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PREPARATION AND CRYSTAL STRUCTURE OF DIOXOTETRACHLORO-(*N,N'*-ETHYLENEBIS(SALICYLIDENEIMINATO)BIS(TRIPHENYLPHOSPHINE)-DIRHENIUM(V) DICHLOROMETHANE SOLVATE

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Summary

The complex $ReOCl_3(PPh_3)_2$ reacts with bis(trimethylsilyl)-*N,N'*-ethylenebis-(salicylideneiminato) to give a complex in which the "salen" ligand bridges two rhenium atoms, viz. dioxotetrachloro(*N,N'*-ethylenebis(salicylideneiminato)bis-(triphenylphosphine)dirhenium(V). Its crystal and molecular structure have been determined by a single crystal X-ray diffraction analysis. The crystals are monoclinic space group $P2_1/c$ with four molecules in a cell of dimensions a 18.609(4), b 16.286(4), c 18.600(4) Å and β 105.00(2)°. Least squares refinement of 5867 observed reflections measured on a diffractometer reached R = 0.045. The "salen" ligand bridges two rhenium atoms which present a distorted octahedral coordination. The two halves of the molecule are approximately related by a non-crystallographic two fold axis perpendicular to the C—C bond of the ethylenic group.

Introduction

The ability of the ethylenebis(salicylideneiminato) ligand (salen) and its derivatives to bridge two metal centers has been demonstrated by several authors [1—9]. In particular, crystal structure determinations have been carried out on $Co_3(3\ MeOsalen)_3$ [2] and $(ApoPd)_2$salophen [9] (Apo = acetophenone oxime), but no studies have been reported on salen derivatives of rhenium.

We have found that the complex *trans*-$ReOCl_3(PPh_3)_2$ (which has previously been the subject of several investigations [10—13]), reacts with the new salen derivative (SiMe$_3$)salen [14] to give the compound Re$_2$O$_4$Cl$_4$(salen)(PPh$_3$)$_2$, which is the subject of this paper.

Experimental

Preparation

1.5 g of *trans*-oxotrichlorobis(triphenylphosphine)rhenium(V), 0.580 ml of bis(trimethylsilyl)-*N*,*N′*-ethylenebis(salycilideneiminate) ((SiMe$_3$)$_2$salen) were refluxed together for one hour in THF. The green powder was filtered hot under nitrogen and washed with THF and pentane. The powder was recrystallized from dichloromethane/ethanol and crystals suitable for X-ray analysis were formed.

Elemental analysis of the crude product (Found: C, 46.78; H, 3.48; Cl, 11.30; N, 2.28, mol. wt. (in 1,2-dichloroethane) 1438. $C_{52}H_{44}Cl_4N_2O_4P_2Re_2$ calcd.: C, 46.71; H, 3.32; Cl, 10.61; N, 2.10%; mol. wt. 1337.07) was in agreement with the formulation without dichloromethane of solvation. The analysis carried out after structure determination on the recrystallized product confirmed the presence of the dichloromethane molecules (Found: C, 44.13; H, 3.37; Cl, 14.60; N, 2.09. $C_{53}H_{46}Cl_6N_2O_4P_2Re_2$ calcd.: C, 44.76; H, 3.26; Cl, 14.96; N, 1.97%).

Crystal data

The crystal used was a regular prism with dimensions 0.09 × 0.17 × 0.18 mm. All X-ray experiments were performed using a single-crystal PW 1100 Philips diffractometer with graphite monochromated MoK$_\alpha$ radiation (λ = 0.7107 Å). The monoclinic unit cell was determined on the basis of 25 strong reflections found by mounting the crystal at random in a reciprocal space position defined by $4° < \theta < 12°$, $6° < \chi < 55°$ and $0° < \phi < 90°$.

For the subsequent determination of precise lattice parameters twenty reflections with $15° < \theta < 20°$ were considered, and the precise diffraction angles θ were evaluated as centres of gravity of their profiles $I = f(\theta)$ averaged over positive and negative θ values. Integrated intensities for the *hkl* reflections with $k, l \geqslant 0$ and $2° < \theta < 23°$ were measured using the $\omega/2\theta$ scan method with a scan speed of 1.8° min^{-1} a scan width of 1.30° and two background counts of duration equal to half the peak scanning time taken at each end of the scan. Of the 7540 reflections collected, the 5867 having a net intensity greater than $3\sigma(I)$ ($\sigma(I)$ is the standard error based on count statistics) were used in structure determination and refinement. Every hour three standard reflections were monitored to check the stability of the crystal, and only statistical variations were observed. [$\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$ where CT is the total integrated peak count obtained in scan time t_c, B_1 and B_2 are background counts each obtained in time $\frac{1}{2}t_b$ and $I = CT - (t_c/t_b)^2(B_1 + B_2)$. A value of 0.04 was assigned to the factor p in the formula to calculate $\sigma(I)$ to allow for other error sources]. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects and for absorption by use of the program ORABS.

