Table 3. *Selected bond distances* (Å) *and angles* (°) *in oxo complexes of* Re^{V} *with bidentate oxygenated ligands with e.s.d.'s in parentheses*

	Re—O$_{oxo}$	Re—O	O *trans* to	Re—N	N *trans* to	Re—P	P *trans* to	Re—Cl	Cl *trans* to	Re—Br	Br *trans* to	Mean angle X_{cis}—Re—O$_{oxo}$	Reference
ReOCl$_2$(PPh$_3$)(acac)	1·69 (1)	2·10 (1)*	O$_{oxo}$			2·431 (4)	O	2·376 (7)	Cl			96·9 (3)‡	(*a*)
		1·99 (1)	P					2·339 (7)	Cl				
Re$_2$O$_2$Cl$_4$(PPh$_3$)(salen)	1·68 (1)	1·92 (1)	O$_{oxo}$	2·15 (1)	Cl	2·466 (4)	Cl	2·367 (3)	N			93·8 (2)	(*b*)
	1·68 (1)	1·93 (1)	O$_{oxo}$	2·15 (1)	Cl	2·472 (4)	Cl	2·365 (3)	N			93·3 (2)	
								2·416 (4)	P				
								2·404 (4)	P				
ReOCl$_2$(PPh$_3$){Ph(O)-CNNCMe$_3$}	1·685 (8)	2·013 (7)	O$_{oxo}$	2·13 (1)	Cl	2·472 (2)	Cl	2·344 (4)	N			94·5 (2)	(*c*)
								2·388 (3)	P				
ReOCl (Me-sal)$_2$	1·680 (4)	1·979 (4)	O$_{oxo}$	2·120 (5)	O			2·399 (2)	N			95·1 (1)	(*d*)
		1·995 (4)	N	2·103 (5)	Cl								
trans-ReOBr$_2$(PPh$_3$)(Ph-sal) monoclinic form	1·683 (5)	1·937 (5)	O$_{oxo}$	2·173 (6)	P	2·465 (2)	N			2·550 (1)	Br	93·9 (1)	(*e*)
										2·562 (1)	Br		
trans-ReOBr$_2$(PPh$_3$)(Ph-sal) triclinic form	1·680 (4)	1·972 (4)	O$_{oxo}$	2·141 (9)	P	2·482 (3)	N			2·545 (1)	Br	94·9 (1)	(*f*)
										2·547 (1)	Br		
trans-ReOCl$_2$(PPh$_3$)(Me-sal)	1·701 (5)	1·949 (5)	O$_{oxo}$	2·125 (6)	P	2·471 (2)	N	2·375 (2)	Cl			94·3 (1)	(*g*)
								2·430 (2)	Cl				
cis-ReOCl$_2$(PPh$_3$)(Me-sal)	1·660 (8)	1·955 (6)	O$_{oxo}$	2·15 (1)	Cl	2·485 (3)	Cl	2·355 (3)	N			94·1 (2)	(*h*)
								2·397 (3)	P				
Weighted mean [σ_m]†	1·683 [3]	1·970 [8]		2·132 [8]		2·470 [4]		2·389 [7]		2·551 [4]		94·5 [3]	

Abbreviations: acac = acetylacetonato; salen = *N,N'*-ethylenebis(salicylideneaminato); Me-sal and Ph-sal = *N*-methyl- and *N*-phenylsalicylideneaminato.

References: (*a*) Lock & Che'ng Wan (1975); (*b*) Bombieri *et al.* (1978); (*c*) Hursthouse *et al.* (1979); (*d*) Gilli *et al.* (1982); (*e*) Bertolasi *et al.* (1982); (*f*) Sacerdoti *et al.* (1984); (*g, h*) present work.

* Not included in the average.

† Averages and their standard errors are calculated by $x_m = \sum f_i x_i / \sum f_i$ and $\sigma_m = \{\sum f_i (x_i - x_m)^2 / [(N-1)\sum f_i]\}^{1/2}$, where $f_i = 1/\sigma_i^2$ and the summation is from 1 to N.

‡ Standard errors of the single angles are calculated by $\sigma'_m = 1/\sum f_i$(average as above).

