with hydrogen atoms included in idealised positions with freely refined isotropic thermal parameters, converged with $R = 0.080$ and $R_g = 0.097$[37] for 617 reflections (those with $I > \sigma_I$) weighted $w = (\sigma_F^2 + 0.01\,F^2)^{-1}$.

The major peaks in the final difference map were close to the vanadium and oxygen atoms, with heights of *ca.* 0.7 e Å^{-3}.

Scattering factors for neutral atoms were taken from ref. 39. Computer programs used are those noted above and in Table 4 of ref. 40 and were run on the MicroVAX II computer in this Laboratory.

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