Structure determination and refinement

The crystals are monoclinic, space group $P2_1/c$. Cell parameters are a 18.609(4), b 16.286(4), c 18.600(4) Å β 105.00(2)° and the calculated density for $Z = 4$ is

1.63 g cm^{-3}. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares techniques. Throughout the refinement the function minimized was $\Sigma\, w(|F_0| - |F_c|)^2$ and a unitary weighting scheme was used.

Atomic scattering factors were taken from ref. 15 and allowance was made for f' and f'' terms of rhenium atoms [16]. The phenyl rings were refined as rigid groups of symmetry D_{6h} (C—C 1.395 Å). At the end of the Fourier refinement the R ($= \Sigma||F_0| - |F_c||/\Sigma|F_0|$) value was 0.20. After a few cycles in the isotropic mode for all the carbon atoms and anisotropic for rhenium, chlorine, oxygen and phosphorous atoms belonging to the rhenium coordination spheres the R value was 6.7%.

A difference Fourier synthesis calculated at this point showed the positions of several hydrogen atoms; in addition, two very broad peaks with electron densities ca. 5—6 electrons $Å^{-3}$ were found, together with two minor peaks of ca. 2 electrons $Å^{-3}$. The two stronger peaks and one of two minor peaks form a roughly isosceles triangle with two edges of 1.7 Å and one of 2.7 Å which correspond well to the C—Cl and Cl · · · Cl distances in dichloromethane. Since the compound was recrystallized from this solvent, the residuals of electron density were attributed to a dichloromethane molecule in the crystal. The second minor peak could be accounted for by an alternative orientation of the CH_2Cl_2 molecule.

The Cl and C (from CH_2Cl_2) atom positions were refined isotropically. Their high thermal parameters (Table 1) as well as the broad peaks in the difference Fourier indicate the presence of some positional disorder as well as high thermal vibration. The introduction of occupancy factors less than one and the refinement of the two alternative orientations of the molecule did not give reliable results and was abandoned. Two final cycles of full-matrix least-squares refinement, isotropic for the chlorine and carbon atoms of the dichloromethane molecule and for the non-coordinated atoms but anisotropic for the atoms belonging to the two coordination polyhedrons, together with introduction of the hydrogens of the phenyl rings at the calculated positions (assuming C—H 0.95 Å and C—C—H 120°), and of the hydrogens belonging to the carbon atoms of the salicylaldimine ligand and of the ethylenic bridge (some in calculated positions and some in the position shown by the difference map) lowered the R factor to the final R value of 0.045.

All data processing and computation were carried out on a CDC 6600 machine using the X-Ray "73" system of programs [17], together with the SHELX package for the rigid groups refinement [18].

Results and discussion

Final positional and thermal parameters of the non group atoms are given in Table 1, along with their standard deviations estimated from the inverse matrix. Similar results for the carbon and hydrogen atoms are listed in Table 2 with the rigid-body coordinates derived from the final group parameters. Tables of observed and calculated structure factors may be obtained from the authors.

The crystal structure is composed of discrete molecules of $(ReCl_2OPPh_3)_2$-salen where the "salen" group acts as bis-bidentate ligand bridging two rhenium

(Continued on p. 58)

TABLE 1

FRACTIONAL COORDINATES (X10^4), ANISOTROPIC ^{a} (X10^4) AND ISOTROPIC (X10^3) TEMPERATURE FACTORS WITH e.s.d.'s IN PARENTHESES

