Formation of Spirocyclic Imidophosphinato Complexes: Crystal Structures of $[V(OPPh_2NPPh_2O)_2O]$ and $[Mo(NPPh_2NPPh_2O)_2Cl_2]$†

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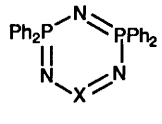
Treatment of tetrahydrofuran (thf) solutions of $[V(NPPh_2NPPh_2N)Cl_2]$ **1b** with Bu^{t}OH, LiOBu^t or $NaOSiPh_3$ affords in small yields the spirocyclic vanadyl complex $[V(OPPh_2NPPh_2O)_2O]$ **2**. This complex is formed in nearly quantitative yield from $[VOCl_2(thf)_2]$ and $Na[OPPh_2NPPh_2O]$. It crystallizes in the monoclinic space group $P2_1/c$ with a = 1572.0(8), b = 1056.3(5), c = 2685.0(13) pm, β = 94.30(2)° and Z = 4. The structure was refined to R = 0.033, R' = 0.044. The nitrogen atoms in **1b** adjacent to the metal have been replaced by oxygen atoms during alcoholysis. The V atom has a square-pyramidal geometry. The d^1 electronic state was confirmed by ESR measurements. Reaction of $MoOCl_4$ and $[H_2NPPh_2NPPh_2NH_2]Cl$ yields the already known $[Mo(NPPh_2NPPh_2N)Cl_3]$ **1a** and the spirocyclic molybdenum compound $[Mo(NPPh_2NPPh_2O)_2Cl_2]$ **3**. The 1:1 MeCN adduct of **3** crystallizes in the acentric space group $P1$ with a = 1087.1(5), b = 1156.4(6), c = 1166.5(6) pm, α = 82.86(2), β = 68.26(2), γ = 64.15(2)° and Z = 1. The Mo atom has a distorted-octahedral geometry with short Mo–N bond lengths (average 177.8 pm).

Metal chelates have been found to be useful catalysts in organic reactions.[1] Their applications are highly dependent on the nature of the metal, its oxidation state and the nature of the ligand. Our interest was in preparing metallaphosphazenes and studying their general and catalytic properties. Recently, we have reported on the synthesis of metallatriazadiphosphorines **1** from the reaction of $[H_2NPPh_2NPPh_2NH_2]Cl$ with metal halides or metal nitride halides in their highest oxidation state, or by passing chlorine through solutions containing lower-valent metal halides.[2] In a previous paper[3] we have outlined studies of the reactions of $[Mo(NPPh_2NPPh_2N)Cl_3]$ **1a** with Bu^{t}OH and Ph_3SiOH leading to cleavage of the

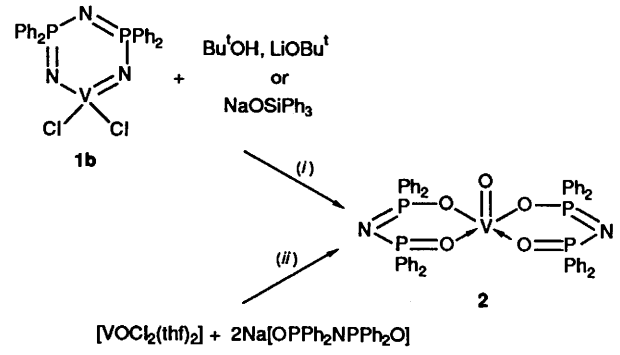


1a X = $MoCl_3$
1b X = VCl_2

Mo–N–P units and subsequent formation of Mo–O–P moieties. In this context and for sake of comparison, the alcoholysis of $[V(NPPh_2NPPh_2N)Cl_2]$ **1b** and the reaction of $[H_2NPPh_2NPPh_2NH_2]Cl$ with $MoOCl_4$ have been studied.

Results and Discussion

The reaction of the compound $[Mo(NPPh_2NPPh_2N)Cl_3]$ **1a** with Bu^{t}OH or Ph_3SiOH affords imidodiphosphinato complexes of molybdenum, where the N atoms of **1a** adjacent to the Mo have been replaced by O atoms.[3] In order to get more insight into the parameters affecting this exchange reaction, we have undertaken studies of related metallatriazadiphosphorines.



Scheme 1 (*i*) thf, 6–18% yield; (*ii*) thf, −2NaCl, 97% yield

The six-membered ring complex $[V(NPPh_2NPPh_2N)Cl_2]$ **1b**[2] was treated with Bu^{t}OH, LiOBu^t or $NaOSiPh_3$, respectively to yield the bicyclic vanadyl bis(imidodiphosphinate) complex **2**. In each case complex **2** could only be isolated in rather low yield (6–18%, referred to P) (Scheme 1). This complex is sparingly soluble in hot MeCN, $MeNO_2$ and $MeCO_2H$. It exhibits a strong absorption (965 cm^{-1}) in the IR spectrum in the range expected for V=O groups. The ^{31}P NMR spectrum of a solution of **2** in MeCN shows a broad single resonance at δ 28.2 (half-linewidth 210 Hz). The molecular ion M^+ was observed in the mass spectrum at m/z 899.

