Syntheses and Molecular Structures of the Tridentate Phosphine Ligand 2-[$Ph_2P(CH_2)_3N$=CH]C_6H_4OH (HL) and Its Rhenium(V) Complex [$ReOCl_2L$]·0.25CH_2Cl_2†

Hilary J. Banbery, Wasif Hussain, Thomas A. Hamor,* Christopher J. Jones,* and Jon. A. McCleverty
Department of Chemistry, University of Birmingham, PO Box 363, Birmingham B15 2TT

The tridentate ligand 2-[$Ph_2P(CH_2)_3N$=CH]C_6H_4OH (HL), which contains both 'hard' and 'soft' potential donor atoms, has been synthesized. Single-crystal *X*-ray diffraction studies show that, in the solid state, this ligand adopts a structure in which the oxygen and nitrogen atoms are linked by an intramolecular hydrogen bond. The reaction of this material with $[ReOCl_4]^-$ to form [$ReOCl_2L$] leads to the replacement of the proton in this hydrogen bond by rhenium(V), and the folding of the trimethylene chain to bring the phosphorus atom [Re–P 2.442(5) Å] into a position which allows the ligand to bind facially to the $\{ReO\}^{3+}$ moiety through all three donor atoms. The co-ordination site *trans* to the Re=O oxygen [Re–O = 1.711(13)Å] is occupied by the phenolic oxygen [Re–O = 1.965(13)Å] and the rhenium atom has a distorted octahedral co-ordination environment.

Although the formal oxidation state of V may normally be considered high for a *d*-block metal, the $\{ReO\}^{3+}$ moiety nonetheless forms stable complexes with ligands containing 'soft' donor atoms which might be expected to favour low oxidation states. Particular examples are provided by the well known complex [$ReOCl_3(PPh_3)_2$][1] and by $[ReO(SPh)_4]^-$.[2] In order to investigate the ways in which ligands containing both 'hard' and 'soft' donor atoms might bind to the $\{ReO\}^{3+}$ moiety, we have been studying the reactions of $[ReOCl_4]^-$ with polydentate ligands which contain sulphur[3] or phosphorus as 'soft' donor atoms in combination with aryloxo and amine or imine nitrogen as 'hard' ligating sites. The monobasic tridentate ligand 2-[$Ph_2P(CH_2)_3N$=CH]C_6H_4OH (HL), derived from the condensation of (3-aminopropyl)diphenylphosphine and salicylaldehyde provides an example of such a ligand. We have determined the solid-state molecular structures of both the free ligand and the rhenium(V) complex [$ReOCl_2L$] to establish whether all three donor atoms bind to the rhenium and, if so, to which co-ordination sites relative to the rhenyl oxo group.

Discussion

Synthetic Studies.—The ligand HL may be readily prepared by the reaction between (3-aminopropyl)diphenylphosphine and salicylaldehyde in dichloromethane. The i.r. spectrum of the white crystalline solid obtained contains bands attributable to the presence of the phenyl and propyl groups in addition to ν(C=N) at 1 638 cm^{-1}. The ^1H n.m.r. spectrum of the ligand contains two complex multiplets of total relative area 11 in the region δ 7.44—7.25 (relative to $SiMe_4$) attributable to the phosphinophenyl protons and one of the salicylaldimine aryl protons. The remaining salicylaldimine aryl protons appear as two doublets at δ 7.21 [^3J(H–H) = 7.4 Hz] and 6.95 [^3J(H–H) = 8.2 Hz] and a triplet at 6.89 [^3J(H–H) = *ca.* 7.5 Hz], each of relative area 1. A singlet of relative area 1 appears at δ 8.27 and may be assigned to the azomethine CH proton. The protons of the 1,3-disubstituted propyl moiety appear as three signals each of relative area 2. The C=N–CH_2 protons give rise to a triplet at δ 3.64 [^3J(H–H) = 6.4 Hz], the P-CH_2 protons to a multiplet at δ 2.11 [^3J(H–H) and ^3J(P–H) unresolved], and finally the C-CH_2-C protons to a multiplet at δ 1.83 which is also not fully resolved. A broad singlet of relative area 1 at δ 13.46 is assigned to the salicylaldimine OH proton. The ^{31}P-{H} n.m.r. spectrum contains a singlet at δ 16.69 p.p.m. (relative to 85% aqueous H_3PO_4). The formulation of this compound as 2-[$Ph_2P(CH_2)_3N$=CH]C_6H_4OH was confirmed by the *X*-ray diffraction study described below.

