

Unexpected Nitrogen–Oxygen Exchange Reactions in Cyclic Metallaphosphazenes; Synthesis and X-Ray Crystal Structures of $[\text{Mo}(\text{OPPh}_2\text{NHPPh}_2\text{O})\text{O}_2\text{Cl}_2]$, $[\text{Mo}(\text{OPPh}_2\text{NPPh}_2\text{O})_2(\text{O})\text{Cl}]$, and $[\text{Mo}(\text{OPPh}_2\text{NPPh}_2\text{O})_2\text{O}_2]$ †

Mathias Rietzel, Herbert W. Roesky,* Kattesh V. Katti, Hans-Georg Schmidt, Regine Herbst-Irmer, Mathias Noltemeyer, and George M. Sheldrick
Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

Martyn C. R. Symons and Atieh Abu-Raqabah

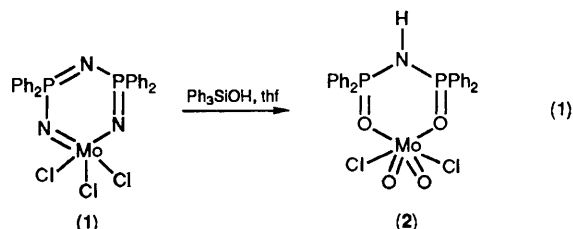
Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH

The reactions of $[\text{Mo}(\text{NPPh}_2\text{NPPh}_2\text{N})\text{Cl}_3]$ with Ph_3SiOH and Bu^tOH lead not to the expected substitution products but to exchange and rearrangement reactions in which the nitrogen atoms which co-ordinate molybdenum are replaced by oxygen. The crystal structures of $[\text{Mo}(\text{OPPh}_2\text{NHPPh}_2\text{O})\text{O}_2\text{Cl}_2]$, $[\text{Mo}(\text{OPPh}_2\text{NPPh}_2\text{O})_2(\text{O})\text{Cl}]$, and $[\text{Mo}(\text{OPPh}_2\text{NPPh}_2\text{O})_2\text{O}_2]$ are reported, together with the synthesis of these unexpected products by more direct routes.

In the course of our investigations of the stabilisation of transition-metal centres in high oxidation states with phosphazene ligands, we reported the synthesis and characterisation of cyclometallaphosphazenes of V, Nb, Mo, W, and Re,^{1–5} and the first eight-membered cyclometallaphosphazenes $[\text{ClV}(\text{O}-\text{SiMe}_3)\text{NPPh}_2\text{N}]_2$ and $(\text{Cl}_2\text{VNPPh}_2\text{N})_2$.⁶ The metal–halogen bonds present in all these cyclometallaphosphazenes facilitate a variety of further reactions. We decided to test the reactivity and stability of $[\text{Mo}(\text{NPPh}_2\text{NPPh}_2\text{N})\text{Cl}_3]$ (1)² by nucleophilic substitution reactions with sterically demanding alcohols. As strong π -donor ligands, alkoxy groups generally increase the stability of higher oxidation states of transition metals.⁷ In this contribution we report reactions of (1) with Ph_3SiOH and Bu^tOH , which led to unexpected products, and the subsequent synthesis of these products by more direct routes.

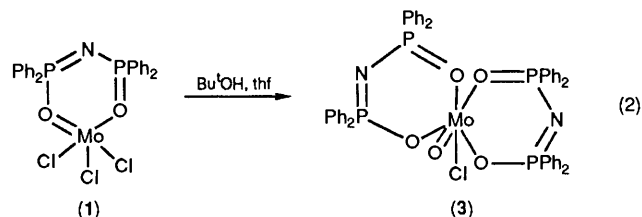
Results and Discussion

Substitution reactions with Ph_3SiOH as nucleophile usually result in the incorporation of the inert Ph_3SiO group.^{8,9} However when compound (1) is treated with Ph_3SiOH in a 1:4 molar ratio at room temperature in tetrahydrofuran (thf), (2) is formed almost quantitatively (according to ³¹P n.m.r. spectroscopy) instead of the expected products [equation (1)]. Pale



green crystals of (2) were isolated directly from the reaction mixture. The ³¹P n.m.r. spectrum ($\text{MeCN}-\text{CD}_3\text{CN}$) exhibits a sharp singlet ($\delta + 37.0$ p.p.m.), indicating the equivalence of the two P atoms. The ¹H n.m.r. spectrum shows signals for phenyl protons ($\delta 7.46$ – 7.88) and for an NH proton ($\delta 2.18$). Although

in the field ionisation (f.i.) mass spectrum the molecular ion was not observed, a fragment of m/z 546 could be identified as $[\text{M} - \text{HCl} - \text{Cl}]$ (correct isotopic pattern). The correct elemental analysis together with the ³¹P n.m.r. spectrum indicate that an N atom is located between the two P atoms, and that ring oxygen atoms co-ordinate Mo. In addition to (2), considerable amounts of colourless crystals were formed from acetonitrile solution and identified as hexaphenyldisiloxane [¹H n.m.r. spectrum, elemental analysis, electron impact (e.i.) mass spectrum]. At room temperature the formation of compound (2) proceeds quite slowly, but attempts to reduce the reaction time by refluxing the reaction mixture in thf led to lower yields (43%) along with many by-products. The dark colour of the heated solution indicated a partial decomposition of the solvent. Compound (2) can be dissolved in thf or in MeCN yielding pale green, (2a), or pale yellow, (2b), crystals, respectively. Although the spectroscopic parameters of (2a) and (2b) are identical, both types of crystals were examined crystallographically (Figure 2).