	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re(1)	2923(0)	5365(0)	607(0)	328(0)	339(0)	285(0)	24(0)	90(0)	−25(0)
Re(2)	1878(0)	3727(0)	3405(0)	306(0)	330(0)	273(0)	−9(0)	85(0)	−25(0)
Cl(11)	2565(3)	3968(2)	246(2)	786(31)	431(24)	451(23)	−69(19)	206(22)	−168(22)
Cl(12)	2867(2)	5653(3)	−654(2)	588(26)	601(27)	322(21)	45(19)	137(19)	−39(21)
P(1)	3420(2)	6750(2)	976(2)	449(24)	346(21)	336(21)	1(17)	148(18)	−38(18)
O(11)	2083(5)	5720(6)	627(5)	415(61)	527(67)	383(58)	127(50)	129(48)	−1(51)
O(12)	3944(5)	5027(6)	785(5)	410(56)	414(58)	405(57)	1(47)	171(46)	−89(46)
N(1)	3072(6)	4989(7)	1743(6)	270(65)	438(69)	286(61)	−50(53)	32(51)	−72(55)
N(2)	2007(6)	3674(7)	2290(6)	237(61)	385(72)	309(66)	97(59)	9(51)	3(55)
Cl(21)	3196(2)	3979(3)	3824(2)	351(22)	732(30)	433(23)	69(21)	41(17)	−53(20)
Cl(22)	1853(2)	3648(3)	4668(2)	657(27)	672(28)	325(20)	−40(20)	186(19)	−38(23)
P(2)	541(2)	3371(3)	3054(2)	310(21)	425(23)	402(22)	7(18)	117(17)	−18(18)
O(21)	1625(6)	4716(6)	3244(5)	483(63)	408(61)	429(60)	−30(50)	181(50)	−58(51)
O(22)	2085(5)	2570(6)	3375(5)	396(58)	416(57)	293(52)	7(44)	114(44)	26(45)
C(11)	4508(8)	4740(9)	1335(8)	40(3)					
C(12)	5239(9)	4661(10)	1235(9)	49(4)					
C(13)	5774(10)	4330(11)	1781(10)	61(6)					
C(14)	5632(11)	4106(13)	2448(11)	68(6)					
C(15)	4961(10)	4222(11)	2580(10)	57(5)					
C(16)	4382(8)	4531(9)	2034(8)	38(4)					
C(17)	3654(8)	4655(9)	2185(7)	36(3)					
C(18)	2445(8)	5115(9)	2085(8)	34(3)					
C(28)	1846(8)	4455(9)	1835(8)	37(3)					
C(21)	2213(8)	2000(9)	2899(8)	33(3)					
C(22)	2281(9)	1185(10)	3114(9)	47(4)					
C(23)	2416(10)	602(12)	2627(10)	66(5)					
C(24)	2516(12)	822(13)	1964(12)	72(6)					
C(25)	2464(10)	1633(11)	1741(10)	58(5)					
C(26)	2309(8)	2238(9)	2203(8)	38(4)					
C(27)	2205(8)	3057(9)	1951(8)	39(4)					
Cl(13)	4208(6)	2393(7)	1331(6)	195(4)					
Cl(14)	4332(8)	801(9)	1165(8)	318(6)					
C(1)	4021(12)	1603(14)	585(12)	140(6)					

	x/a	y/b	z/c
H(12)	5158	4937	694
H(13)	6338	4266	1717
H(14)	6086	3815	2892
H(15)	4873	4072	3115
H(17)	3623	4603	2730
H(182)	2233	5741	1986
H(181)	2717	5017	2666
H(281)	1784	4299	1248
H(282)	1306	4690	1879
H(22)	2302	979	3596
H(23)	2504	20	2897
H(24)	2781	425	1592
H(25)	2459	1700	1151
H(27)	2337	3258	1566

[a] In the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{12}a^*b^*hk + \ldots)]$.

TABLE 2

GROUP'S DERIVED PARAMETERS [a]