The reaction between $NBu^n{}_4[ReOCl_4]$ and HL proceeded smoothly in refluxing ethanol in the absence of air to produce a green complex. The i.r. spectrum of this material contains bands consistent with the presence of the ligand L and includes ν(C=N) at 1 600 cm^{-1} in addition to ν(Re=O) at 958 cm^{-1}. The ^1H n.m.r. spectrum of the complex was obtained in $(CD_3)_2SO$ since the material was insufficiently soluble in less-polar solvents. It contains two complex multiplets of total relative area 11 in the region δ 7.56—7.36 attributable to the phosphinophenyl protons and one of the salicylaldimine aryl protons. The remaining salicylaldimine aryl protons appear as two overlapping triplets of total relative area 2 at δ 7.10 and a doublet of relative area 1 at δ 6.61 [^3J(H–H) = 7.9 Hz]. A singlet of relative area 1 appears at δ 8.17 and may be assigned to the azomethine CH proton. The protons of the 1,3-disubstituted propyl moiety in the complex are diastereotopic and should give rise to six signals of relative area 1. However, two of these are apparently obscured by signals at δ 3.34 and 2.50 due to residual Me_2SO and water in the solvent. The remaining four protons are observed as a singlet at δ 5.76, a doublet at δ 4.54, and two triplets at δ 4.07 and 3.63; all of these signals contained further unresolved couplings so that their apparent multiplicity was an artefact. The ^{31}P-{^1H} n.m.r. spectrum contains a signal at 21.8 p.p.m. relative to 85% aqueous H_3PO_4 attributable to the phosphine phosphorus. No molecular ion was observed in the electron-impact mass spectrum of the complex, instead the most intense ion was observed at m/z = 584 (^{186}Re, ^{36}Cl, ^{31}P) corresponding with $[M - Cl]^+$. The formulation of this complex as [$ReOCl_2L$] was confirmed by the X-ray study described below.

Structural Studies.—The structure of the ligand HL is illustrated in Figure 1,[4] which also shows the atomic numbering.

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† Dichloro{2-[3′-(diphenylphosphino)propyliminomethyl]phenolato-*NOP*}oxorhenium(V)–dichloromethane(4/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for HL

Atom	x	y	z	Atom	x	y	z
P	1 997(1)	8 581(3)	−896(1)	C(11)	856(3)	10 275(14)	−2 172(4)
O	712(2)	7 483(10)	1 148(3)	C(12)	1 215(2)	10 287(13)	−1 666(3)
N	1 098(2)	4 743(12)	521(3)	C(13)	1 918(2)	5 858(12)	−476(3)
C(1)	2 443(2)	7 790(12)	−1 271(3)	C(14)	1 515(2)	6 168(13)	−196(3)
C(2)	2 708(2)	5 784(14)	−1 145(3)	C(15)	1 463(2)	4 271(13)	234(4)
C(3)	3 056(2)	5 448(15)	−1 440(4)	C(16)	771(2)	3 295(15)	470(3)
C(4)	3 137(3)	7 016(17)	−1 853(4)	C(17)	406(2)	3 784(14)	761(3)
C(5)	2 876(3)	9 009(17)	−1 991(4)	C(18)	67(2)	2 152(15)	716(3)
C(6)	2 534(3)	9 364(15)	−1 700(3)	C(19)	−283(2)	2 567(18)	984(4)
C(7)	1 516(2)	8 474(13)	−1 567(3)	C(20)	−302(3)	4 600(19)	1 303(4)
C(8)	1 445(2)	6 625(13)	−1 984(3)	C(21)	34(3)	6 205(17)	1 360(4)
C(9)	1 084(2)	6 620(16)	−2 494(3)	C(22)	387(2)	5 844(15)	1 077(3)
C(10)	796(2)	8 458(17)	−2 591(3)				