† Dichloro(1,3-dioxo-1,1,3,3-tetraphenyldi- λ^5 -phosphazene-*OO'*)dioxo-, chlorobis(*N*-diphenylphosphoryl-*PP*-diphenylphosphinimidato-*OO'*)oxo-, and bis(*N*-diphenylphosphoryl-*PP*-diphenylphosphinimidato-*OO'*) dioxo-molybdenum.

Supplementary data available: complete bond lengths and angles, structure factors and thermal parameters have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, West Germany. Any request for this material should quote the reference numbers CSD 54055 and 54285 and the full literature citation.

Non-S.I. unit employed: $G = 10^{-4}$ T.

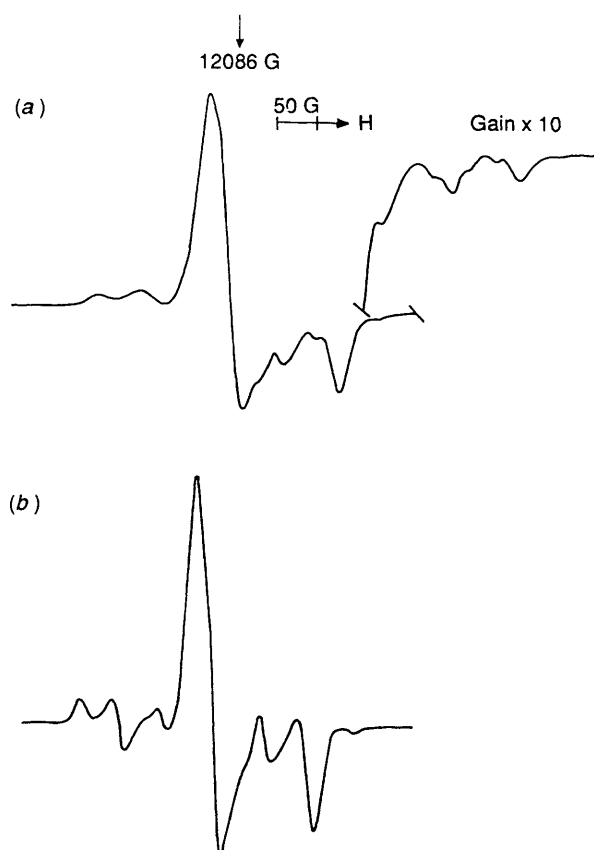


Figure 1. Q-Band e.s.r. spectrum for compound (3) at ca. 100 K. (a) A computer simulation using the parameters given in Table 1 is shown in (b)

Table 1. E.s.r. parameters for compound (3), estimated from the Q-band spectrum

	x	y	z
g	1.942	1.938	1.919
$A(^{95}\text{Mo})^*/\text{G}$	(-) 55	(-) 51	(-) 93

* Using $2B^o \approx 31\text{G}$ (J. R. Morton and K. F. Preston, *J. Magn. Reson.*, 1978, **30**, 577). We obtain a $4d$ population of ca. 87% using negative signs. Other sign combinations give impossible values.

When compound (1) reacts with 3 equivalents of Bu^tOH in thf the spirocyclic compound (3) is obtained in a 36% yield [equation (2)]. Green, air-stable crystals of (3) were isolated directly from the reaction mixture. The f.i. mass spectrum shows a molecular ion with the expected isotopic pattern. The ^{31}P n.m.r. spectrum ($\text{MeCN}-\text{C}_6\text{D}_6$) of redissolved single crystals of (3) consists of three signals: a singlet (δ 34.5 p.p.m., $w_{\frac{1}{2}}$ 30 Hz) and two broad unresolved doublets (δ 31.9 and 27.9, p.p.m., $w_{\frac{1}{2}}$ 70 Hz) of approximately equal intensity. The P-P coupling constant of the doublets was about 20 Hz, but could not be determined accurately because of the large linewidths. This spectrum did not show any change between +40 and -60 °C. It can best be explained in terms of an AMX_2 spin pattern for the four phosphorus atoms. We suggest that the strong *trans* effect of the exocyclic $\text{Mo}=\text{O}$ bond weakens the ring $\text{Mo}-\text{O}$ bond *trans* to it and gives rise to a significant ^{31}P chemical shift difference in one ring. Probably the two phosphorus atoms in the other ring have accidentally degenerate chemical shifts, since the *trans* effect of Cl and ring O are similar. The general broadness of the signals is attributed to the paramagnetism of

(3). E.s.r. measurements verified the paramagnetism of (3) expected for Mo^V .

E.S.R. Spectra for Compound (3).—Spectra were obtained at X and Q-band frequencies, the latter being better defined [Figure 1(a)]. It was necessary to use well powdered samples to avoid effects from small crystals. Powder spectra were almost unchanged on cooling to ca. 77 K showing that there is no extensive librational motion at room temperature.

The spectra comprise intense single features which give g_x , g_y , and g_z accurately, the x - y splitting being only resolved at Q-band frequencies. Satellite features from $^{95/97}\text{Mo}$ were also well defined, but no ligand hyperfine coupling was resolved. Although a single-crystal e.s.r. study was not undertaken, spectra for small crystallites were examined over a range of orientations. These gave g values and $^{95/97}\text{Mo}$ coupling constants which all fell within the limits defined by the powder spectra, thus supporting the analysis. This is also strongly supported by the computer fit shown in Figure 1(b).