Group	Derived phenyl-group carbon atoms					Derived phenyl-group hydrogen atoms			
	Atom	*x/a*	*y/b*	*z/c*	*U*	Atom	*x/a*	*y/b*	*z/c*
Group 1	C(110)	3360(5)	8331(7)	362(7)	66(6)	H(110)	3862	8384	645
	C(111)	2998(5)	8997(7)	−48(7)	91(7)	H(111)	3253	9503	−45
	C(112)	2260(5)	8920(7)	−463(7)	92(7)	H(112)	2014	9374	−743
	C(113)	1885(5)	8178(7)	−469(7)	79(6)	H(113)	1383	8125	−751
	C(114)	2248(5)	7512(7)	−58(7)	54(4)	H(114)	1992	7006	−62
	C(19)	2985(5)	7589(7)	357(7)	47(4)				
Group 2	C(116)	4616(6)	6628(7)	368(5)	53(5)	H(116)	4249	6439	−55
	C(117)	5357(6)	6686(7)	343(5)	71(5)	H(117)	5495	6535	−96
	C(118)	5897(6)	6963(7)	964(5)	71(6)	H(118)	6401	7003	948
	C(119)	5695(6)	7184(7)	1610(5)	77(6)	H(119)	6062	7373	2033
	C(120)	4954(6)	7127(7)	1635(5)	63(5)	H(120)	4816	7277	2075
	C(115)	4414(6)	6849(7)	1014(5)	45(3)				
Group 3	C(122)	2717(6)	7588(7)	1922(6)	63(4)	H(122)	2420	7832	1481
	C(123)	2582(6)	7769(7)	2609(6)	84(6)	H(123)	2194	8137	2635
	C(124)	3019(6)	7410(7)	3257(6)	87(7)	H(124)	2927	7533	3724
	C(125)	3589(6)	6870(7)	3218(6)	79(6)	H(125)	3886	6626	3659
	C(126)	3724(6)	6689(7)	2531(6)	58(5)	H(126)	4112	6321	2505
	C(121)	3288(6)	7048(7)	1883(6)	45(4)				
Group 4	C(210)	−367(5)	2010(7)	2902(5)	56(4)	H(210)	−672	2297	2490
	C(211)	−596(5)	1251(7)	3112(5)	72(6)	H(211)	−1056	1022	2843
	C(212)	−148(5)	830(7)	3717(5)	71(6)	H(212)	−304	313	3860
	C(213)	528(5)	1167(7)	4112(5)	62(5)	H(213)	832	880	4524
	C(214)	756(5)	1926(7)	3902(5)	54(4)	H(214)	1217	2156	4171
	C(29)	309(5)	2347(7)	3297(5)	43(4)				
Group 5	C(216)	42(7)	4902(7)	3381(7)	74(6)	H(216)	341	5115	3080
	C(217)	−360(7)	5435(7)	3717(7)	100(8)	H(217)	−336	6011	3645
	C(218)	−798(7)	5123(7)	4159(7)	102(8)	H(218)	−1072	5486	4388
	C(219)	−833(7)	4277(7)	4266(7)	111(8)	H(219)	−1131	4064	4567
	C(220)	−431(7)	3744(7)	3930(7)	74(6)	H(220)	−455	3169	4001
	C(215)	7(7)	4057(7)	3488(7)	51(4)				
Group 6	C(222)	406(5)	2913(6)	1597(6)	46(4)	H(222)	811	2560	1812
	C(223)	108(5)	2923(6)	828(6)	68(5)	H(223)	310	2577	518
	C(224)	−486(5)	3442(6)	512(6)	79(6)	H(224)	−689	3449	−12
	C(225)	−783(5)	3951(6)	966(6)	74(6)	H(225)	−1187	4305	752
	C(226)	−485(5)	3941(6)	1736(6)	63(5)	H(226)	−686	4288	2045
	C(221)	110(5)	3422(6)	2051(6)	43(4)				

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[a] Fractional coordinates (X10^4), temperature factors (X10^3).

atoms. The molecules are separated by Van der Waals contacts and their packing diagram is presented in Fig. 1. The packing is an efficient one, as evidenced by the "graphitic" packing of the phenyl rings and by the relatively low solubility of the compound in various solvents. A view of the molecule with the atomic labelling scheme (in the phenyls rings only the carbon bonded to the phosphorous atom are labelled) is given in Fig. 2. Bond distances and angles are listed in Table 3.

The two rhenium atoms display the same octahedral coordination configuration in both halves of the molecule. A chlorine and the oxygen (oxo) atoms are coordinated in the plane of the bidentate ligand while the second chlorine and the phosphorous atom of the PPh_3 group are in apical positions.

The two halves of the molecule are approximately related by a non crystallographic two fold axis perpendicular to the C—C bond of the ethylenic group.

The IR stretching vibration in the $\nu(Re{=}O)$ region, at 968 cm^{-1}, suggests a similar configuration and geometry of the two octahedral groups. Its position, equal to the $\nu(Re{=}O)$ 969 cm^{-1} found for the *trans*-$ReOCl_3(PPh_3)_2$ complex [13], predicts similar chemical behaviour of their Re=O bonds.