Table 2. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for HL

P–C(1)	1.828(7)	C(8)–C(9)	1.389(9)
P–C(7)	1.842(6)	C(9)–C(10)	1.362(11)
P–C(13)	1.859(7)	C(10)–C(11)	1.377(10)
O–C(22)	1.356(9)	C(11)–C(12)	1.379(10)
N–C(15)	1.447(8)	C(13)–C(14)	1.526(9)
N–C(16)	1.290(9)	C(14)–C(15)	1.479(9)
C(1)–C(2)	1.399(9)	C(16)–C(17)	1.454(9)
C(1)–C(6)	1.386(9)	C(17)–C(18)	1.390(10)
C(2)–C(3)	1.398(10)	C(17)–C(22)	1.379(10)
C(3)–C(4)	1.347(11)	C(18)–C(19)	1.373(11)
C(4)–C(5)	1.388(11)	C(19)–C(20)	1.369(12)
C(5)–C(6)	1.376(10)	C(20)–C(21)	1.370(11)
C(7)–C(8)	1.387(9)	C(21)–C(22)	1.396(10)
C(7)–C(12)	1.376(9)		
C(1)–P–C(7)	100.2(3)	C(9)–C(10)–C(11)	119.8(7)
C(1)–P–C(13)	102.9(3)	C(10)–C(11)–C(12)	120.4(7)
C(7)–P–C(13)	101.6(3)	C(7)–C(12)–C(11)	120.7(7)
C(15)–N–C(16)	121.2(7)	P–C(13)–C(14)	108.8(5)
P–C(1)–C(2)	125.6(5)	C(13)–C(14)–C(15)	113.6(6)
P–C(1)–C(6)	116.7(6)	N–C(15)–C(14)	111.3(6)
C(2)–C(1)–C(6)	117.7(6)	N–C(16)–C(17)	120.7(7)
C(1)–C(2)–C(3)	119.9(7)	C(16)–C(17)–C(18)	119.4(7)
C(2)–C(3)–C(4)	120.8(8)	C(16)–C(17)–C(22)	121.4(7)
C(3)–C(4)–C(5)	120.3(7)	C(18)–C(17)–C(22)	119.2(7)
C(4)–C(5)–C(6)	119.3(8)	C(17)–C(18)–C(19)	120.8(8)
C(1)–C(6)–C(5)	121.8(8)	C(18)–C(19)–C(20)	120.2(8)
P–C(7)–C(8)	122.3(5)	C(19)–C(20)–C(21)	119.6(8)
P–C(7)–C(12)	119.4(5)	C(20)–C(21)–C(22)	121.0(9)
C(8)–C(7)–C(12)	118.2(6)	O–C(22)–C(17)	121.9(6)
C(7)–C(8)–C(9)	121.0(7)	O–C(22)–C(21)	118.9(8)
C(8)–C(9)–C(10)	119.8(7)	C(17)–C(22)–C(21)	119.1(8)

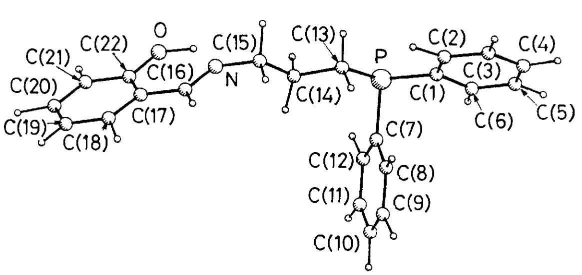

Figure 1. A view of the free ligand HL showing the atom numbering

Fractional atomic co-ordinates, bond lengths and angles are given in Tables 1 and 2 respectively. The *X*-ray analysis confirmed that HL is a neutral, monomeric compound, containing three potential donor atoms which might co-ordinate to a metal atom. The geometry around the phosphorus atom is distorted trigonal pyramidal, with C–P–C angles of 100.2(3), 102.9(3), and 101.6(3)°.

As expected, the P–C bond lengths are not equivalent being 1.859(7) Å for the sp^3-hybridized carbon atom, and 1.828(7) and 1.842(6) Å for the two sp^2-hybridized carbon atoms. The N · · · H-O distance of 2.638 Å (N · · · H 1.66 Å and N · · · H-O 152° based on H in the calculated position) indicate a strong hydrogen-bond interaction between the imine nitrogen and the hydroxyl hydrogen of the salicylaldehyde ring. This distance is shorter than the literature value[5] of 2.77 Å (N · · · H 1.91 Å and N · · · H-O 140°). The strong hydrogen bond produces rigidity in the salicylaldimine moiety, contributing to the linear conformation of the molecule (Figure 1).

