

Substitution of Nitrido by the Oxo Group in Reactions of $[\text{ReNCl}_2(\text{PPh}_3)_2]$ with Multidentate N,O⁻-donor Chelates. Crystal Structure of $[\text{ReOCl}_2(\text{PPh}_3)(\text{HL})]$ [$\text{H}_2\text{L} = 2,6\text{-bis}(\text{hydroxymethyl})\text{pyridine}$][†]

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The complex $[\text{ReNCl}_2(\text{PPh}_3)_2]$ reacts with the potentially bidentate 8-hydroxyquinoline (Hquin) and *N*-phenylsalicylideneimine (Hpsal), and potentially terdentate ligands di-2-pyridyl ketone and 2,6-bis(hydroxymethyl)pyridine (H_2L) to form the products $[\text{ReOCl}(\text{quin})_2]$, $[\text{ReOCl}_2(\text{PPh}_3)(\text{psal})]$, $[\text{ReOCl}_2\{(\text{C}_5\text{H}_4\text{N})_2\text{C}(\text{O})(\text{OH})\}]$ and *cis*- $[\text{ReOCl}_2(\text{PPh}_3)(\text{HL})]$, respectively. The first three products are identical to those isolated earlier by the reactions of *trans*- $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with these ligands, while in the latter product the HL^- ligand acts as a bidentate N,O⁻-donor, spanning one axial (O⁻ *trans* to Re=O) and one equatorial co-ordination site. These reactions present an alternative synthetic route to monooxorhenium(v) complexes. The complex *cis*- $[\text{ReOCl}_2(\text{PPh}_3)(\text{HL})]$ crystallizes in the orthorhombic space group $P2_12_12_1$ with cell parameters $a = 10.019(3)$, $b = 12.457(6)$, $c = 19.53(1)$ Å, $U = 2436.5$ Å³, $Z = 4$, $R = 0.059$ and $R' = 0.074$ for 1330 reflections with $F_o > 4\sigma(F_o)$.

The renewed interest in the co-ordination chemistry of rhenium is partly due to the recent use of the β-emitting nuclides ¹⁸⁶Re ($\beta^- = 1.07$ MeV, *ca.* 1.71×10^{-13} J, $t_{1/2} = 90$ h) and ¹⁸⁸Re ($\beta^- = 2.12$ MeV, *ca.* 3.40×10^{-13} J, $t_{1/2} = 17$ h) as suitable candidates for therapeutic applications in nuclear medicine.^{1,2}

We have recently reported³ the crystal structure of $[\text{ReOCl}_2\{(\text{C}_5\text{H}_4\text{N})_2\text{C}(\text{O})(\text{OH})\}]$, which was synthesized by the reaction of *trans*- $[\text{ReOCl}_3(\text{PPh}_3)_2]$ with di-2-pyridyl ketone (dpk) in benzene, containing trace amounts of water. It was shown that the co-ordinated dpk ligand had undergone nucleophilic addition of water at the carbonyl carbon atom, and that the $(\text{C}_5\text{H}_4\text{N})_2\text{C}(\text{O})(\text{OH})$ moiety acts as a uninegative terdentate N,O,N-donor ligand, with the diolate oxygen in the position *trans* to the oxorhenium(v) group. As an extension to this work, we have decided to prepare the analogous nitridorhenium(v) complex, by using $[\text{ReNCl}_2(\text{PPh}_3)_2]$ and dpk as starting materials.

We have reasoned that initial N,N-co-ordination of dpk to ReN^{2+} , followed by nucleophilic attack of water at the ketonic carbon of dpk, will necessarily place one of the resulting two *gem*-diols in a position close to the octahedral co-ordination site *trans* to the rhenyl nitrido group. An unusual *trans* N≡Re–O arrangement would then be obtained. However, we found that the aerobic reaction of $[\text{ReNCl}_2(\text{PPh}_3)_2]$ with dpk in benzene led to the isolation of the known complex $[\text{ReOCl}_2\{(\text{C}_5\text{H}_4\text{N})_2\text{C}(\text{O})(\text{OH})\}]$, *i.e.* the $\text{Re}\equiv\text{N}^{2+}$ group was lost and was replaced by the $\text{Re}=\text{O}^{3+}$ group. This result appeared totally unexpected, considering the relative stability of the ReN^{2+} core.