Structure of Compound **2**.—Suitable crystals for a structural analysis were obtained by recrystallization of the crude product

† Bis(*N*-diphenylphosphoryl-*P*,*P*-diphenylphosphinimidato-κ^2O,O')-oxovanadium(IV) and dichlorobis(3-oxo-1,1,3,3-tetraphenyl-1λ^5,3λ^5-diphosphazenylimido-κ^2N,O)molybdenum(VI).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.
Non-SI unit employed: G = 10^{-4} T.

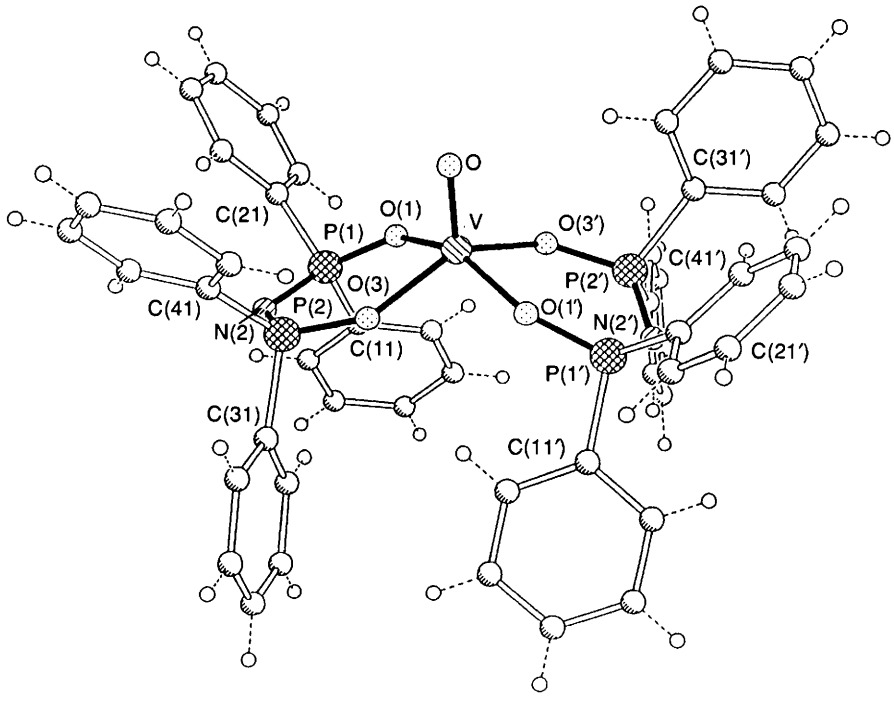


Fig. 1 The molecule of compound **2** with the unique atoms labelled

Table 1 Selected bond lengths (pm) and angles (°) for compound **2**

V–O	157.5(2)	V–O(1)	198.2(2)
V–O(3)	198.4(2)	V–O(1′)	198.7(2)
V–O(3′)	197.7(2)	O(1)–P(1)	151.9(2)
P(1)–N(2)	158.9(2)	P(1)–C(11)	179.9(3)
P(1)–C(21)	180.1(2)	N(2)–P(2)	158.6(2)
P(2)–O(3)	152.7(2)	P(2)–C(31)	180.9(3)
P(2)–C(41)	179.9(3)	O(1′)–P(1′)	152.6(2)
P(1′)–N(2′)	158.6(2)	P(1′)–C(11′)	179.6(3)
P(1′)–C(21′)	181.0(2)	N(2′)–P(2′)	159.2(2)
P(2′)–O(3′)	152.9(2)	P(2′)–C(31′)	180.1(3)
P(2′)–C(41′)	179.9(3)		
O–V–O(1)	103.7(1)	O–V–O(3)	108.8(1)
O(1)–V–O(3)	87.6(1)	O–V–O(1′)	104.0(1)
O(1)–V–O(1′)	152.3(1)	O(3)–V–O(1′)	83.9(1)
O–V–O(3′)	107.6(1)	O(1)–V–O(3′)	82.5(1)
O(3)–V–O(3′)	143.6(1)	O(1′)–V–O(3′)	88.8(1)
V–O(1)–P(1)	137.3(1)	O(1)–P(1)–N(2)	115.7(1)
P(1)–N(2)–P(2)	123.7(1)	N(2)–P(2)–O(3)	117.1(1)
V–O(3)–P(2)	135.4(1)	V–O(1′)–P(1′)	135.9(1)
O(1′)–P(1′)–N(2′)	115.5(1)	P(1′)–N(2′)–P(2′)	124.2(1)
N(2′)–P(2′)–O(3′)	115.1(1)	V–O(3′)–P(2′)	135.2(1)

from hot MeCN. The molecular structure of compound **2** is shown in Fig. 1 and selected bond distances and angles in Table 1. The square-pyramidal co-ordination of the V atom is a typical feature of vanadyl compounds.[4] Atoms O(1), O(3), O(3′), O(1′) are displaced from the least-squares plane passing through them by not more than 7.1 pm, and the V atom lies 54.6 pm above this plane. The apical V–O bond length [157.5(2) pm] may be compared with that (157.1 pm) in $[VO(acac)_2]$[5] (acac = acetylacetonate).