The compound [ReOCl$_2$L] crystallizes with two crystallographically independent molecules of the complex, and half a molecule of dichloromethane, per equivalent position. Corresponding bond lengths and angles at Re differ by no more than 0.03 Å and 3° and the overall conformations of the two molecules are quite similar, so only one of these is shown in Figure 2.[4] Fractional atomic co-ordinates and selected bond lengths and angles are given in Tables 3 and 4. The rhenium atom is in an approximately octahedral co-ordination environment. The phenolic oxygen ligand lies *trans* to the oxo group in accord with the well established tendency of oxygen donor atoms in polydentate ligands to co-ordinate at this site.[3,6,7] The phosphorus atom occupies a site *trans* to a chlorine and *cis* to the rhenyl oxo ligand. The tridentate ligand shows substantial distortion from the solid-state structure it adopts in the free state. This brings the phosphorus atom into a position in which, in combination with the aryloxo and imine ligating groups, it can complete facial co-ordination to the rhenium. This contrasts with the meridional co-ordination obtained with more rigid tridentate Schiff-base ligands.[7]

The largest deviations from octahedral geometry occur in the linear angles Cl(2)–Re(1)–N(1) and Cl(2′)–Re(1′)–N(1′), which have values of 169.3(4) and 171.4(4)° respectively. These result in a maximum angular distortion of 10.7 and 8.6° for molecules 1 and 2 respectively. The angles subtended at rhenium by the nitrogen atom and the aryl oxygen atom, involving a more rigid six-membered chelate ring containing an aromatic bond and a C=N double bond, also deviate considerably from the ideal value of 90°; N(1)–Re(1)–O(1) is 83.0(5)° and N(1′)–Re(1′)–O(1′) is 82.7(5)°. For both molecules the Re–Cl(1) bond is longer than Re–Cl(2) by approximately 0.04 Å. This may be due to a *trans* effect of the stronger Re–N bond [2.109(13) and 2.136(17) Å in the two molecules] compared with the Re–P interaction [2.442(5) and 2.451(6) Å]. A comparison of the geometry around the phosphorus atom with that for the free ligand shows that angles at phosphorus have increased, with C–P–C angles in