We have investigated this phenomenon further, and have found that the reaction of $[\text{ReNCl}_2(\text{PPh}_3)_2]$ with 2,6-bis(hydroxymethyl)pyridine (H_2L) in ethanol gave the product *cis*- $[\text{ReOCl}_2(\text{PPh}_3)(\text{HL})]$ with the ligand HL^- behaving as a uninegative bidentate chelate, with a negatively charged oxygen *trans* to the oxorhenium(v) group. The nitrido group in

$[\text{ReNCl}_2(\text{PPh}_3)_2]$ was also substituted by the oxo group in the reactions with 8-hydroxyquinoline (Hquin) and *N*-phenylsalicylideneimine (Hpsal), with the known compounds⁴ $[\text{ReOCl}(\text{quin})_2]$ and $[\text{ReOCl}_2(\text{PPh}_3)(\text{psal})]$ being isolated respectively.

In this report, we describe the reactions by which the nitrido group is substituted by the oxo group, as well as the crystal structure of *cis*- $[\text{ReOCl}_2(\text{PPh}_3)(\text{HL})]$.

Experimental

Materials.—Solvents were purified and dried before use. All reactions were carried out under aerobic conditions. Literature methods were used for the preparation of $[\text{ReNCl}_2(\text{PPh}_3)_2]$ ⁵ and *trans*- $[\text{ReOCl}_3(\text{PPh}_3)_2]$,⁶ and the ligands di-2-pyridyl ketone (Aldrich), 8-hydroxyquinoline (BDH) and 2,6-bis(hydroxymethyl)pyridine (H_2L) (Ega-Chemie) were purchased. *N*-Phenylsalicylideneimine was prepared by the condensation of aniline and salicylaldehyde in ethanol–benzene (50% v/v). Infrared spectra were recorded on a Shimadzu FTIR-4100 and a Nicolet 20 DXC spectrophotometer in the range 4000–250 cm^{-1} in KBr pellets and ¹H NMR spectra on a Varian Gemini 200 MHz spectrometer. Peak positions are relative to SiMe_4 as an external reference. Electronic spectra were obtained with a Shimadzu UV-3100 spectrophotometer, conductivity data with a Phillips PW 9509 conductometer, and elemental analyses were performed on a Heraeus Rapid Analyzer.

Preparations.— $[\text{ReOCl}_2\{(\text{C}_5\text{H}_4\text{N})_2\text{C}(\text{O})(\text{OH})\}]$. Di-2-pyridyl ketone (0.26 mmol) was added to a benzene solution (20 cm^3) of $[\text{ReNCl}_2(\text{PPh}_3)_2]$ (0.13 mmol), and the mixture was heated under reflux for 10 min. Within a few minutes the red-brown solution turned blue and a blue precipitate began to form. After cooling to room temperature, the blue precipitate was removed by filtration and washed with diethyl ether. Recrystallization from acetonitrile gave the product as dark blue crystals, yield 76%; m.p. 288 °C (Found: C, 27.7; H, 2.0; N, 5.8. $\text{C}_{11}\text{H}_9\text{Cl}_2\text{N}_2\text{O}_3\text{Re}$ requires C, 27.9; H, 1.9; N, 5.9%); $\tilde{\nu}/\text{cm}^{-1}$ (KBr) 955vs (Re=O), 1616s ($\text{C}_5\text{H}_4\text{N}$), 3395w (OH), 323m (ReCl) and 1094s (C–O); $\lambda_{\text{max}}/\text{nm}$ [dimethylformamide

[†] Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

(dmf)] 273 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 4800), 321 (sh), 349 (2700) and 384 (2700); δ_{H} [200 MHz, solvent (CD_3)₂SO, standard SiMe₄] 9.07 (1 H, br s, OH), 8.45 (2 H, d, 2CH), 8.06 (2 H, t, 2CH), 8.02 (2 H, d, 2CH) and 7.82 (2 H, t, 2CH).