Bridging by the salen ligand is achieved by twisting the two "sal" moieties [N(1), O(12), C(11), · · · C(17) and N(2), O(22), C(21), · · · C(27)] about the ethylene bridge C(18)—C(28) which presents a torsional angle of 84.3°, the "sal"

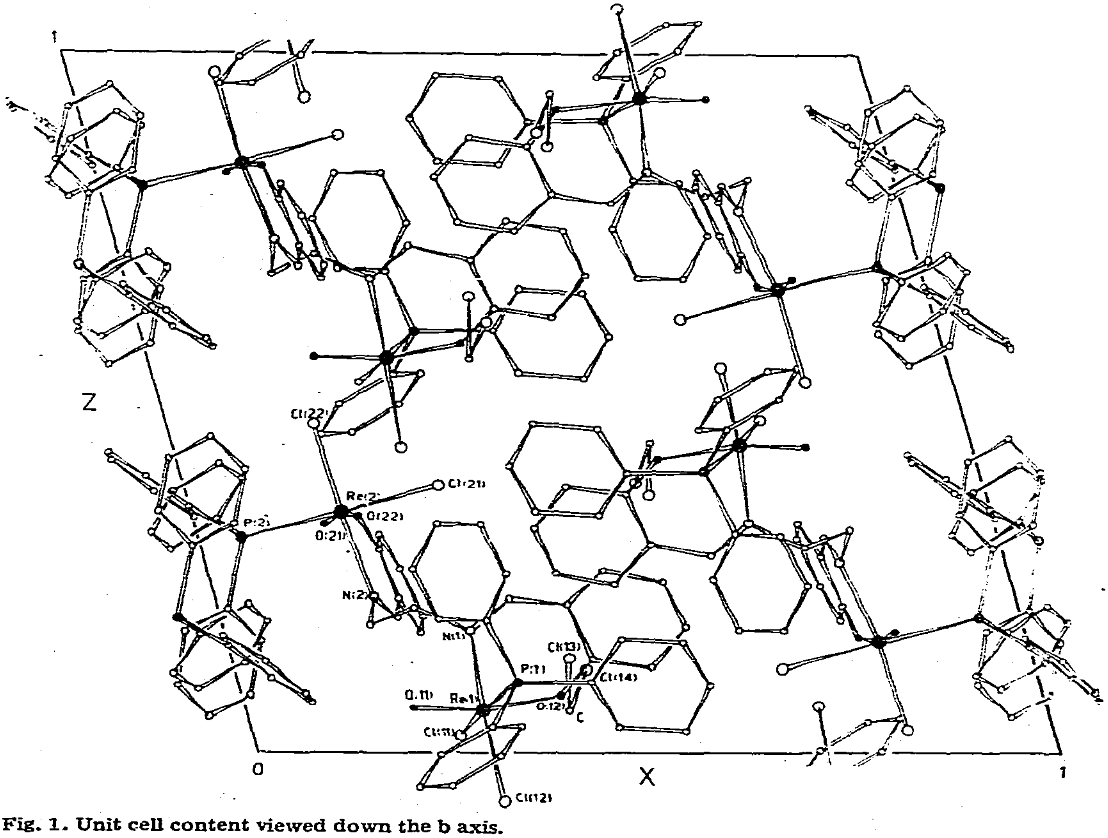

Fig. 1. Unit cell content viewed down the b axis.

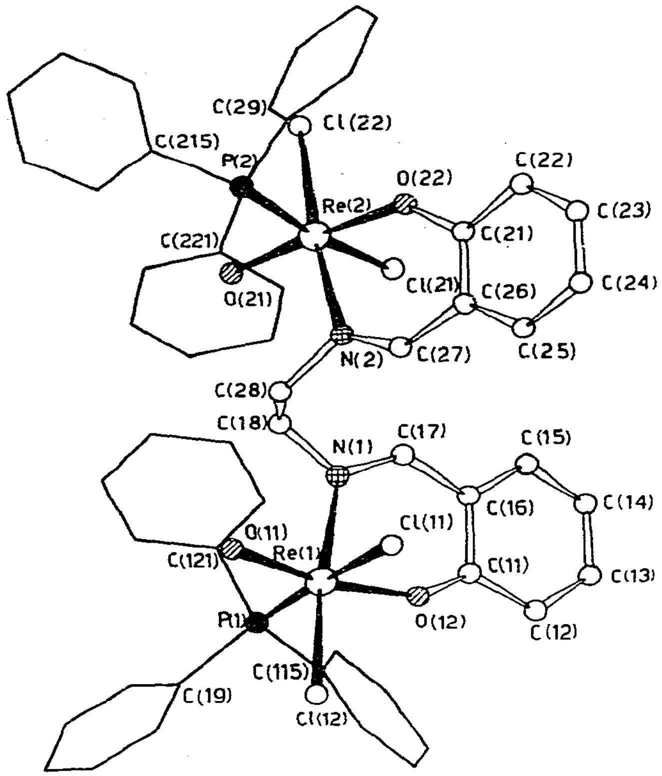

Fig. 2. Perspective view of the molecule.