Table 3. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for $[ReOCl_2L]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	1 916(1)	−1 283(1)	−2 108(1)	Re(1′)	3 267(1)	905(1)	1 271(1)
Cl(1)	2 188(4)	−2 074(4)	−3 003(2)	Cl(1′)	4 215(3)	−229(4)	980(2)
Cl(2)	395(3)	−1 002(4)	−2 708(3)	Cl(2′)	3 823(3)	2 081(4)	737(3)
N(1)	3 159(9)	−1 758(10)	−1 531(7)	N(1′)	2 958(9)	−129(11)	1 857(8)
O(1)	1 503(7)	−2 465(9)	−1 874(5)	O(1′)	4 277(7)	1 119(8)	2 030(6)
O(2)	2 354(7)	−273(9)	−2 274(5)	O(2′)	2 352(8)	626(8)	664(6)
P(1)	1 831(3)	−621(3)	−1 108(2)	P(1′)	2 320(3)	1 923(3)	1 668(2)
C(1)	1 847(13)	−3 287(15)	−1 646(8)	C(1′)	4 787(12)	580(13)	2 490(9)
C(2)	1 286(14)	−4 049(16)	−1 627(9)	C(2′)	5 648(13)	848(16)	2 832(9)
C(3)	1 695(22)	−4 872(16)	−1 347(13)	C(3′)	6 200(14)	307(17)	3 267(10)
C(4)	2 552(18)	−4 926(20)	−1 061(12)	C(4′)	5 848(14)	−532(17)	3 441(10)
C(5)	3 106(19)	−4 191(19)	−1 085(13)	C(5′)	4 989(16)	−808(16)	3 113(11)
C(6)	2 758(16)	−3 365(14)	−1 352(9)	C(6′)	4 435(13)	−249(14)	2 643(9)
C(7)	3 381(13)	−2 582(13)	−1 291(9)	C(7′)	3 533(14)	−530(14)	2 334(9)
C(8)	3 866(11)	−1 037(14)	−1 281(8)	C(8′)	2 015(12)	−389(13)	1 703(10)
C(9)	3 760(12)	−628(14)	−665(9)	C(9′)	1 515(13)	294(14)	1 987(10)
C(10)	2 952(12)	−53(14)	−740(9)	C(10′)	1 356(12)	1 253(14)	1 646(10)
C(11)	1 040(12)	292(12)	−1 145(8)	C(11′)	1 871(12)	2 953(15)	1 195(9)
C(12)	828(12)	890(14)	−1 652(9)	C(12′)	1 689(15)	2 876(14)	533(11)
C(13)	303(13)	1 646(14)	−1 668(10)	C(13′)	1 334(17)	3 645(19)	154(12)
C(14)	−45(13)	1 818(14)	−1 163(10)	C(14′)	1 175(18)	4 459(18)	417(13)
C(15)	113(15)	1 187(17)	−663(10)	C(15′)	1 336(17)	4 495(17)	1 059(15)
C(16)	705(12)	440(14)	−646(9)	C(16′)	1 715(16)	3 766(18)	1 465(10)
C(17)	1 665(11)	−1 474(12)	−557(8)	C(17′)	2 805(13)	2 289(14)	2 497(10)
C(18)	2 265(13)	−1 552(14)	62(9)	C(18′)	3 617(14)	2 760(15)	2 624(11)
C(19)	2 113(14)	−2 245(13)	470(9)	C(19′)	4 013(18)	3 057(19)	3 250(13)
C(20)	1 435(16)	−2 825(14)	268(13)	C(20′)	3 634(26)	2 925(22)	3 718(14)
C(21)	833(16)	−2 763(14)	−332(13)	C(21′)	2 751(22)	2 496(16)	3 549(12)
C(22)	937(12)	−2 081(12)	−761(8)	C(22′)	2 293(17)	2 180(16)	2 925(8)
Cl(3)*	4 537(9)	1 202(10)	4 936(6)	C(23)*	5 131(32)	1 136(29)	4 396(21)
Cl(4)*	5 933(11)	1 907(13)	4 500(8)				

* Atom of solvent molecule, site occupation factor 0.53(1).

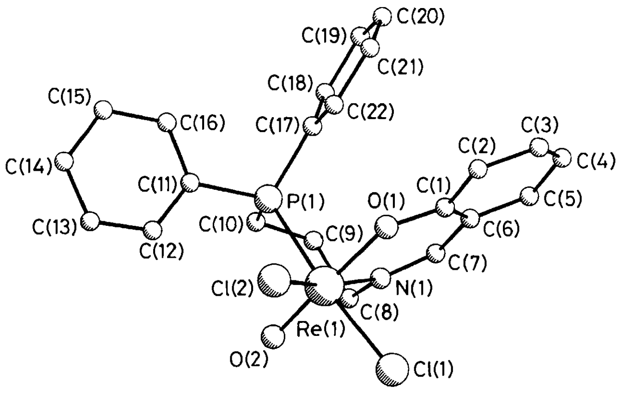

Figure 2. A view of the complex $[ReOCl_2L]$ showing the atom numbering, H atoms have been omitted for clarity

the range 104.0(8)—108.6(8)°. This corresponds with a change from the trigonal pyramidal geometry of the free ligand to a tetrahedral geometry for the complex, and the co-ordination of the sterically bulky lone pair of electrons on phosphorus to the rhenium atom.

The Re–P–C angles range from 104.8(7) to 118.4(6)° and there is a marked systematic difference between these angles. Those involving rhenium and an sp^3-hybridized carbon atom are much smaller with a mean of 105.2°, compared to a mean of 115.9° for Re–P–C(sp^2). This effect may be due to conjugation between the phosphorus lone pair and the aromatic systems, which increases the Re–P–C(sp^2) angles.