The liquid-phase spectrum comprised a poorly resolved 1:2:1 triplet ($A_{\text{iso}} = 6\text{G}$). Solutions saturated in thf were unfortunately too dilute to show molybdenum satellite features. Data are given in Table 1. The fact that all three g values are less than the free-spin value (2.0023) establishes that the centre has a $4d^1(d_{xy}^1)$ configuration. The nearly axial g and A tensors suggest that the centre is a co-ordinated molybdenyl ion, the parallel (z) axis lying along the $\text{Mo}=\text{O}$ direction, and the values obtained are typical of such structures. The g_z value derived from the $^{95/97}\text{Mo}$ features exactly equals that for the non-magnetic isotope centres showing that g_z and A_z are coaxial as expected for a molybdenyl centre. However there are small deviations for the x and y g -values derived from the hyperfine features compared with those for the non-magnetic isotope features. The latter are the true values, and the former values probably deviate because the 'x' and 'y' directions are not quite equal.¹⁰ In view of the low symmetry of these centres this is to be expected. The deviations are too small to allow significant estimates of relative angles. For a d^1 centre, A_{iso} ($^{95/97}\text{Mo}$) is expected to be negative, and the anisotropic coupling should take the form $-2B$, $+B$, $+B$ along the z , x , y axes to a first approximation. Using the signs indicated in Table 1, these conditions are fulfilled. The anisotropic coupling corresponds to an approximate $4d$ orbital population of 0.87. The magnitude of the negative isotropic coupling is normal for d^1 complexes and suggests a negligible contribution from direct admixture of the outer s orbitals.

Absence of coupling to $^{35/37}\text{Cl}$ nuclei shows that there is very little π delocalisation into chlorine despite the probable d - p overlap. The isotropic coupling to only two of the four ^{31}P nuclei accords well with the structure, the coupling being assigned to the ligand in the xy plane. The coupling of 6 G corresponds to a very low spin density on phosphorus, which probably arises through spin polarisation rather than direct delocalisation. There was no indication of any coupling from ^{14}N . Careful scrutiny of the single-crystal features over a range of orientations gave no indication of any extra splittings.

Because of the poor solubility of compound (3) in common organic solvents, ^{15}N and ^{95}Mo n.m.r. measurements were unsuccessful. The ^1H n.m.r. spectrum (CD_3CN) shows signals only in the phenyl region (δ 7.24–8.02). In the i.r. spectrum the most obvious difference compared to (1) is the shift of the $\nu(\text{P}=\text{N})$ towards lower frequencies (from 1 245 to 1 174 cm^{-1}). A strong absorption at 917 cm^{-1} is assigned to $\nu(\text{Mo}=\text{O})$. The modest yield of (3) may be a consequence of a complex reaction mechanism. Except for NH_4Cl , no other product could be isolated. Variations of the reaction conditions, especially of the molar ratio of the starting materials, resulted in lower yields. Whilst compound (3) is only sparingly soluble in MeCN , it is

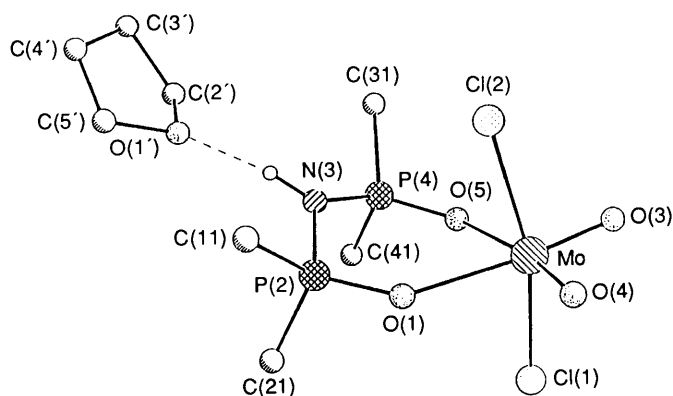


Figure 2. The molecule of (2a) showing the hydrogen bond to the thf solvent molecule. Phenyl rings are represented by a single carbon atom for clarity

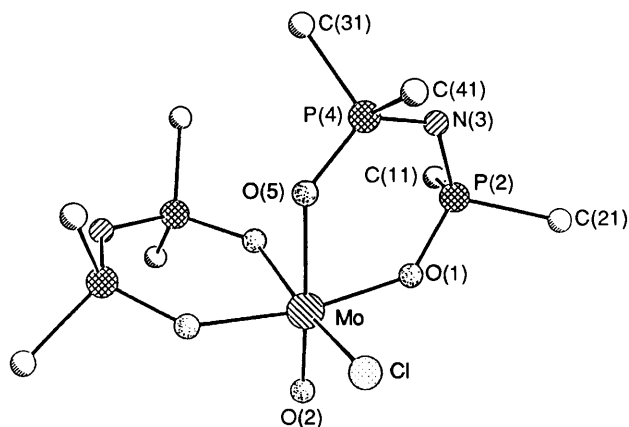


Figure 3. The molecule of (3) with the unique atoms labelled. The terminal oxygen and chlorine atoms are disordered. Phenyl rings are represented by single carbon atoms for clarity

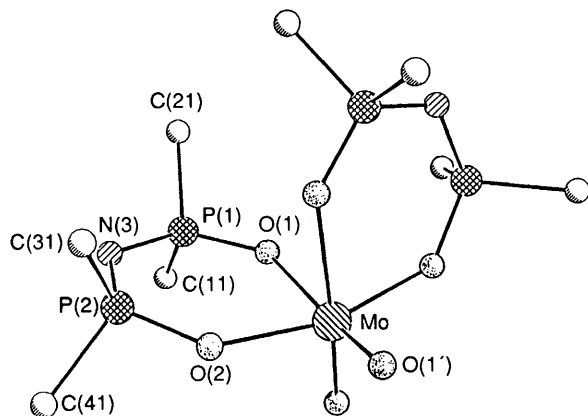


Figure 4. The molecule of (6a) with the unique atoms labelled. Phenyl rings are represented by single carbon atoms for clarity

quantitatively oxidised to (6) when dissolved in boiling thf or dimethylformamide (dmf) (see below). Suitable crystals for an X-ray crystal structure analysis of (3) were grown from MeCN (Figure 3).