[ReOCl(quin)₂]. A solution of 8-hydroxyquinoline (0.60 mmol) in ethanol (10 cm³) was added to a benzene solution (5 cm³) of [ReNCl₂(PPh₃)₂] (0.15 mmol). The mixture was heated under reflux for 45 min, with the solution changing from red-brown to green. After heating was discontinued, the green solution was cooled to room temperature, and filtered to yield a green crystalline precipitate. The slow evaporation of the mother-liquor at room temperature gave another batch of green crystals, total yield 81%; m.p. 329 °C (decomp.) (Found: C, 41.2; H, 2.4; N, 5.3. C₁₈H₁₂ClN₂O₃Re requires C, 41.1; H, 2.3; N, 5.3%); $\tilde{\nu}/\text{cm}^{-1}$ (KBr) 967vs (Re=O), 1318s (C–O) and 308m (ReCl).

[ReOCl₂(PPh₃)(psal)]. A mixture of [ReNCl₂(PPh₃)₂] (63 μmol) and *N*-phenylsalicylideneimine (130 μmol) in ethanol (15 cm³) was heated under reflux for 1 h. After cooling to room temperature, the green precipitate was removed by filtration and washed with ethanol and diethyl ether. Recrystallization from dichloromethane–pentane gave emerald-green plates, yield 79%; m.p. 173 °C (Found: C, 50.7; H, 3.6; N, 2.1. C₃₁H₂₅Cl₂NO₂PRE requires C, 50.9; H, 3.4; N, 1.9%); $\tilde{\nu}/\text{cm}^{-1}$ (KBr) 970s (Re=O), 1601s (HC=N), 1302s (C–O), 313s and 320m (ReCl); δ_{H} [200 MHz, solvent (CD_3)₂SO, standard SiMe₄] 8.57 (1 H, d), 7.75 (6 H, m), 7.62 (15 H, m, PPh₃), 7.29 (1 H, t), 7.16 (1 H, t) and 5.84 (1 H, d).

cis-[ReOCl₂(PPh₃)(HL)]. A quantity of H₂L (0.16 mmol), dissolved in ethanol (5 cm³), was added dropwise to a stirred ethanolic solution (15 cm³) of [ReNCl₂(PPh₃)₂] (0.15 mmol). The mixture was heated under reflux for 10 min, and after about 3 min the orange-brown solution turned blue. After heating was stopped, the hot solution was filtered, and left to evaporate slowly at room temperature. After 48 h the purple crystals were removed by filtration and washed with acetone and diethyl ether, yield 78%; m.p. 188–190 °C (decomp.) (Found: C, 44.4; H, 3.6; N, 2.3. C₂₅H₂₃Cl₂NO₃PRE requires C, 44.6; H, 3.4; N, 2.1%); $\tilde{\nu}/\text{cm}^{-1}$ (KBr) 959vs (Re=O), 1613s (C₅H₄N), 3415w (OH), 323, 328 (ReCl) and 1077s (C–O); $\lambda_{\text{max}}/\text{nm}$ (MeCN) 271 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 7550), 325 (3800), 360 (sh) and 564 (100); δ_{H} [200 MHz, solvent (CD_3)₂SO, standard SiMe₄] 5.05 (1 H, br s, OH), 4.89 (4 H, s, 2CH₂), 7.92 (2 H, d, H² and H⁴), 8.56 (1 H, t, H³) and 7.59 (15 H, m, PPh₃).

The complex *cis*-[ReOCl₂(PPh₃)(HL)] was also prepared from *trans*-[ReOCl₃(PPh₃)₂] under exactly the same conditions, except that heating was continued for 30 min. The melting point, infrared, ¹H NMR and electronic spectra and other physical characteristics were identical to the product prepared from [ReNCl₂(PPh₃)₂].

Crystallography.—A purple parallelepiped (0.08 × 0.12 × 0.16 mm) crystal of [ReOCl₂(PPh₃)(HL)], grown by slow cooling of an ethanol solution, was fixed on a glass capillary and mounted on a Siemens Nicolet R3m/V diffractometer. Cell parameters were refined by using 50 computer-centred reflections from diverse regions of reciprocal space.

Crystal data. C₂₅H₂₃Cl₂NO₃PRE, *M* = 673.5, orthorhombic, space group *P*2₁2₁2₁, *a* = 10.019(3), *b* = 12.457(6), *c* = 19.53(1) Å, *U* = 2436.5 Å³, *Z* = 4, *D*_c = 1.835 g cm⁻³, $\lambda(\text{Mo-K}\alpha)$ = 0.710 73 Å, μ = 53.0 cm⁻¹, *F*(000) = 1312, *T* = 296 K.