In contrast to reported hydrolysis reactions of metal imido complexes,[6–10] we have not observed the formation of ammonia in the alcoholysis reactions of **1a** and **2**. In recent publications Pickett and co-workers[6,11] have shown by means of cyclic voltammetry that the reversible primary reduction of $[MoO(Cl)(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$) occurs at more positive potentials (>300 mV) than that of its imido analogue. This result might explain the fact that the V atom in

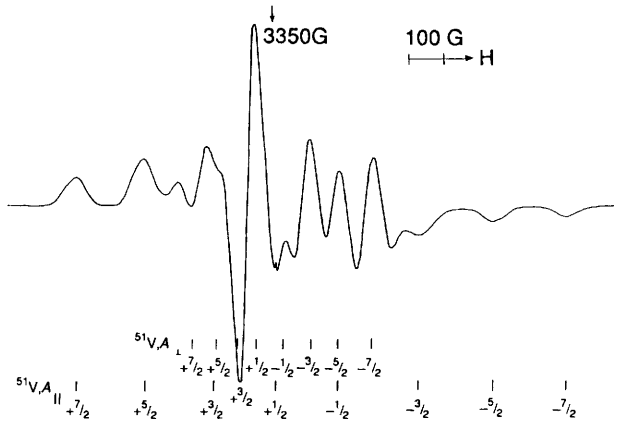


Fig. 2 First-derivative, X-band ESR spectrum for compound **2** at 298 K, showing parallel and perpendicular features from ^{51}V hyperfine coupling

1b is reduced (+IV) in the course of the reaction. We assume a similar mechanism for the formation of compound **2** as discussed by Pickett and co-workers[6,11] for the hydrolysis of *trans*-$[W(NH)(OMe)(dppe)_2]^+X^-$ (X = Cl, Br or I). The initial step may be either an addition of the nucleophile at the metal centre or an attack at the phosphorus atoms. A subsequent rearrangement reaction leads to a metal–oxygen multiple bond or a phosphine oxide, respectively. Finally, the metal fragment and the bis(diphosphine oxide) recombine to generate transition-metal imidophosphinato complexes.

In order to provide compound **2** in higher yields and to facilitate further studies we looked for a more elegant route towards **2**. We treated $[VOCl_2(thf)_2]$[12] (thf = tetrahydrofuran) with $Na[OPPh_2NPPh_2O]$ in the appropriate stoichiometry (Scheme 1). The two components were mixed in thf and the mixture was heated under reflux for 1 d. Separation of NaCl gave **2** in high yield (97%).

ESR Investigations of Compound **2**.—An X-band powder spectrum for compound **2** obtained at room temperature is shown in Fig. 2, together with line assignments. The spectrum at 77 K was almost identical. The Q-band spectrum gave identical

Table 2 ESR parameters for compound **2**

	Hyperfine coupling constant/MHz				
	$A_{\parallel}$	$A_{\perp}$	A_{iso}	$g_{\parallel}$	$g_{\perp}$
X Band	505	211	309	1.920	1.978
Q Band	505	215	312	1.920	1.975

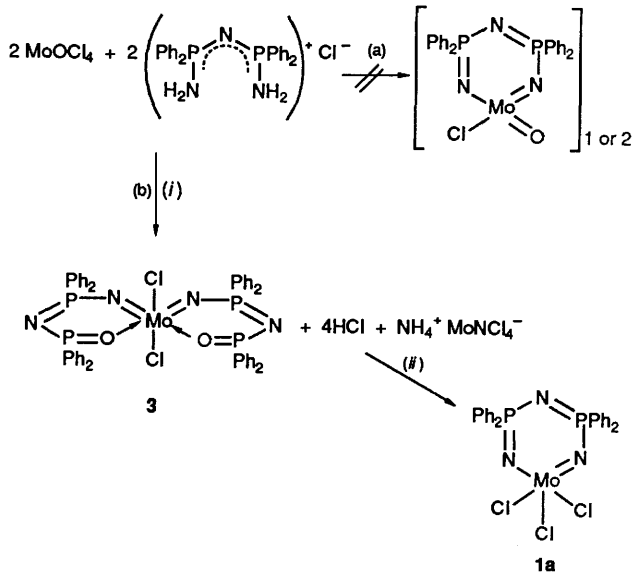
Table 3 Selected bond lengths (pm) and angles (°) for compound **3**