In order to confirm these unexpected nitrogen–oxygen exchange reactions, we tried to synthesise the metallacycles (2) and (3) by independent routes, e.g. by treating the tetraphenylimidodiphosphinate ligand with the appropriate metal halide oxides. The direct synthesis of (2) was attempted by the reaction of the imidodiphosphinic acid $\text{OPPh}_2\text{NPPh}_2\text{OH}$ (4)¹¹ with MoO_2Cl_2 . Indeed compound (2) could be prepared

successfully in this way by using acetic anhydride as solvent. In more common organic solvents (thf, dmf, diethyl ether, MeCN) either MoO_2Cl_2 or (4) was insoluble at ambient temperature, and heating of the reaction mixtures always produced a complex mixture of products, possibly initiated by elimination of HCl. In acetic anhydride the formation of (2) proceeds almost quantitatively (>95% yield). The identity of the reaction product as (2) was confirmed by the ^{31}P n.m.r. f.i. mass spectra and elemental analysis. Attempts to synthesise compound (3) directly by treatment of MoOCl_3 with 2 equivalents of (4) were unsuccessful, so we prepared the salt $\text{Na}[\text{OPPh}_2\text{NPPh}_2\text{O}]$ (5) from (4) and NaH. The synthesis of (3) was accomplished by treating MoOCl_3 with 2 equivalents of (5) in dimethoxyethane (dme) at room temperature. Under these conditions (3) is formed in 63% yield as a pale green crystalline solid. Nevertheless, whenever this reaction was carried out in thf, dmf, pyridine, or chlorobenzene a different product $[\text{Mo}(\text{OPPh}_2\text{NPPh}_2\text{O})_2\text{O}_2]$ (6) was formed predominantly instead of (3). As this compound is nearly exclusively produced in thf, it could easily be isolated and purified by recrystallisation from this solvent. The ^{31}P n.m.r. spectrum (thf- C_6D_6) of the colourless crystalline solid shows two sharp doublets at δ 30.6 and 25.6 p.p.m. ($^2J_{\text{PP}} = 3.0$ Hz), respectively. In the f.i. mass spectrum the highest fragment was found at m/z 962 (100%), which suggested the composition $[\text{Mo}(\text{OPPh}_2\text{NPPh}_2\text{O})_2\text{O}_2]$. The correct isotopic pattern as well as the elemental analysis [(6b), 1:1 adduct of (6) with thf] confirm the supposed composition. Furthermore, (6) was prepared straightforwardly in excellent yield by the reaction of MoO_2Cl_2 with 2 equivalents of (5) in thf solution. Suitable crystals for an X-ray crystal structure analysis were obtained by recrystallisation from thf [(6a); (6b), 1:1 adduct of (6) with thf] (Figure 4).

Crystal Structures.—The ring dimensions in compound (2a) are essentially different to those in (3) and (6a) because the nitrogen is protonated, resulting in longer P–N and shorter P–O bonds (Table 2). This hydrogen atom could be found in a difference electron-density synthesis and makes a hydrogen bond to the oxygen atom of the thf solvent molecule ($\text{N} \cdots \text{O}$ 275 pm, Figure 2). The co-ordination about Mo in (2a) closely resembles that found¹² in both crystalline modifications of $[\text{Mo}\{(\text{Me}_2\text{N})_3\text{PO}\}_2\text{O}_2\text{Cl}_2]$. In the structure of (3), a crystallographic two-fold axis through Mo requires that the terminal O and Cl are disordered, reducing the usefulness of the structural parameters, although the structure determination clearly conforms with the proposed composition.

In each of the compounds studied the Mo–O bonds *trans* to terminal oxygen are about 220 pm and may be regarded as primarily dative bonds; the Mo–O bonds *trans* to a ring oxygen are about 200 pm. The distance of 211.7(5) pm in (3) is an average of the distances *trans* to terminal O and *trans* to Cl. The terminal Mo=O bonds are all slightly shorter than the mean of 170.4 pm reported in a recent survey¹³ of *cis*-dioxomolybdenum complexes, but fall well within the expected range.

Conclusion

It did not prove possible to substitute the Cl atoms of the cyclomolybdaphosphazene (1) using Ph_3SiOH or Bu^tOH . Instead, new metallacycles were formed in which oxygen had formally replaced the nitrogen atoms adjacent to Mo, suggesting that the metallacyclic ring had been opened during the reaction. Molybdenum in its higher oxidation states (IV–VI) is predominantly oxophilic, but the strong tendency to bind oxo ligands is well balanced by its capacity to lose an oxygen atom during oxo-transfer reactions.^{14,15} Except for the nitrogenases,

all other biomolybdenum species catalyse reactions which result in addition or removal of an oxygen atom. The new metallacycles (2), (3), and (6) provide the first examples of imidodiphosphinato complexes with early transition metals. Schmidpeter and co-workers^{16,17} have already reported examples of spirocyclic compounds such as (3) or (6) containing Zn or Cu, but without structural investigation. Recently the synthesis and X-ray crystal structure of a tricyclic imidodiphosphinato lanthanum complex has been published.¹⁸