Data collection and processing, structure analysis and refinement. Intensity data (up to 2 θ = 45°) were collected by using the ω -scan technique (variable scan range 2.1–14.6° min⁻¹), and to verify sample integrity, two standard reflections were monitored after each 200 reflections; no signal decomposition was observed. An empirical absorption correction, generated from the intensities of six reflections measured at 10° increments about the diffraction vector, was applied to the data (transmission factors: 0.78–1.00). The rhenium atom position was obtained in an origin-removed

Table 1 Atomic coordinates ($\times 10^4$) for [ReOCl₂(PPh₃)(HL)] with estimated standard deviations (e.s.d.s) in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Re	3997(1)	−802(1)	6713(1)
Cl(1)	6131(10)	−1577(9)	7012(6)
Cl(2)	4854(10)	−204(7)	5659(5)
P	1901(7)	157(6)	6472(4)
O(1)	3306(24)	−1974(18)	6366(12)
O(2)	4399(25)	417(19)	7203(14)
O(3)	2556(37)	−4022(28)	8031(17)
N	3387(31)	−1226(23)	7745(16)
C(1)	2878(44)	−2150(33)	8055(23)
C(2)	2489(46)	−2136(39)	8655(27)
C(3)	2349(49)	−1344(40)	9135(28)
C(4)	3012(49)	−326(37)	8830(25)
C(5)	3523(38)	−317(31)	8218(25)
C(6)	4188(55)	453(36)	7910(25)
C(7)	2835(43)	−3103(29)	7597(21)
C(8)	767(26)	−548(20)	5932(14)
C(9)	1315(34)	−1144(24)	5410(17)
C(10)	499(36)	−1738(29)	4927(20)
C(11)	−911(39)	−1631(27)	5025(19)
C(12)	−1442(37)	−1080(27)	5566(19)
C(13)	−649(27)	−479(21)	6027(16)
C(14)	2039(31)	1484(22)	6036(16)
C(15)	1068(33)	1867(21)	5674(14)
C(16)	1191(38)	2850(24)	5307(17)
C(17)	2311(40)	3416(32)	5424(20)
C(18)	3305(37)	3090(28)	5807(19)
C(19)	3201(37)	2074(26)	6175(18)
C(20)	990(33)	442(21)	7264(14)
C(21)	1156(36)	1409(26)	7614(17)
C(22)	524(43)	1589(36)	8250(25)
C(23)	−153(47)	701(38)	8561(23)
C(24)	−264(45)	−273(34)	8203(25)
C(25)	312(34)	−451(25)	7614(18)

Patterson synthesis and the remaining non-hydrogen atoms were located by the usual combination of Fourier synthesis and full-matrix least-squares refinements. Of the 1861 unique reflections only 1330, having $F_o > 4\sigma(F_o)$, were used in the refinements, where the function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w^{-1} = \sigma^2(F) + 0.0017F^2$. Owing to the paucity of diffraction data anisotropy was applied only to Re, Cl and P atoms; the final agreement indices *R*, *R'* and 'goodness of fit' were 0.059, 0.074 and 1.54, respectively, and the refined model proved to be the correct enantiomorph. The calculations⁷ were terminated when all shift/e.s.d. ratios were less than 0.3 and the largest peaks remaining in a final Fourier-difference synthesis were associated with the heavy atom. Atomic positional parameters are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results

[ReOCl₂{(C₅H₄N)₂C(O)(OH)}].—This oxorhenium(v) complex was formed in high yield by the reaction of [ReNCl₂(PPh₃)₂] with a two-fold molar excess of the ligand di-2-pyridyl ketone (dpk) in benzene, containing trace amounts of water, under slight heating. The complex was also prepared in the solvents dichloromethane and acetonitrile, from which suitable crystals for X-ray diffraction were obtained.

The melting point, infrared, ¹H NMR and electronic spectra of the complex were identical to that of [ReOCl₂{(C₅-H₄N)₂C(O)(OH)}], which was prepared previously³ by the reaction of *trans*-[ReOCl₃(PPh₃)₂] with dpk in a variety of solvents.