units being inclined each other at 60.9°. The bridging arrangement gives an intramolecular Re · · · Re distance of 5.99 Å, which excludes any metal—metal bonding interaction.

The most significant differences in the coordination polyhedra do not appear in the inner sphere, where bond distances and angles are the same whether the limit of the error, but in the outer sphere. Thus the relative orientations of the phenyl rings in the two triphenylphosphine moieties are different, as shown in Table 4, where the values of the angles between phenyl rings as well as between the "sal" planes are listed.

The Re—N(1) and Re—N(2) bond distances (2.15(1) and 2.15(1) Å) are significantly longer (0.22 Å) than Re(1)—O(12) and Re(2)—O(22) (1.92(1) and 1.93(1) Å) and much greater than suggested by the difference in covalent radii [19]. This fact has been noticed in several "salen" compounds, for example in $Ti^{IV}Cl_2$salen [20] and in Fe^{III}Clsalen [21], with a difference of 0.25 and 0.20 Å, respectively, this has been explained in terms of Pearson's hard and soft acid—base concept [22,23]. Since the nitrogen is a softer base than oxygen, weaker bonds are formed with nitrogen by rather hard acids Ti^{IV}, Fe^{III} and Re^{V}.

The coordination octahedra are rather irregular, as indicated by bond angles and least squares planes. In particular the basal plane constituted by Re, N and O of the "sal" ligand, Cl and O (oxo) atoms, show deviations of the atoms from planarity of ±0.09 Å.

(Continued on p. 62)