These structural studies establish that the potentially tridentate ligand HL can bind to the $\{ReO\}^{3+}$ moiety through all three donor atoms, and that the ligand is sufficiently flexible to achieve facial co-ordination. This behaviour may be compared with that of some facultative ligands which are potentially quinque or sexi-dentate. The ligands $(2\text{-}HOC_6H_4CH{=}NCH_2CH_2)_2S$,[3] $2\text{-}(HNC_4H_3CH{=}NCH_2CH_2)_2NMe$,[8] and $(2\text{-}HOC_6H_4CH{=}NCH_2CH_2OCH_2)_2$[9] react with $[ReOCl_4]^-$ to form complexes in which they function as quadridentate ligands. Thus in $[ReO(OEt)\{(2\text{-}OC_6H_4CH{=}NCH_2CH_2)_2S\}]$[3] the sulphur atom does not bind to rhenium. One phenolic oxygen is bound *trans* to the rhenyl oxo-group so that the next two co-ordinating atoms in the ligand chain must complete a *fac* co-ordination arrangement as indicated in Figure 3(*a*). A similar arrangement is found in $[ReO(Cl)\{2\text{-}OC_6H_4CH{=}NCH_2CH_2OCH_2)_2\}]$,[6] and in $[TcO\{(2\text{-}OC_6H_4CH{=}NCH_2CH_2)_2NH\}]^+$ [Figure 3(*b*)].[9] These findings suggest that it is the preference for binding a phenolic oxygen *trans* to the rhenyl oxo-group which dictates the co-ordination geometries observed in these complexes. Such a preference requires that the next two donor atoms in the sequence should complete mutually *fac* co-ordination. In contrast the ligand $(2\text{-}HNC_4H_3CH{=}NCH_2CH_2)_2NMe$, which lacks phenolic oxygen donor atoms, adopts an arrangement in $[ReO(OMe)\{2\text{-}NC_4H_3CH{=}N(CH_2)_3NMe(CH_2)_3N{=}CHC_4H_3NH\text{-}2\}]$ where only mutually *mer* sites are occupied.[8] An MeO^- ligand then completes six-co-ordination by occupying the site *trans* to the rhenyl oxo-group as shown in Figure 3(*c*). Thus when trying to achieve particular structural arrangements for the binding of facultative ligands to the $\{ReO\}^{3+}$ moiety, the selection of the donor atom type appears to be crucial.

Table 4. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for [ReOCl$_2$L]