Experimental

Manipulations were carried out under an atmosphere of dry

nitrogen using standard Schlenk-tube techniques. Solvents and Bu^tOH 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, ³¹P and ¹H n.m.r. spectra on Bruker AM 250 and WP 80SY spectrometers using 85% H₃PO₄ as external and SiMe₄ as internal standards respectively, and mass spectra performed on Finnigan MAT 8230 and Varian MAT CH5 instruments. E.s.r. 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. Room-temperature solution spectra for saturated solutions in thf were obtained at X-band frequencies only. Melting points were determined in sealed capillaries and are uncorrected. Elemental analyses were by Institut Beller, Göttingen.

The compounds [Mo(NPPPh₂NPPPh₂N)Cl₃] (1), OPPh₂NPPPh₂OH (4), and [MoOCl₃(thf)₂] were prepared by the published methods.^{2,11,19} The sodium salt Na[OPPh₂NPPh₂O] (5) was prepared by treatment of (4) with an equimolar amount of NaH using thf as solvent. The compounds MoO₂Cl₂ and Ph₃SiOH were commercial products.

Preparations.—[Mo(OPPh₂NHPPPh₂O)O₂Cl₂] (2) from [Mo(NPPPh₂NPPPh₂N)Cl₃] (1) and Ph₃SiOH. The compound Ph₃SiOH (2.12 g, 7.68 mmol) in thf (20 cm³) was added to a stirred solution of 1.18 g of (1) (1.92 mmol) in acetic anhydride (60 cm³) at room temperature. The colour of the solution slowly changed from orange-red to pale green (2 d). Filtration through Celite and concentration of the solvent volume to 20 cm³ gave pale green crystals of (2) (1.08 g, yield 82%), m.p. 231 °C (decomp.) Single crystals were obtained either from thf, (2a), or from MeCN, (2b). The spectroscopic parameters of (2a) and (2b) were identical Found: C, 49.3; H, 4.3; N, 2.1; P, 8.8. Calc. for C₂₈H₂₉Cl₂MoNO₅P₂, (2a) 1:1 adduct with thf: C,

Table 2. Selected bond lengths (pm) and angles (°)

	(2a)	(3)	(6a)
Mo=O	167.9(10) 168.9(10)	169.7(23)	168.0(2)
Mo—Cl	237.5(4) 239.5(4)	212.1(8)*	—
Mo—O	221.2(9) 220.0(9)	211.7(5) _d 200.5(4) _r	218.3(2) _i 200.9(2) _r
P—O	149.8(10) 150.0(10)	152.3(5) _d 153.8(5) _r	151.0(2) _i 153.5(2) _r
P—N	165.5(12) 165.7(12)	159.6(5) _d 156.9(6) _r	159.1(2) _i 157.2(3) _r
P—C (mean)	176.7(13)	179.6(7)	180.1(3)
N—P—O (mean)	110.6(5)	116.7(3)	116.7(1)
P—N—P	123.2(6)	125.7(4)	125.3(2)
P—O—Mo (mean)	140.6(5)	136.1(3)	137.7(1)
O—Mo—O (ring)	78.3(3)	86.0(2)	83.4(1)

t = *trans* to terminal O, r = *trans* to ring O, and d = *trans* to disordered terminal O/Cl. * This unreasonable short value may well be an artefact caused by disorder (see text).

Table 3. Crystal data for complexes

Compound	(2a)	(2b)	(3)	(6a)	(6b)
Formula	C ₂₈ H ₂₉ Cl ₂ MoNO ₅ P ₂	C ₂₆ H ₂₄ Cl ₂ MoN ₂ O ₄ P ₂	C ₄₈ H ₄₀ ClMoN ₂ O ₅ P ₄	C ₄₈ H ₄₀ MoN ₂ O ₆ P ₄	C ₅₂ H ₄₈ MoN ₂ O ₇ P ₄
<i>M</i>	688.3	657.3	980.1	960.7	1 032.8
Space group	<i>P</i> 4 ₂ <i>c</i>	<i>Pbca</i>	<i>I</i> 4 ₁ <i>cd</i>	<i>I</i> 4 ₁ <i>cd</i>	<i>P</i> 2 ₁ <i>c</i>
<i>a</i> /pm	1 785.2(5)	1 631.6(8)	2 008.3(6)	2 001.3(3)	1 157.4(6)
<i>b</i> /pm	1 785.2(5)	1 748.3(7)	2 008.3(6)	2 001.3(3)	2 347.4(12)
<i>c</i> /pm	1 936.4(7)	2 131.8(8)	2 244.9(8)	2 202.9(4)	1 809.5(9)
β/°	90	90	90	90	102.06(2)
<i>U</i> /nm ³	6.171	6.081	9.054	8.823	4.808
<i>Z</i>	8	8	8	8	4
<i>D</i> _c /Mg m ⁻³	1.48	1.44	1.45	1.45	1.43
μ/mm ⁻¹	0.73	0.73	0.53	0.48	0.45
Crystal size/mm	0.2 × 0.2 × 0.2	0.3 × 0.4 × 0.4	0.2 × 0.2 × 0.8/ 0.2 × 0.4 × 0.6	0.5 × 0.5 × 0.5	0.4 × 0.3 × 0.2
<i>F</i> (000)	2 800	2 656	4 008	3 936	2 128
No. of reflections					
measured	2 359	8 406	14 084	5 473	8 295
independent	2 240	3 962	4 298	2 851	6 222
observed					
[<i>F</i> > <i>pσ</i> (<i>F</i>)]	1 703	3 091	2 944	2 780	4 523
<i>p</i>	3	3	4	3	4
Maximum 2θ/°	45	45	55	45	45
<i>R</i>	0.0636	0.0988	0.0587	0.0219	0.0535
<i>R</i> ' [<i>w</i> ⁻¹ = σ ² (<i>F</i>) + <i>g</i> (<i>F</i>) ²]	0.0523	0.0966	0.0537	0.0234	0.0480
<i>g</i>	0.0004	0.001	0.0002	0.0001	0.0003
Number of parameters	309	334	278	275	578
Residual electron density/10 ⁻⁶ e pm ⁻³					
maximum	0.60	1.58	0.83	0.27	0.94
minimum	-0.48	-0.81	-0.92	-0.43	-0.66