In order to establish the nature of the complex [ReOCl₂{(C₅H₄N)₂C(O)(OH)}] beyond doubt, an X-ray

crystal structure analysis was undertaken. The results showed that the structure is identical to that reported earlier.³ The $(C_5H_4N)_2C(O)(OH)$ moiety acts as a uninegative, terdentate N, O^- , N -donor ligand to the rhenium(v) ion, which resides in a highly distorted octahedral environment. The two *cis* chlorides and the two nitrogen donors occupy the equatorial sites, with the deprotonated diolate oxygen *trans* to the oxo oxygen ligand.

$[ReOCl_2(quin)_2]$ and $[ReOCl_2(PPh_3)(psal)]$.—These two complexes were prepared in good yield by the reaction of $[ReNCl_2(PPh_3)_2]$ with the corresponding ligands Hquin and Hpsal in ethanol. Their formulations are supported by elemental analyses and infrared data, which, together with their melting points and colour, are identical to those of the compounds prepared earlier⁴ from *trans*- $[ReOCl_3(PPh_3)_2]$ and the ligands Hquin and Hpsal in benzene or tetrahydrofuran (thf). There is no infrared band which could be ascribed to the $Re\equiv N$ stretch in any of the complexes.

$[ReOCl_2(PPh_3)(HL)]$.—The monooxorhenium(v) complex *cis*- $[ReOCl_2(PPh_3)(HL)]$ (*cis* refers to the relative positions of the chloride ligands) was prepared by the reaction of $[ReNCl_2(PPh_3)_2]$ with H_2L in a 1 : 1 ligand to metal molar ratio in ethanol, under aerobic conditions, with slight heating. It was obtained as purple crystals from the slow evaporation of the reaction solution at room temperature, in 78% yield. It was also prepared in good yield (72%) by the reaction of *trans*- $[ReOCl_3(PPh_3)_2]$ with H_2L under reflux in ethanol.

The complex is poorly soluble in polar organic solvents, with highest solubility in acetonitrile, dmf and dimethyl sulfoxide, in which it dissolves to give blue solutions. It is stable in solution for days, and for months in the solid state.

Intense and characteristic stretching vibrations in the infrared spectrum of the complex are consistent with the exhibited core. The $\nu(Re=O)$ is displayed at 959 cm^{-1} , and there is no band in the range $1040\text{--}1090\text{ cm}^{-1}$ which can be attributed to the $Re\equiv N^{2+}$ group. A reasonably strong band at 1077 cm^{-1} is assigned to the C–O stretching and O–H deformation vibrations of the unco-ordinated $-CH_2OH$ group. Two bands of medium intensity at 323 and 328 cm^{-1} are assigned to $\nu(Re-Cl)$.

The 1H NMR spectrum of *cis*- $[ReOCl_2(PPh_3)(HL)]$ was recorded in $(CD_3)_2SO$. The methylene protons result in a singlet at δ 4.89, and the unco-ordinated OH group exhibits a broad singlet centred at δ 5.05. The protons on the pyridine ring are reflected as a two-proton doublet at δ 7.92 and as a triplet at δ 8.56. The co-ordinated PPh_3 results in a multiplet at δ ca. 7.59.

The electronic spectrum of the complex in acetonitrile is dominated by an intense absorption (at 271 nm) due to the $\pi\rightarrow\pi^*$ electronic transition of the pyridine ring in the ligand HL^- . There are additional peaks at 325 and 564 nm, assignable to the oxo oxygen-to-rhenium(v) and chloride-to-rhenium(v) charge-transfer transitions, respectively.

Crystal Structure of cis-(ReOCl₂(PPh₃)(HL)).—The structure is found to contain discrete monomeric neutral molecules in which the metal atom has distorted octahedral geometry, as can be seen in Fig. 1, with the two oxygen atoms *trans* to each other. Only two of the three potential donor atoms of 2,6-bis(hydroxymethyl)pyridine (H_2L) are co-ordinated to rhenium; the ligand acting as a uninegative, bidentate N, O^- -donor. The resulting five-membered metalocycle is not exactly planar, but has a slight envelope conformation with the Re atom 0.05 \AA out of the $O(2)C(6)C(5)N$ plane, which is virtually normal (85.4°) to the equatorial plane. This plane is formed by the two *cis*-chlorides, the N and P atoms. The metal is displaced from the mean equatorial plane by 0.13 \AA , towards the oxo-O(1) atom. In the O_2NCl_2P co-ordination polyhedron the Re atom is $+1.14\text{ \AA}$ from the $Cl(1)NO(1)$ plane and -1.24 \AA from the $O(2)Cl(2)P$ plane, the angle between the two triangular faces being 5.2° . The maximum angular deviation from ideal octahedral values is shown by the $O(1)\text{--}Re\text{--}O(2)$ angle (167°).