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES

Distances			
Re(1)—Cl(11)	2.416(4)	Re(2)—Cl(21)	2.409(4)
Re(1)—Cl(12)	2.367(3)	Re(2)—Cl(22)	2.365(3)
Re(1)—P(1)	2.466(4)	Re(2)—P(2)	2.472(4)
Re(1)—O(11)	1.68(1)	Re(2)—O(21)	1.68(1)
Re(1)—O(12)	1.92(1)	Re(2)—O(22)	1.93(1)
Re(1)—N(1)	2.15(1)	Re(2)—N(2)	2.15(1)
O(12)—C(11)	1.35(2)	O(22)—C(21)	1.35(2)
N(1)—C(17)	1.30(2)	N(2)—C(27)	1.29(2)
N(1)—C(18)	1.48(2)	N(2)—C(28)	1.51(2)
C(17)—C(16)	1.47(2)	C(27)—C(26)	1.41(2)
C(16)—C(11)	1.42(2)	C(26)—C(21)	1.41(2)
C(11)—C(12)	1.43(2)	C(21)—C(22)	1.38(2)
C(12)—C(13)	1.34(2)	C(22)—C(23)	1.38(2)
C(13)—C(14)	1.38(2)	C(23)—C(24)	1.34(2)
C(14)—C(15)	1.35(2)	C(24)—C(25)	1.38(2)
C(15)—C(16)	1.37(2)	C(25)—C(26)	1.39(2)
P(1)—C(19)	1.83(1)	P(2)—C(29)	1.81(1)
P(1)—C(115)	1.84(1)	P(2)—C(215)	1.82(1)
P(1)—C(121)	1.83(1)	P(2)—C(221)	1.83(1)
C(18)—C(28)	1.53(2)	C(1)—Cl(13)	1.86(2)
C(1)—Cl(14)	1.70(2)		
Angles			
N(1)—Re(1)—Cl(12)	172.9(3)	N(2)—Re(2)—Cl(22)	172.5(3)
O(11)—Re(1)—O(12)	168.7(4)	O(21)—Re(2)—O(22)	168.4(4)
O(12)—Re(1)—N(1)	83.0(4)	O(22)—Re(2)—N(2)	81.9(4)
O(12)—Re(1)—Cl(12)	90.9(3)	O(22)—Re(2)—Cl(22)	91.8(3)
Cl(12)—Re(1)—O(11)	98.8(3)	Cl(22)—Re(2)—O(21)	98.8(3)
O(11)—Re(1)—N(1)	87.7(4)	O(21)—Re(2)—N(2)	87.9(4)
Cl(11)—Re(1)—N(1)	87.8(3)	Cl(21)—Re(2)—N(2)	87.8(3)
O(11)—Re(1)—Cl(11)	98.0(3)	O(21)—Re(2)—Cl(21)	96.3(3)
O(12)—Re(1)—Cl(11)	88.1(3)	O(22)—Re(2)—Cl(21)	89.0(3)
Cl(11)—Re(1)—Cl(12)	88.5(1)	Cl(21)—Re(2)—Cl(22)	88.2(1)
P(1)—Re(1)—Cl(12)	90.7(1)	P(2)—Re(2)—Cl(22)	88.4(1)
P(1)—Re(1)—O(11)	87.9(3)	P(2)—Re(2)—O(21)	87.8(3)
P(1)—Re(1)—N(1)	92.5(3)	P(2)—Re(2)—N(2)	95.3(3)
P(1)—Re(1)—O(12)	86.1(3)	P(2)—Re(2)—O(22)	87.6(3)
Cl(11)—Re(1)—P(1)	174.1(1)	Cl(21)—Re(2)—P(2)	175.0(1)
Re(1)—N(1)—C(18)	118(1)	Re(2)—N(2)—C(28)	117(1)
Re(1)—N(1)—C(17)	128(1)	Re(2)—N(2)—C(27)	128(1)
C(17)—N(1)—C(18)	114(1)	C(27)—N(2)—C(28)	115(1)
Re(1)—O(12)—C(11)	141(1)	Re(2)—O(22)—C(21)	140(1)
N(1)—C(18)—C(28)	111(1)	N(2)—C(28)—C(18)	113(1)
N(1)—C(17)—C(16)	127(1)	N(2)—C(27)—C(26)	127(1)
C(17)—C(16)—C(11)	121(1)	C(27)—C(26)—C(21)	122(1)
O(12)—C(11)—C(16)	120(1)	O(22)—C(21)—C(26)	120(1)
C(17)—C(16)—C(15)	120(1)	C(27)—C(26)—C(25)	120(1)
C(15)—C(16)—C(11)	119(1)	C(25)—C(26)—C(21)	118(1)
O(12)—C(11)—C(12)	121(1)	O(22)—C(21)—C(22)	119(1)
C(16)—C(11)—C(12)	119(1)	C(26)—C(21)—C(22)	121(1)
C(11)—C(12)—C(13)	119(1)	C(21)—C(22)—C(23)	119(1)
C(12)—C(13)—C(14)	121(2)	C(22)—C(23)—C(24)	121(2)
C(13)—C(14)—C(15)	122(2)	C(23)—C(24)—C(25)	121(2)
C(14)—C(15)—C(16)	120(2)	C(24)—C(25)—C(26)	120(2)
Re(1)—P(1)—C(19)	115.7(3)	Re(2)—P(2)—C(29)	116.1(3)
Re(1)—P(1)—C(115)	113.0(3)	Re(2)—P(2)—C(215)	111.5(4)
Re(1)—P(1)—C(121)	111.6(4)	Re(2)—P(2)—C(221)	113.8(3)
C(19)—P(1)—C(115)	103.6(5)	C(29)—P(2)—C(215)	105.2(5)
C(19)—P(1)—C(121)	103.8(5)	C(29)—P(2)—C(221)	103.1(5)
C(115)—P(1)—C(121)	108.3(4)	C(215)—P(2)—C(221)	106.1(5)
Cl(14)—C(1)—Cl(13)	95(1)		

TABLE 4

LEAST-SQUARES PLANES WITH THE DEVIATIONS (Å) OF THE RELEVANT ATOMS IN SQUARE BRACKETS (The equations of the planes in direct space are given by $PX + QY + RZ = S$) AND ANGLES BETWEEN THE PLANES