Table 4. Atomic co-ordinates ($\times 10^4$) for compound (**2a**)

Atom	x	y	z	Atom	x	y	z
Mo	7 908(1)	7 575(1)	9 056(1)	C(25)	4 955	8 963	9 597
Cl(1)	7 146(2)	7 614(3)	10 061(2)	C(26)	5 622	8 858	9 234
Cl(2)	8 355(2)	7 534(3)	7 890(2)	C(31)	6 622(7)	6 097(7)	7 448(6)
O(1)	7 070(5)	8 369(4)	8 642(5)	C(32)	6 394	5 354	7 518
P(2)	6 448(2)	8 394(2)	8 121(2)	C(33)	6 557	4 836	7 000
N(3)	6 355(6)	7 579(6)	7 722(5)	C(34)	6 949	5 061	6 413
P(4)	6 444(2)	6 762(2)	8 119(2)	C(35)	7 177	5 804	6 342
O(5)	7 044(5)	6 809(4)	8 658(5)	C(36)	7 014	6 322	6 860
O(3)	8 424(6)	6 839(5)	9 313(6)	C(41)	5 582(7)	6 555(7)	8 524(5)
O(4)	8 449(6)	8 309(6)	9 288(6)	C(42)	4 933	6 465	8 132
C(11)	6 582(7)	9 039(6)	7 452(6)	C(43)	4 241	6 389	8 458
C(12)	6 295	9 761	7 527	C(44)	4 197	6 404	9 177
C(13)	6 442	10 303	7 025	C(45)	4 846	6 494	9 570
C(14)	6 876	10 122	6 450	C(46)	5 539	6 570	9 243
C(15)	7 163	9 400	6 376	O(1')	2 535(14)	502(8)	1 542(7)
C(16)	7 016	8 858	6 877	C(2')	1 850(16)	216(12)	1 254(12)
C(21)	5 603(8)	8 612(6)	8 551(5)	C(3')	1 860(26)	275(20)	480(13)
C(22)	4 918	8 472	8 230	C(4')	2 696(24)	244(16)	401(16)
C(23)	4 251	8 577	8 593	C(5')	3 127(18)	359(21)	1 058(20)
C(24)	4 270	8 822	9 277				

Table 5. Atomic co-ordinates ($\times 10^4$) for compound (**3**)

Atom	x	y	z
Mo	5 000	10 000	5 000
O(1)	4 497(2)	9 143(2)	5 085(2)
P(2)	4 064(1)	8 808(1)	5 564(1)
N(3)	3 734(3)	9 275(2)	6 040(3)
P(4)	3 872(1)	10 053(1)	6 115(1)
O(5)	4 411(2)	10 348(2)	5 717(2)
O(2)	5 546(11)	9 642(12)	4 520(10)
Cl	5 698(4)	9 582(4)	4 398(3)
C(11)	4 572(3)	8 186(3)	5 895(3)
C(12)	4 381(4)	7 891(4)	6 426(4)
C(13)	4 796(6)	7 410(4)	6 701(5)
C(14)	5 378(5)	7 233(4)	6 432(5)
C(15)	5 558(5)	7 504(4)	5 919(5)
C(16)	5 167(3)	7 991(4)	5 658(4)
C(21)	3 425(3)	8 375(3)	5 159(3)
C(22)	3 605(4)	7 907(4)	4 735(4)
C(23)	3 132(6)	7 623(5)	4 383(5)
C(24)	2 494(7)	7 764(6)	4 453(6)
C(25)	2 290(5)	8 203(5)	4 872(6)
C(26)	2 760(4)	8 525(4)	5 232(4)
C(31)	4 074(3)	10 236(3)	6 877(3)
C(32)	4 356(3)	10 841(4)	7 011(4)
C(33)	4 472(4)	10 999(4)	7 594(5)
C(34)	4 318(4)	10 575(5)	8 038(4)
C(35)	4 040(6)	9 973(5)	7 906(5)
C(36)	3 920(4)	9 805(4)	7 325(4)
C(41)	3 103(3)	10 503(3)	5 986(3)
C(42)	2 532(5)	10 302(5)	6 231(5)
C(43)	1 939(5)	10 644(7)	6 181(6)
C(44)	1 945(7)	11 210(7)	5 844(7)
C(45)	2 509(7)	11 425(5)	5 590(5)
C(46)	3 095(5)	11 066(4)	5 647(4)

Table 6. Atomic co-ordinates ($\times 10^4$) for compound (**6a**)