Mo–Cl	242.0(3)	Mo–O	210.5(8)
Mo–N(1)	176.8(10)	Mo–O(1′)	209.7(9)
Mo–N(1′)	178.7(8)	Mo–Cl′	239.0(4)
O–P	157.7(7)	P–N	159.6(12)
P–C(11)	180.4(12)	P–C(21)	180.0(14)
N–P(1)	157.4(13)	P(1)–N(1)	165.4(8)
P(1)–C(31)	178.8(11)	P(1)–C(41)	179.6(13)
O(1′)–P(1′)	156.0(7)	P(1′)–N′	158.2(13)
P(1′)–C(31′)	178.2(12)	P(1′)–C(41′)	181.0(14)
N′–P′	156.4(14)	P′–N(1′)	164.0(7)
P′–C(11′)	180.4(9)	P′–C(21′)	176.1(13)
Cl–Mo–O	84.9(2)	Cl–Mo–N(1)	95.1(3)
O–Mo–N(1)	89.6(4)	Cl–Mo–O(1′)	84.5(2)
O–Mo–O(1′)	78.9(3)	N(1)–Mo–O(1′)	168.5(4)
Cl–Mo–N(1′)	92.4(3)	O–Mo–N(1′)	169.1(4)
N(1)–Mo–N(1′)	101.2(4)	O(1′)–Mo–N(1′)	90.3(4)
Cl–Mo–Cl′	166.7(1)	O–Mo–Cl′	85.2(2)
N(1)–Mo–Cl′	93.6(3)	O(1′)–Mo–Cl′	85.0(2)
N(1′)–Mo–Cl′	95.7(3)	Mo–O–P	132.2(6)
O–P–N	114.5(5)		

parameters which provided good reconstructions for both spectra. These results show that the g and A components show common directions and are effectively axial. The hyperfine coupling constants and g values (Table 2) are normal for vanadyl complexes, and confirm that the configuration is essentially $3d^1$, with only minor delocalization at the ligands. The linewidths in the X- and Q-band spectra are such that small hyperfine couplings to ^{31}P would not be resolved. We therefore studied a wide range of single-crystal spectra at arbitrary orientations. Several features were observed with widths of *ca.* 10 G, but never less than this, and with no sign of resolution. This confirms that the ^{31}P hyperfine coupling must be small, and hence that delocalization is not extensive.

The observation of nitrogen–oxygen exchange processes in metal complexes of type **1** prompted us to study the reaction between transition-metal oxyhalides and $[H_2NPPh_2NPPh_2NH_2]Cl$.[13–15] In an attempt to obtain a molybdatriazadiphosphorine with an exocyclic metal–oxygen bond, we allowed $[H_2NPPh_2NPPh_2NH_2]Cl$ to react with $MoOCl_4$ (Scheme 2). The reaction proceeds according to the unexpected pathway (b). From a heated $CHCl_3$ solution of the two reactants a brown precipitate was isolated which proved to be a mixture of two products **1a** and **3**. The ^{31}P NMR spectrum showed two singlets (δ 38.1 and 43.0 respectively). By fractional crystallization from MeCN a separation of the two products was achieved. The compound which gave the signal at δ 43.0 was identical with the six-membered ring **1a** previously prepared by the reaction of $MoNCl_3$ with $[H_2NPPh_2NPPh_2NH_2]Cl$.[2] Therefore we suppose that $MoNCl_3$ or $MoNCl_4^-$ is an intermediate product resulting in the idealized equation (b) (Scheme 2). The field-ionization mass spectrum of the second compound **3** gave the parent ion at m/z 996 indicative of a composition with one molybdenum atom and two Cl atoms. Characteristic absorptions for P–N bonds were found at 1175 cm^{-1} in the IR spectrum. However, the structure of **3** could only be elucidated by an X-ray crystal structure analysis.