	P	*Q*	*R*	*S*
Plane 1: Re(1), O(12), N(1), Cl(12), O(11) [Re(1) —0.013, O(12) 0.083, N(1) —0.086, Cl(12) —0.068, O(11) 0.084, Cl(11) —2.421, P(1) 2.453]	5.2565	14.9572	3.6172	9.7934
Plane 2: Re(2), O(22), N(2), Cl(22), O(21) [Re(1) 0.003, O(22) —0.077, N(2) 0.085, Cl(2) 0.067, O(21) —0.078, Cl(21) 2.408 P(2) —2.465]	17.1826	3.7492	1.0758	4.9871
Plane 3: O(12), C(11), C(13), C(14), C(15), C(16), C(17), N(1) [O(12) —0.064, C(11) —0.021, C(12) 0.061, C(13) 0.025, C(14) —0.021, C(15) —0.011, C(16) —0.024, C(17) —0.011, N(1) 0.066]	3.4520	15.0571	5.0877	9.3935
Plane 4: O(22), C(21), C(22), C(23), C(24), C(25), C(26), C(27, N(2) [O(22) 0.057, C(21) 0.010, C(22) —0.018, C(23) —0.059, C(24) —0.008, C(25) 0.044, C(26) 0.050, C(27) 0.010, N(2) —0.086]	16.9194	2.4499	2.5980	4.9769
Plane 5: $\underline{\text{C(19)}}$ [a], C(110), C(111), C(112), C(113), C(114)	—9.9481	4.9088	16.7585	1.3538
Plane 6: $\underline{\text{C(115)}}$, C(116), C(117), C(118), C(119), C(120)	—1.3706	15.3011	—5.6546	9.3013
Plane 7: $\underline{\text{C(121)}}$, C(122), C(123), C(124), C(125), C(126)	11.7494	12.4916	—0.9880	12.4811
Plane 8: $\underline{\text{C(29)}}$, C(210), C(211), C(212), C(213), C(214)	—11.9725	7.5037	14.0814	6.0341
Plane 9: $\underline{\text{C(215)}}$, C(216), C(217), C(218), C(219), C(220)	11.0054	1.0033	11.5981	4.4598
Plane 10: $\underline{\text{C(221)}}$, C(222), C(223), C(224), C(225), C(226)	12.8013	11.7426	—4.8049	3.1732

Angles (deg.) between the planes

(1)—(2)	56.1	(1)—(3)	6.4	(2)—(4)	6.6	(3)—(4)	64.1°
(5)—(6)	86.6	(6)—(7)	50.5	(5)—(7)	89.1		
(8)—(9)	82.0	(9)—(10)	67.4	(8)—(10)	80.7		
(5)—(3)	63.7	(6)—(3)	42.0	(7)—(3)	30.2	(8)—(5)	15.1
(8)—(4)	73.8	(9)—(4)	30.8	(10)—(4)	45.4	(10)—(7)	12.1
(9)—(6)	75.3						

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[a] The underlined carbon atoms are attached to the phosphorous.

The two Re—O_{oxo} bond lengths are the same viz., 1.68(1) Å, and the value is indicative of a triple bond, as reported for other octahedral rhenium(V) compounds such as the $[ReO(H_2O)Cl_2tu_2]^+$ cation [1.654(10) Å] [24] and $[(enH_2)ReOCl_5]$[1.689(10) Å] [25].

In addition the two bond distances Re(1)—O(12) [1.92(1) Å] and Re(2)—O(22) [1.93(1) Å], each *trans* to the multiply bonded oxo ligand, are shorter than the shortest Re—O(2) bond distance, viz. 1.99(1) Å, found in $[ReOCl_2(C_5H_7O_2)P(C_6H_5)_3]$ [26]. This excludes bonding weakening due to the strong π-bonding of the *trans* Re—O_{oxo} group postulated by Johnson et al. [27], but is consistent with Bright and Ibers' explanation [28] that any lengthening of this bond is essentially caused by steric repulsion of other ligands; in our case no significant inter- and intra-molecular contact involves the two O(12) and O(21) atoms.

The two independent Re—P distances of 2.466(5) and 2.472(5) Å agree satisfactorily with those of 2.442, 2.469 and 2.490 Å found in the $[ReNCl_2(P(C_2H_5)_2C_6H_5)_3]$ [29] and with those of 2.45 and 2.48 Å found in $[ReOCl_3(P(C_2H_5)_2C_6H_5)_2]$ [30].

The Re—Cl bond length *trans* to the triphenylphosphine ligand is slightly but significantly longer than the Re—Cl bond length *trans* to the nitrogen by (on average) 0.05 Å, reflecting once again the *trans* influence of a coordinated tertiary phosphine ligand on a M—Cl bond length in an octahedral complex.

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