Atom	x	y	z
Mo	10 000	5 000	8 033
O(1')	10 542(1)	4 635(1)	7 554(1)
O(1)	9 404(1)	5 353(1)	8 798(1)
O(2)	9 487(1)	4 149(1)	8 164(1)
P(1)	8 887(1)	5 059(1)	9 220(1)
P(2)	9 067(1)	3 812(1)	8 660(1)
N(3)	8 758(1)	4 278(1)	9 161(1)
C(11)	8 108(2)	5 504(1)	9 100(1)
C(12)	8 075(2)	6 042(2)	8 719(2)
C(13)	7 468(3)	6 389(2)	8 656(2)
C(14)	6 921(2)	6 200(2)	8 963(2)
C(15)	6 945(2)	5 668(2)	9 333(2)
C(16)	7 545(2)	5 319(2)	9 408(2)
C(21)	9 092(1)	5 256(2)	9 992(1)
C(22)	8 952(2)	4 824(2)	10 467(2)
C(23)	9 081(2)	5 012(2)	11 054(2)
C(24)	9 346(2)	5 624(2)	11 176(2)
C(25)	9 495(2)	6 049(2)	10 717(2)
C(26)	9 368(2)	5 869(2)	10 122(1)
C(31)	9 592(1)	3 179(1)	8 986(1)
C(32)	10 189(2)	3 014(2)	8 721(2)
C(33)	10 593(2)	2 530(2)	8 980(2)
C(34)	10 407(3)	2 220(2)	9 498(2)
C(35)	9 822(3)	2 375(2)	9 769(2)
C(36)	9 406(2)	2 859(2)	9 518(2)
C(41)	8 418(2)	3 377(1)	8 254(1)
C(42)	8 593(2)	2 909(2)	7 822(2)
C(43)	8 111(3)	2 612(2)	7 471(2)
C(44)	7 459(3)	2 773(3)	7 549(3)
C(45)	7 274(2)	3 218(2)	7 982(3)
C(46)	7 753(2)	3 527(2)	8 335(2)

48.8; H, 4.25; N, 2.0; P, 9.0%. ^1H N.m.r. (CD_3CN): δ 2.18 (1 H, br s, =NH) and 7.46–7.88 (20 H, m, Ph). F.i. mass spectrum: m/z 546 ($M - \text{HCl} - \text{Cl}$, 60) and 417 ($\text{OPh}_2\text{NPPh}_2\text{OH}$, 100%).

Compound (2) from $\text{OPPh}_2\text{NPPh}_2\text{OH}$ (**4**) and MoO_2Cl_2 . A solution of MoO_2Cl_2 (0.47 g, 2.36 mmol) in acetic anhydride (25 cm^3) was added to a solution of compound (**4**) (0.98 g, 2.35 mmol) in acetic anhydride (60 cm^3) room temperature. After stirring for 30 min a pale green precipitate appeared and was filtered off. After concentration of the solvent volume to 20 cm^3

a second portion of the solid was isolated. Recrystallisation of both portions from MeCN gave analytically pure (**2b**) (1.42 g, 97%).

$[\text{Mo}(\text{OPPh}_2\text{NPPh}_2\text{O})_2(\text{O})\text{Cl}]$ (**3**) from (**1**) and Bu^tOH. A solution of Bu^tOH (0.54 g, 7.32 mmol) in thf (20 cm^3) was added to a stirred solution of compound (**1**) (1.50 g, 2.44 mmol) in thf (60 cm^3) at room temperature. Within 3 d the colour of the solution changed from orange-red to green. After further standing for 2 d a white precipitate (NH_4Cl) appeared. Filtration and concentration of the solvent volume to 30 cm^3

gave green crystals of (3), which were recrystallized from hot MeCN (0.43 g; 36% yield, referred to P), m.p. 244–246 °C (decomp.) (Found: C, 58.7; H, 4.2; Cl, 3.7; N, 2.8. Calc. for $C_{48}H_{40}ClMoN_2O_5P_4$: C 58.8; H, 4.1; Cl, 3.6; N, 2.9%). F.i. (field ionisation) mass spectrum: m/z 981 (M , 80%) and 946 ($M - Cl$, 100%).

Compound (3) from Na[OPPh₂NPPh₂O] (5) and MoOCl₃. A solution of compound (5) (1.67 g, 3.80 mmol) in dme (80 cm³) was added to a suspension of [MoCl₃(thf)₂] (0.68 g, 1.88 mmol) in dme (60 cm³) at room temperature. After stirring for 2 h a bright green precipitate appeared, which was isolated by filtration. The solid which contained sodium chloride was subjected to Soxhlet extraction using MeCN (300 cm³) for 1.5 d. Removal of the solvent yielded 1.17 g of analytically pure (3) (63% yield).

[Mo(OPPh₂NPPh₂O)₂O₂] (6). A solution of compound (5) (1.34 g, 3.05 mmol) in thf (50 cm³) was added to a solution of MoO₂Cl₂ (0.30 g, 1.53 mmol) in thf (35 cm³) at room temperature. After stirring for 4 h a turbidity started to form. After concentration of the solvent volume to 20 cm³ the white precipitate was filtered off by using Celite. Cooling of the pale yellow solution to –20 °C gave colourless crystals of (6), which were recrystallised from thf (1.40 g, 95% yield), m.p. 251 °C (decomp.) [Found: C, 60.9; H, 4.6; N, 2.8; P, 12.3. Calc. for $C_{52}H_{48}MoN_2O_7P_4$, 1:1 adduct of (6) with thf: C, 60.45; H, 4.7; N, 2.7; P, 12.0%]. Mass spectrum: m/z 962 (M , 100%) and 946 ($M - O$, 10%).