Structure of Compound **3**·MeCN.—Suitable crystals of compound **3** were obtained by repeated crystallization from MeCN. The structure of the 1:1 adduct formed with MeCN is shown in Fig. 3, and selected bond distances and angles are given in Table 3. It is readily apparent that the Mo atom has a distorted-octahedral structure with two Cl atoms in *trans* positions. The equatorial positions are occupied by two N and two O atoms from $O{=}PPh_2NPPh_2N$ ligands. The Mo–N bond lengths [Mo–N(1) 176.8(10), Mo–N(1′) 178.7(8) pm] indicate a strong double-bond character; they are close to those in other molybdenum(VI) imido complexes[2] (average lengths in **1a** 177.8 pm). By means of the *cis* arrangement of the two Mo–N bonds the most efficient π bonding is achieved. The coplanar arrangement of the two $O{=}PPh_2NPPh_2N$ ligands may be explained by a *trans* effect of the metal imido groups, as the two oxygen-donor atoms should be more weakly bound than the Cl atoms. To our knowledge this is the first example of a bicyclic phosphorane iminato complex. The elemental analysis confirmed the composition of **3**, although the data obtained from three independent determinations differed slightly due to variable amounts of MeCN in the crystals. The ^{31}P NMR spectrum of compound **3** is puzzling in the light of this structure. Even at lower temperatures (215 K) the sharp singlet does not split into two signals expected for the different phosphorus atoms. Nitrogen-15 and ^{95}Mo NMR measurements were not successful due to the low solubility of **3** in common organic solvents.



Scheme 2 (*i*) $CHCl_3$; (*ii*) $[H_2NPPh_2NPPh_2NH_2]Cl$, $-2NH_4Cl$

Experimental

Manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk-tube techniques. Solvents and Bu^{t}OH were dried by standard methods and degassed prior to use. Infrared spectra were obtained using Nujol mulls between KBr plates and Perkin-Elmer 180 and 325 spectrophotometers, ^{31}P NMR spectra on a Bruker AM 250 spectrometer using 85% H_3PO_4 as external standard, and mass spectra on Finnigan MAT 8230 and Varian MAT CH5 instruments. The ESR spectra were measured using a Varian E109 X-band and a Bruker ER 200D Q-band spectrometer at *ca.* 293 and between 77 and 100 K. Samples were either very finely powdered, or comprised a small number of well defined crystals. Melting points were determined in sealed capillaries and are uncorrected. Elemental analyses were done by Beller, Göttingen.

The compounds $[V(NPPh_2NPPh_2N)Cl_2]$ **1b**,[2] $NaOSiPh_3$,[16]

Table 4 Crystal data, intensity measurement and refinement (SHELX)

Compound	**2**	**3**
Formula	$C_{48}H_{40}N_2O_5P_4V$	$C_{48}H_{40}Cl_2MoN_4O_2P_4{\cdot}CH_3CN$
M	899.7	1 036.7
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/pm	1 572.0(8)	1 087.1(5)
b/pm	1 056.3(5)	1 156.4(6)
c/pm	2 685.0(13)	1 166.5(6)
α/°	90	82.86(2)
β/°	94.30(2)	68.26(2)
γ/°	90	64.15(2)
U/nm^3	4.4459	1.2247
Z	4	1
D_c/Mg m^{-3}	1.34	1.41
μ(Mo-Kα)/mm^{-1}	0.40	0.54
Crystal size/mm	0.3 × 0.3 × 0.3	0.3 × 0.4 × 0.5
Absorption corrections by azimuthal scans, R_ψ	0.022–0.013	0.013–0.010
Minimum, maximum transmission	0.24, 0.27	0.56, 0.61
Reflections up to $2\theta_{max}$/°	45	45
Measured reflections	13 259	4 432
Unique reflections	5 806 (R_{int} 0.019)	4 431 —
Observed (m) reflections with $\|F_o\| > 3\sigma\|F_o\|$	5 224	4 318
Refined parameters (n)	541	569
Goodness of fit $[\Sigma w(\|F_o\| - \|F_c\|)^2/(m-n)]^{\frac{1}{2}}$	2.04	2.8
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.033	0.064
$R' = R_g = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}$	0.044	0.077
Weighting scheme $w^{-1} = [\sigma^2(\|F_o\|) + g\|F_o\|^2]$	0.0002	0.0004
η in Rodgers refinement	—	0.6(2)
Residual electron density/10^{-6} e pm^{-3} maximum	0.4	3.2 } near Mo
minimum	−0.3	−0.3 } near Mo