Re(1)–Cl(1)	2.431(6)	Re(1′)–Cl(1′)	2.444(5)
Re(1)–Cl(2)	2.402(5)	Re(1′)–Cl(2′)	2.389(6)
Re(1)–N(1)	2.109(13)	Re(1′)–N(1′)	2.136(17)
Re(1)–O(1)	1.965(13)	Re(1′)–O(1′)	1.955(10)
Re(1)–O(2)	1.711(13)	Re(1′)–O(2′)	1.693(11)
Re(1)–P(1)	2.442(5)	Re(1′)–P(1′)	2.451(6)
N(1)–C(7)	1.31(2)	N(1′)–C(7′)	1.30(2)
N(1)–C(8)	1.51(2)	N(1′)–C(8′)	1.48(2)
O(1)–C(1)	1.35(2)	O(1′)–C(1′)	1.34(2)
P(1)–C(10)	1.90(2)	P(1′)–C(10′)	1.80(2)
P(1)–C(11)	1.81(2)	P(1′)–C(11′)	1.84(2)
P(1)–C(17)	1.81(2)	P(1′)–C(17′)	1.83(2)
Cl(1)–Re(1)–Cl(2)	91.7(2)	Cl(1′)–Re(1′)–Cl(2′)	90.5(2)
Cl(1)–Re(1)–N(1)	88.2(4)	Cl(1′)–Re(1′)–N(1′)	87.3(5)
Cl(2)–Re(1)–N(1)	169.3(4)	Cl(2′)–Re(1′)–N(1′)	171.4(4)
Cl(1)–Re(1)–O(1)	87.3(4)	Cl(1′)–Re(1′)–O(1′)	85.7(4)
Cl(2)–Re(1)–O(1)	86.3(3)	Cl(2′)–Re(1′)–O(1′)	88.8(4)
N(1)–Re(1)–O(1)	83.0(5)	N(1′)–Re(1′)–O(1′)	82.7(5)
Cl(1)–Re(1)–O(2)	93.0(5)	Cl(1′)–Re(1′)–O(2′)	94.5(5)
Cl(2)–Re(1)–O(2)	98.1(4)	Cl(2′)–Re(1′)–O(2′)	98.0(5)
N(1)–Re(1)–O(2)	92.6(5)	N(1′)–Re(1′)–O(2′)	90.5(6)
O(1)–Re(1)–O(2)	175.6(4)	O(1′)–Re(1′)–O(2′)	173.2(6)
Cl(1)–Re(1)–P(1)	171.3(2)	Cl(1′)–Re(1′)–P(1′)	173.2(2)
Cl(2)–Re(1)–P(1)	96.2(2)	Cl(2′)–Re(1′)–P(1′)	95.7(2)
N(1)–Re(1)–P(1)	83.3(4)	N(1′)–Re(1′)–P(1′)	86.1(5)
O(1)–Re(1)–P(1)	89.7(4)	O(1′)–Re(1′)–P(1′)	91.6(4)
O(2)–Re(1)–P(1)	89.4(4)	O(2′)–Re(1′)–P(1′)	87.5(5)
Re(1)–N(1)–C(7)	128.9(12)	Re(1′)–N(1′)–C(7′)	124.8(14)
Re(1)–P(1)–C(10)	104.8(7)	Re(1′)–P(1′)–C(10′)	105.6(7)
Re(1)–P(1)–C(11)	118.4(6)	Re(1′)–P(1′)–C(11′)	117.6(7)
C(10)–P(1)–C(11)	104.0(8)	C(10′)–P(1′)–C(11′)	104.4(9)
Re(1)–P(1)–C(17)	113.1(6)	Re(1′)–P(1′)–C(17′)	114.5(7)
C(10)–P(1)–C(17)	108.6(8)	C(10′)–P(1′)–C(17′)	106.2(10)
C(11)–P(1)–C(17)	107.1(9)	C(11′)–P(1′)–C(17′)	107.4(9)

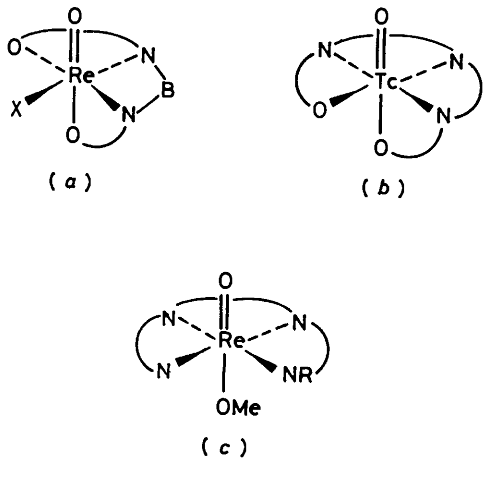

Figure 3. Structural arrangements in a technetium(v) and some rhenium (v) complexes: (*a*) [ReO(OEt){(2-OC$_6$H$_4$CH=NCH$_2$CH$_2$)$_2$S}][3] and [ReOCl{(2-OC$_6$H$_4$CH=NCH$_2$CH$_2$OCH$_2$)$_2$}][6] [X = OEt, B = (CH$_2$CH$_2$)$_2$S; X = Cl, B = (CH$_2$CH$_2$OCH$_2$)$_2$]; (*b*) [TcO{(2- OC$_6$H$_4$CH=NCH$_2$CH$_2$}$_2$NH}]$^+$;[9] and (*c*) [ReO(Cl){(2-NC$_4$H$_3$CH=N(CH$_2$)$_3$NMe(CH$_2$)$_3$N=CHC$_4$H$_3$NH-2}](R = CHC$_4$H$_3$NH-2)[8]

Experimental

Synthetic Studies.—Commercial reagents were used as supplied; (3-aminopropyl)diphenylphosphine[10] and NBu$^n_4$[ReOCl$_4$][11] were prepared according to previously described procedures. Methanol and ethanol were dried over magnesium and redistilled before use but other solvents were used as received without further purification.