X-Ray Structure Determinations.—Crystal data are presented in Table 3. For each of compounds (2) and (6) two different solvates were studied. The structure determinations showed that (2b) and (6b) contained disordered solvent molecules, with the result that these structures were much less precise than those of (2a) and (6a). Thus only the results for the latter two will be presented. For (3) two crystals were also measured, but the refined structures were essentially identical (including the same O/Cl disorder), so the data sets were merged (choosing the combination of polar-axis directions which gave the smaller merging R index: 0.0510 rather than 0.0531), and the refinement repeated with the merged data.

Data collection and processing. Stoe-Siemens four-circle diffractometer, monochromated Mo- K_{α} radiation ($\lambda = 0.71069$ Å), profile-fitted intensities.²⁰ Absorption correction based on ψ scans. Programs SHELXS 86 and SHELX 76 (modified by the author) used for all calculations.

Structure analysis and refinement. Structures solved by the heavy-atom method and refined with all non-hydrogen atoms anisotropic. Riding model with idealised geometry and fixed isotropic U for H [the H on N in (2a) was refined with loosely restrained N–H distance and fixed U]. Final atomic coordinates for (2a), (3), and (6a) are given in Tables 4–6. For the two non-centrosymmetric structures the absolute structure was established by means of an η refinement.²¹

The refinement of compound (3) posed severe crystallographic problems. In the space group $I4_1cd$ a two-fold axis through Mo forces the terminal oxygen and chlorine atoms to be disordered. Free refinement of these two atoms with half occupancies produced the lowest R index but unreasonable bond lengths, so it was necessary to apply restraints to the Mo=O and Mo–Cl distances, and to equate the anisotropic thermal parameters for the two atoms. The chemical analysis and e.s.r. spectrum of (3) provide convincing evidence for Mo^v, but since (3) and (6a) are isostructural a mixed phase of intermediate composition

cannot be ruled out. Refinement of an occupation factor appears to depend strongly on the restraints applied to the bond lengths and thermal parameters. We also successfully solved and refined the structure in the lower-symmetry space group $Fdd2$ only to be faced with the same disorder. Since even the collection of two independent data sets from two different crystals did not resolve the problem, we report the results of a refinement with half occupancies for both atoms and very light restraints, even though this results in an unreasonably short Mo–Cl distance.

In each structure the refinements were performed first with the same scattering factors for the three light atoms in the ring, but the thermal parameters showed unambiguously that the atoms joining two P atoms should be assigned as N and the rest as O, as in the final refinements. In (3) and (6a) no Fourier difference peak could be found which could have been assigned to a hydrogen atom attached to N or O⁺.

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

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support, and the Alexander von Humboldt Foundation for a Fellowship (to K. V. K.).

References

- H. W. Roesky, K. V. Katti, U. Seseke, M. Witt, E. Egert, R. Herbst, and G. M. Sheldrick, *Angew. Chem.*, 1986, **98**, 447; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 477.
- H. W. Roesky, K. V. Katti, U. Seseke, H. G. Schmidt, E. Egert, R. Herbst, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1987, 847.
- K. V. Katti, H. W. Roesky, and M. Rietzel, *Inorg. Chem.*, 1987, **26**, 4032.
- K. V. Katti, U. Seseke, and H. W. Roesky, *Inorg. Chem.*, 1987, **26**, 814.
- R. Herbst, K. V. Katti, H. W. Roesky, and G. M. Sheldrick, *Z. Naturforsch., Teil B*, 1987, **42**, 1387.
- M. Witt, H. W. Roesky, M. Noltemeyer, and G. M. Sheldrick, *Angew. Chem.*, 1988, **100**, 852; *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 851.
- M. H. Chrisholm, *Chem. Soc. Rev.*, 1985, **14**, 69.
- W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, 1980, **19**, 777.
- E. A. Babamaian, D. C. Hrcir, S. G. Bott, and J. L. Atwood, *Inorg. Chem.*, 1986, **25**, 4818.
- J. A. De Cray and P. H. Rieger, *Bull. Magn. Reson.*, 1987, **8**, 95.
- E. Fluck and F. L. Goldmann, *Chem. Ber.*, 1963, **96**, 3091.
- B. Viosat, P. Khodadad, and N. Rodier, *Acta Crystallogr., Sect. B*, 1977, **33**, 2523, 3793.
- J. M. Mayer, *Inorg. Chem.*, 1988, **27**, 3899.
- E. I. Stiefel, *Prog. Inorg. Chem.*, 1977, **22**, 1.
- C. D. Garner and S. Bristow, in 'Molybdenum Enzymes,' ed. T. G. Spiro, Wiley, New York, 1985, p. 343.
- A. Schmidpeter, R. Böhm, and H. Groeger, *Angew. Chem.*, 1964, **76**, 860; *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 704.
- H. J. Keller and A. Schmidpeter, *Z. Naturforsch., Teil B*, 1967, **22**, 231.
- I. Rodriguez, C. Alvarez, J. Gomez-Lara, R. A. Toscano, N. Platzler, C. Mulheim, and H. Rudler, *J. Chem. Soc., Chem. Commun.*, 1987, 1502.
- W. E. Cleland jr., K. M. Barnhart, K. Yamanouchi, D. Collison, F. E. Mabbs, R. B. Ortega, and J. H. Enemark, *Inorg. Chem.*, 1987, **26**, 1017.
- W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
- D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.

Received 22nd August 1989,
revised manuscript received 19th February 1990,
Paper 9/03597D