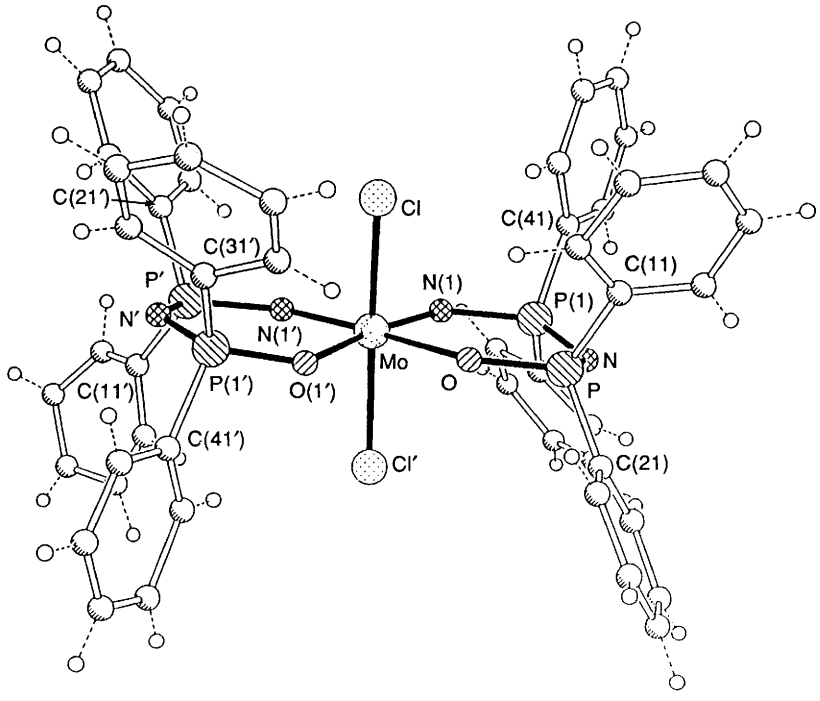


Fig. 3 The molecule of compound **3** with the unique atoms labelled

$[VOCl_2(thf)_2]$,[12] $MoOCl_4$,[17] and the salt $[H_2NPPh_2NPPh_2NH_2]Cl$[15] were prepared as described in the literature, LiOBu^t was freshly prepared from Bu^{t}OH and LiBu in hexane and $Na[OPPh_2NPPh_2O]$ was prepared by treatment of $OPPh_2NPPh_2OH$[18] with an equimolar amount of NaH in thf.

Preparations.—$[V(OPPh_2NPPh_2O)_2O]$ **2**. (*a*) *From* $[V(NPPh_2NPPh_2N)Cl_2]$ **1b** *and* Bu^{t}OH. A dark red stirred solution of compound **1b** (1.95 g, 3.65 mmol) in MeCN (100 cm^3) was cooled to −40 °C, and a solution of Bu^{t}OH (0.81 g, 10.9 mmol) in MeCN (20 cm^3) was added. The mixture was

Table 5 Atomic coordinates (× 10^4) for compound **2**

Atom	x	y	z	Atom	x	y	z
V	7 871(1)	4 272(1)	1 034(1)	C(41)	7 099(2)	6 925(3)	2 109(1)
O	8 116(1)	5 474(2)	728(1)	C(42)	6 406(2)	7 676(3)	2 208(1)
O(1)	6 611(1)	4 200(2)	929(1)	C(43)	6 502(3)	8 979(3)	2 261(1)
P(1)	5 853(1)	4 317(1)	1 245(1)	C(44)	7 275(3)	9 521(4)	2 218(1)
N(2)	6 044(1)	4 967(2)	1 775(1)	C(45)	7 969(3)	8 811(4)	2 121(1)
P(2)	6 976(1)	5 246(1)	2 018(1)	C(46)	7 889(2)	7 510(3)	2 067(1)
O(3)	7 722(1)	4 791(2)	1 732(1)	C(11′)	9 555(1)	1 692(2)	1 904(1)
O(1′)	8 987(1)	3 613(2)	1 321(1)	C(12′)	9 039(2)	2 123(3)	2 265(1)
P(1′)	9 483(1)	2 377(1)	1 290(1)	C(13′)	9 135(2)	1 654(3)	2 748(1)
N(2′)	9 090(1)	1 379(2)	896(1)	C(14′)	9 747(2)	760(3)	2 870(1)
P(2′)	8 378(1)	1 706(1)	461(1)	C(15′)	10 253(2)	310(3)	2 520(1)
O(3′)	7 798(1)	2 818(2)	570(1)	C(16′)	10 157(2)	752(3)	2 035(1)
C(11)	5 434(1)	2 747(3)	1 315(1)	C(21′)	10 568(1)	2 741(2)	1 158(1)
C(12)	4 755(2)	2 542(3)	1 600(1)	C(22′)	10 815(2)	2 634(3)	675(1)
C(13)	4 441(3)	1 320(4)	1 650(2)	C(23′)	11 626(2)	2 977(4)	564(1)
C(14)	4 796(3)	333(4)	1 419(2)	C(24′)	12 199(2)	3 406(4)	935(1)
C(15)	5 454(2)	526(3)	1 138(2)	C(25′)	11 973(2)	3 501(3)	1 416(1)
C(16)	5 780(2)	1 728(3)	1 079(1)	C(26′)	11 159(2)	3 174(3)	1 531(1)
C(21)	5 027(1)	5 194(2)	896(1)	C(31′)	8 865(1)	2 068(2)	−108(1)
C(22)	4 452(2)	4 590(3)	558(1)	C(32′)	8 940(2)	3 310(3)	−261(1)
C(23)	3 867(2)	5 281(3)	259(1)	C(33′)	9 455(2)	3 609(3)	−642(1)
C(24)	3 854(2)	6 570(3)	289(1)	C(34′)	9 893(2)	2 669(4)	−871(1)
C(25)	4 420(2)	7 181(3)	623(1)	C(35′)	9 808(2)	1 439(3)	−734(1)
C(26)	5 005(2)	6 497(3)	929(1)	C(36′)	9 296(2)	1 124(3)	−354(1)
C(31)	7 092(2)	4 498(3)	2 625(1)	C(41′)	7 732(1)	313(2)	354(1)
C(32)	7 599(2)	5 008(3)	3 015(1)	C(42′)	7 179(2)	199(3)	−71(1)
C(33)	7 717(2)	4 368(5)	3 465(1)	C(43′)	6 643(2)	−830(3)	−131(1)
C(34)	7 346(3)	3 240(5)	3 528(1)	C(44′)	6 650(2)	−1 750(3)	226(1)
C(35)	6 827(3)	2 713(4)	3 149(1)	C(45′)	7 196(2)	−1 667(3)	645(1)
C(36)	6 698(2)	3 350(3)	2 695(1)	C(46′)	7 738(2)	−637(3)	711(1)