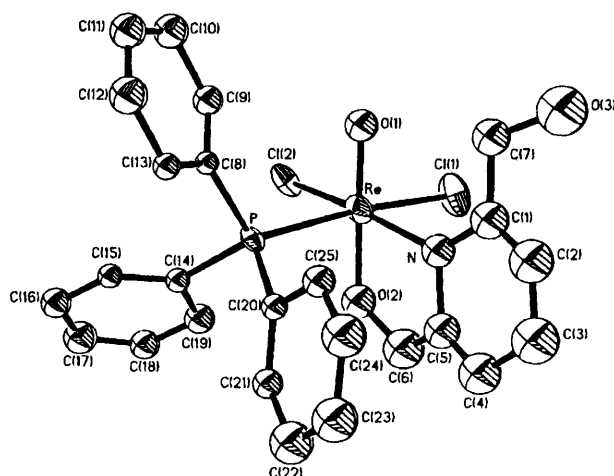


Fig. 1 An ORTEP⁸ view of the complex $[ReOCl_2(PPh_3)(HL)]$, showing the atom numbering and the thermal ellipsoids at 40% probability

Table 2 Bond lengths (\AA) and angles ($^\circ$) in the inner core of $[ReOCl_2(PPh_3)(HL)]$

Re–Cl(1)	2.42(1)	Re–O(1)	1.75(2)
Re–Cl(2)	2.35(1)	Re–O(2)	1.84(2)
Re–P	2.462(8)	Re–N	2.17(3)
Cl(1)–Re–Cl(2)	90.9(4)	P–Re–O(2)	83.4(8)
Cl(1)–Re–P	174.0(3)	O(1)–Re–O(2)	167(1)
Cl(2)–Re–P	89.5(3)	Cl(1)–Re–N	85.8(9)
Cl(1)–Re–O(1)	96.3(8)	Cl(2)–Re–N	172.9(8)
Cl(2)–Re–O(1)	94.0(8)	P–Re–N	93.1(8)
P–Re–O(1)	89.6(8)	O(1)–Re–N	92(1)
Cl(1)–Re–O(2)	90.6(8)	O(2)–Re–N	77(1)
Cl(2)–Re–O(2)	96.6(8)		

The structural properties of *cis*- $[ReOCl_2(PPh_3)(HL)]$ (Table 2) are typical of numerous six-co-ordinate octahedral monooxo complexes of Re^V ,⁹ and are not further commented on. Nevertheless, with regard to bond lengths, a comparison in strictly similar complexes (Table 3) shows that the $Re=O(1)$ distance (1.75 \AA) is quite long compared to the mean value of 1.69 \AA ($\sigma = 0.025\text{ \AA}$), calculated by Mayer¹³ for a large sample of monooxorhenium(v) compounds, while the $Re-O(2)$ distance (1.84 \AA) is somewhat shorter than the expected value (1.92 \AA). Although these differences are not dramatic (within three e.s.d.s), and do not seem of any chemical significance, there appear to be no features of the packing (Fig. 2), governed by van der Waals contacts, which would seem to cause these.

Discussion

The syntheses of the complexes $[ReOCl_2\{(C_5H_4N)_2C(O)(OH)\}]$, $[ReOCl_2(quin)_2]$, $[ReOCl_2(PPh_3)(psal)]$ and $[ReOCl_2(PPh_3)(HL)]$ from $[ReNCl_2(PPh_3)_2]$, with the concomitant easy displacement of the nitrido by an oxo group, is surprising and remarkable. We believe it occurs by deprotonation and co-ordination of a hydroxy group of the chelate ligands in the position *trans* to the nitrido group. This axial co-ordination of the hard base O^- will weaken the $Re\equiv N$ bond considerably, and will 'pull' the rhenium atom into the equatorial plane. The large steric requirements of the nitrido ligand¹⁴ will lead to additional $Re\equiv N$ bond weakening, and its substitution by the smaller oxide (present as H_2O in solvent and air) will be promoted.