Infra-red spectra were recorded using a PE 297 instrument, ^{1}H and ^{31}P n.m.r. spectra using JEOL GX 270 (270 MHz) and FX90Q (36.4 MHz ^{31}P) instruments respectively, and mass spectra using a Kratos MS80 instrument. Microanalyses were performed by the Microanalytical Service, School of Chemistry, University of Birmingham.

2-[Ph$_2$P(CH$_2$)$_3$N=CH]C$_6$H$_4$OH (HL). Salicylaldehyde (1.25 g, 10.2 mmol) was added to a solution of 1-amino-3-diphenylphosphinopropane (2.48 g, 10.2 mmol) in dichloromethane (30 cm^3). The mixture was then stirred for 20 h at room temperature in the presence of dry magnesium sulphate (1 g). The mixture was filtered and the solvent removed from the filtrate under reduced pressure to afford a yellow oil. This was treated with pentane (15 × 2 cm^3) and the combined extracts allowed to stand at room temperature for 0.5 h during which time a yellow solid deposited. This was combined with the solid remaining from the pentane extraction and the whole was recrystallized from ethanol to afford bright yellow needles (2.2 g, 62%) (Found: C, 76.1; H, 6.6; N, 3.9. C$_{22}$H$_{22}$NOP requires C, 76.1; H, 6.3; N, 4.0%).

[ReOCl$_2$L]. The salt NBu$_4$[ReOCl$_4$] (114 mg, 0.33 mmol) was added to a solution of HL (200 mg, 0.33 mmol) in dry ethanol (20 cm^3) and the mixture heated under reflux for 3 h. The green solution which formed was allowed to stand at room temperature for a further 3 h during which time a green solid was deposited. This material was recrystallized from dichloromethane–methanol (1:1) to give bright green needles (90 mg, 44%) (Found: C, 42.6; H, 3.6; N, 2.2. C$_{22}$H$_{21}$Cl$_2$NO$_2$PRe requires C, 42.7; H, 3.4; N, 2.3%).

Structural Studies.—Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with Mo-K_α radiation up to $\theta = 25°$.

Crystal data. HL, $M = 347.4$, monoclinic, space group $C2/c$, $a = 30.928(4)$, $b = 5.717(4)$, $c = 22.171(3)$ Å, $\beta = 103.62(1)°$, $U = 3810$ Å^3, $Z = 8$. $D_c = 1.211$ g cm^{-3}, λ(Mo-K_α) = 0.71069 Å, $\mu = 1.48$ cm^{-1}, $F(000) = 1\,472$, $T = 298$ K.

[ReOCl$_2$L]·0.25CH$_2$Cl$_2$, $M = 640.7$, monoclinic, space group $P2_1/c$, $a = 15.726(3)$, $b = 14.470(9)$, $c = 21.880(12)$Å, $\beta = 107.74(4)°$, $U = 4742$Å^3, $Z = 8$, $D_c = 1.795$ g cm^{-3}, λ(Mo-K_α) = 0.71069Å, $\mu = 57.72$ cm^{-1}, $F(000) = 2484$, $T = 297$ K.

The structures were solved using Patterson and Fourier methods. Positional and anisotropic thermal parameters for the non-hydrogen atoms of the complex were refined by least squares. Hydrogen atoms were placed in calculated positions, riding on their respective carbon atoms, and were assigned an overall isotropic thermal parameter of 0.07 Å^2. The calculations[12] were terminated when all shift/estimated standard deviation (e.s.d) ratios were less than 0.15. Unit weights resulted in a satisfactory weighting analysis for [ReOCl$_2$L], residual electron density +1.1 to −1.6 e Å^{-3}. The weighting scheme used for HL was $w = 1/[\sigma^2(F) + 0.002F^2]$, residual electron density +0.3 to −0.3 e Å^{-3}. An empirical absorption correction was applied to [ReOCl$_2$L] using DIFABS.[13] Final values of R for HL and [ReOCl$_2$L] are 0.067 for 1 554 observed and 0.051 for 4 017 [$F > 5\sigma(F)$] reflections, respectively.

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

Acknowledgements

We are grateful to the S.E.R.C. and Amersham International plc for their support (to H.B. and W.H.).

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Received 22nd March 1989; *Paper* 9/01242G