Table 6 Atomic coordinates (× 10^4) for compound **3**

Atom	x	y	z	Atom	x	y	z
Mo	4 990	4 992	21	C(42)	9 783(15)	3 263(13)	−936(14)
Cl	6 168(3)	3 434(3)	1 303(3)	C(43)	10 983(18)	2 804(16)	−617(15)
O	5 755(9)	3 387(7)	−1 147(6)	C(44)	12 057(19)	3 231(20)	−1 158(16)
P	7 069(3)	2 853(3)	−2 408(3)	C(45)	11 899(17)	4 088(17)	−1 997(21)
N	7 934(10)	3 731(9)	−2 952(8)	C(46)	10 669(17)	4 588(14)	−2 358(15)
P(1)	7 954(3)	4 753(3)	−2 194(3)	C(11′)	1 460(12)	8 343(9)	2 381(10)
N(1)	6 548(9)	5 257(8)	−880(8)	C(12′)	1 233(39)	9 307(21)	2 831(41)
O(1′)	3 317(7)	4 375(7)	828(6)	C(13′)	102(40)	10 533(21)	2 996(34)
P(1′)	2 069(3)	4 669(3)	2 119(3)	C(14′)	−496(23)	10 845(18)	2 116(20)
N′	1 875(11)	5 813(10)	2 885(9)	C(15′)	−9(40)	9 944(18)	1 405(31)
P′	2 690(3)	6 706(3)	2 498(3)	C(16′)	846(45)	8 721(17)	1 595(33)
N(1′)	4 085(9)	6 247(8)	1 192(7)	C(21′)	3 389(10)	6 753(9)	3 625(9)
Cl′	3 650(3)	6 162(3)	−1 291(3)	C(22′)	2 994(23)	6 289(17)	4 785(12)
C(11)	8 264(14)	1 264(11)	−2 129(13)	C(23′)	3 546(27)	6 341(17)	5 675(14)
C(12)	7 868(23)	747(16)	−1 083(14)	C(24′)	4 436(20)	6 890(14)	5 454(14)
C(13)	8 830(31)	−580(18)	−916(22)	C(25′)	4 879(16)	7 352(16)	4 310(16)
C(14)	10 170(30)	−1 150(21)	−1 862(37)	C(26′)	4 347(14)	7 274(12)	3 404(13)
C(15)	10 511(19)	−545(16)	−2 860(30)	C(31′)	2 408(13)	3 254(12)	2 986(11)
C(16)	9 561(14)	658(13)	−3 083(17)	C(32′)	1 812(13)	3 302(11)	4 256(11)
C(21)	6 405(11)	2 660(8)	−3 542(9)	C(33′)	1 988(16)	2 222(12)	4 935(13)
C(22)	6 547(19)	3 305(15)	−4 613(14)	C(34′)	2 828(23)	1 063(13)	4 345(15)
C(23)	6 021(25)	3 109(19)	−5 457(15)	C(35′)	3 584(22)	961(14)	3 051(15)
C(24)	5 394(15)	2 360(15)	−5 296(14)	C(36′)	3 360(18)	2 049(12)	2 398(14)
C(25)	5 255(18)	1 710(18)	−4 289(18)	C(41′)	403(11)	5 061(10)	1 841(10)
C(26)	5 745(15)	1 898(14)	−3 381(13)	C(42′)	−528(15)	4 525(15)	2 417(14)
C(31)	7 893(12)	6 132(9)	−3 098(10)	C(43′)	−1 764(19)	4 868(21)	2 197(18)
C(32)	7 793(18)	7 216(13)	−2 569(15)	C(44′)	−2 085(16)	5 719(21)	1 366(18)
C(33)	7 891(22)	8 201(13)	−3 330(20)	C(45′)	−1 255(18)	6 317(19)	741(18)
C(34)	7 991(22)	8 163(16)	−4 550(16)	C(46′)	109(17)	5 925(16)	1 026(18)
C(35)	8 101(15)	7 166(13)	−5 014(13)	N(3)	5 128(33)	9 297(32)	231(28)
C(36)	8 123(12)	6 090(11)	−4 331(11)	C(1)	4 388(45)	9 514(37)	−495(35)
C(41)	9 574(11)	4 162(11)	−1 811(10)	C(2)	3 782(39)	9 396(34)	−1 386(42)