Although the substitution of a nitrido by a monooxo group in

Table 3 Comparison of bond lengths (Å) in mononuclear octahedral complexes containing the linear [O=Re–O]²⁺ core and nitrogen pyridine-type donors

Compound	Donor set	Re=O	Re–O	Re–Cl	Re–N	Ref.
[ReOCl ₂ {(C ₅ H ₄ N) ₂ C(O)(OH)}]	O ₂ N ₂ Cl ₂	1.67	2.00	2.31	2.14	3
[{ReOCl ₂ [(C ₅ H ₄ N) ₂ C(O)(OH)] ₂ Cl}] [–]	O ₂ N ₂ Cl ₂	1.67	1.96	2.34	2.15	10
[ReOCl ₂ (OEt)(py) ₂]	O ₂ N ₂ Cl ₂	1.68	1.90	2.37, 2.44	2.14	11
[ReOCl ₂ (OSiMe ₃)(py) ₂]	O ₂ N ₂ Cl ₂	1.68	1.89	2.40	2.13	12
[ReOCl ₂ (L'·OH)]*	O ₂ N ₂ Cl ₂	1.69	1.95	2.37	2.14	9
[ReOCl ₂ (HL)(PPh ₃)]	O ₂ NCl ₂ P	1.75	1.84	2.35	2.17	This work
				2.42 (<i>trans</i> P)		

* L' = 2,3-bis(2-pyridyl)benzo[*g*]quinoxaline.

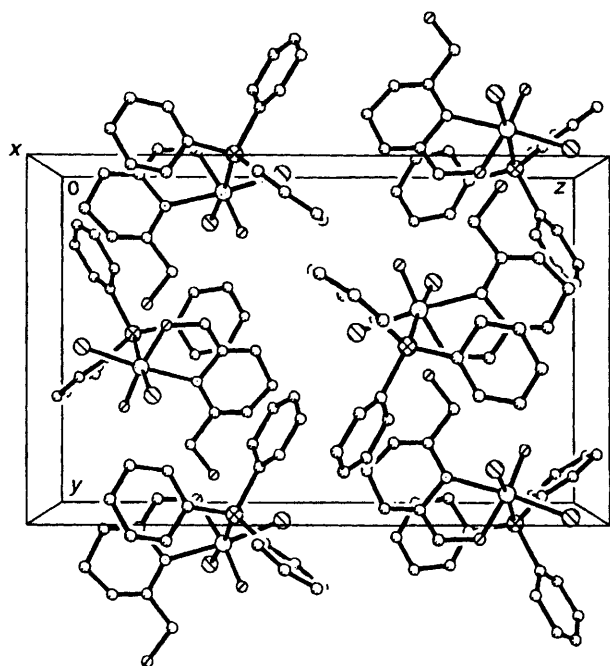


Fig. 2 Packing of the molecules in the unit cell

rhenium(v) complexes has not been reported before, a recent account¹⁵ mentioned the replacement of the Re≡N²⁺ group by the *trans*-dioxo [O=Re=O]⁺ group in reactions of [ReNCl₂(PPh₃)₂] with bi- and tetra-dentate chelating amines.

The bidentate N,O[–]-co-ordination of the potentially terdentate ligand 2,6-bis(hydroxymethyl)pyridine in the complex [ReOCl₂(PPh₃)(HL)] is unusual. It was found that quasi-rigid terdentate ligands with an O,N,X (X = O or S) donor atom set co-ordinate in the equatorial plane *cis* to the oxo group in rhenium(v) complexes, and that a small oxygenated molecule (like H₂O or MeOH) occupies the position *trans* to Re=O in such complexes.^{16–18}

Another surprising feature of the structure is that the co-ordination of the pyridine nitrogen of HL[–] occurs *cis* to the PPh₃ molecule, which contrasts with the *trans* geometry found in the starting complexes [ReNCl₂(PPh₃)₂] and

[ReOCl₃(PPh₃)₂]. All efforts to isolate the *trans* isomer were unsuccessful. Isomerization in monooxorhenium(v) complexes has recently been reported.¹⁹

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