allowed to warm to room temperature and stirred. Within 1 d its colour slowly changed to green and turquoise crystals formed (0.11 g, 6% yield, referred to P). The supernatant liquid was decanted, and the crystals were recrystallized from hot MeCN, m.p. 232 °C (decomp.) (Found: C, 63.5; H, 4.40; N, 3.05. Calc. for $C_{48}H_{40}N_2O_5P_4V$: C, 64.1; H, 4.50; N, 3.10%). ^{31}P NMR

(MeCN, C_6D_6): δ 28.2 (br s, $W_{\frac{1}{2}}$ = 210 Hz). Electron-impact mass spectrum: *m/z* 899 (M^+, 100%). IR spectrum (KBr): 1430s, 1340vs, 1220s, 1110s, 1060m, 965vs and 540vs cm^{-1}. By treatment of compound **1b** with $LiOBu^t$ or $NaOSiPh_3$ (1:3 stoichiometry, thf as solvent), **2** could be obtained in 18 and 10% yields, respectively (referred to P).

(*b*) *From* $[VOCl_2(thf)_2]$ *and* $Na[OPPh_2NPPh_2O]$. A solution of $Na[OPPh_2NPPh_2O]$ (1.41 g, 3.20 mmol) in thf (60 cm^3) was added to a stirred solution of $[VOCl_2(thf)_2]$ (0.45 g, 1.60 mmol) in thf (20 cm^3) at room temperature. The initially clear green solution was heated under reflux for 1 d, cooled to ambient temperature, and the solvent was reduced *in vacuo* to one fourth of its volume (20 cm^3). After removal of NaCl by filtration through Celite, the solvent was completely evaporated to obtain a bright green powder (1.40 g, 97% yield). Recrystallization from MeCN gave analytically pure crystalline material. The ^{31}P NMR and the mass spectra were the same as listed in (*a*).

$[Mo(NPPh_2NPPh_2O)_2Cl_3]$ **3**. A stirred suspension of freshly sublimed $MoOCl_4$ (2.95 g, 11.6 mmol) in $CHCl_3$ (150 cm^3) was cooled to −20 °C, and an ice-cooled solution of $[H_2NPPh_2NPPh_2NH_2]Cl$ (5.24 g, 11.6 mmol) in $CHCl_3$ (100 cm^3) was added. The mixture was stirred at 0 °C for 6 h and subsequently heated under reflux for 24 h. Removal of the solvent *in vacuo* yielded a brown powder (4.51 g). By recrystallization from hot MeCN an orange precipitate of compound **3** was isolated (2.93 g, 51% yield). Work-up of the supernatant liquid and recrystallization from MeCN gave **1a**·MeCN (1.67 g, 22% yield). Repeated crystallization of compound **3** from MeCN yielded transparent pale yellow crystals, m.p. 165 °C (decomp.), which were suitable for an X-ray crystal structure analysis. The single crystals contained one molecule of MeCN, which is the reason that the crystal system is non-centrosymmetric [Found (mean values of three determinations): C, 56.4; H, 4.00; Cl, 6.65; N, 6.60. Calc. for $C_{50}H_{43}Cl_2MoN_5O_2P_4$, **3**·MeCN: C, 57.9; H, 4.20; Cl, 6.85; N, 6.75%]. ^{31}P NMR (MeCN, CD_3CN): δ 38.1 (s). Field-ionization mass spectrum: *m/z* 996 (M^+, 0.8), 977 (M^+ − Cl + O, 100) and 961 (M^+ − Cl, 60%). IR spectrum (KBr): 1435vs, 1175vs, 1120vs, 1040vs, 1025s, 995m, 945m (sh), 915s (br), 550s and 310m cm^{-1}.

Crystal Structure Analyses.—Intensities were measured for both compounds on a Stoe-Siemens four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 71.069 pm) at 20 °C and a profile-fitting procedure.[19] The details of the X-ray analyses, data collections and structure refinements for both structures are listed in Table 4. Final atomic coordinates for the non-hydrogen atoms are listed in Tables 5 and 6 for **2** and **3**, respectively. Crystallographic calculations were performed using software written by Sheldrick.[20] In the case of **3** a refinement of anomalous dispersion according to Rodgers[21] assured the absolute structure.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

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