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The Structure of *cis*-Dichlorobis[dimethyl(phenyl)phosphine](*N*-phenylsalicylideneaminato)rhenium(III), [Re(C$_{13}$H$_{10}$NO)Cl$_2${P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$]

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Abstract. $M_r = 729·6$, monoclinic, $P2_1/c$, $a = 17·411$ (3), $b = 10·710$ (3), $c = 20·967$ (4) Å, $\beta = 129·58$ (4)°, $U = 3013$ (2) Å^3, $Z = 4$, $D_x = 1·61$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 4·13$ mm^{-1}, $F(000) = 1440$, $T = 298$ K, $R = 0·036$ for 3895 reflections having $I > 3\sigma(I)$. The coordination is nearly octahedral with the two Cl in *cis* and the two P atoms in *trans* positions. Re^{III}—X (X = O, N, Cl, P) distances are compared with $\mathrm{Re^V}$–X distances and the differences are interpreted in terms of Pearson's hard–soft acid–base theory.

Introduction. We have recently reported a number of crystal-structure determinations of quasi-octahedral oxorhenium(V) complexes with Schiff bases such as Ph-sal and Me-sal (*N*-phenyl- and *N*-methylsalicylideneaminato) (Gilli, Sacerdoti, Bertolasi & Rossi, 1982; Bertolasi, Sacerdoti, Gilli & Mazzi, 1982; Sacerdoti, Bertolasi, Gilli & Duatti, 1984; Bertolasi, Ferretti, Sacerdoti & Marchi, 1984) and salen [*N*,*N*′-ethylenebis(salicylideneaminato)] (Bombieri, Mazzi, Gilli & Hernàndez-Cano, 1978).* *cis*-$\mathrm{Re^VO}X_2L(\mathrm{PPh_3})$ (X = Cl or Br; L = Ph-sal or Me-sal) is easily reduced by $\mathrm{PMe_2Ph}$ in boiling benzene to give mononuclear quasi-octahedral complexes of $\mathrm{Re^{III}}$ with the same X and L ligands, that is $\mathrm{Re^{III}}X_2L(\mathrm{PMe_2Ph})_2$ (Duatti, Rossi, Marchi, Magon, Roncari & Mazzi, 1981). We report here the first crystal structure in this class of compounds, that is that of *cis*-$\mathrm{Re^{III}Cl_2(PPhMe_2)_2}$(Ph-sal).

Experimental. Red prism, 0·19 × 0·12 × 0·08 mm, automatic Siemens AED diffractometer, Zr-filtered Mo $K\alpha$, cell parameters from 20 reflections in the range $12 < \theta < 15°$, $\omega/2\theta$ scan, $2 \leq \theta \leq 26°$, 5501 independent reflections ($-16 \leq h \leq 16$, $0 \leq k \leq 13$, $0 \leq l \leq 20$), 3895 having $I > 3\sigma(I)$ considered observed, one standard reflection monitored every 50 reflections, crystal stable through data collection, geometrical absorption correction (0·75 ≤ transmission factor ≤ 1); Patterson and Fourier methods, blocked (2 blocks) matrix least squares on F, anisotropic non-H's, calculated H's, $1{\cdot}74/w = \sigma_F^2 + 0{\cdot}000322|F|^2$, max. Δ/σ 0·4, $R = 0{\cdot}036$, $R_w = 0{\cdot}037$, $S = 1{\cdot}22$, scattering factors from *International Tables for X-ray Crystallography* (1974), final $\Delta\rho$ excursions −0·4–0·5 e Å^{-3} outside the first Re coordination sphere; all calculations done with *SHELX*76 (Sheldrick, 1976).

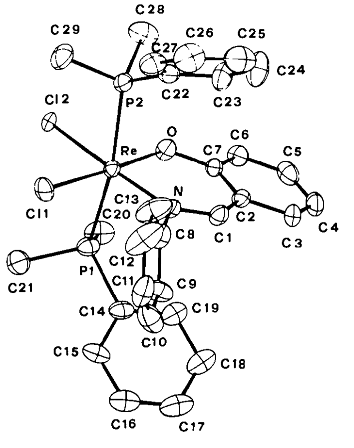

Fig. 1. An *ORTEP* (Johnson, 1971) view of the molecule showing the thermal ellipsoids at 40% probability.

Table 1. *Positional* ($\times 10^4$) *and thermal* (Å$^2 \times 10^3$) *parameters* (*Hamilton,* 1959) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}
Re	2466·4 (2)	3038·0 (2)	7878·7 (2)	33·0 (1)
Cl(1)	2614 (2)	4661 (2)	7185 (1)	52 (1)
Cl(2)	2766 (1)	4526 (1)	8915 (1)	34 (1)
P(1)	4280 (2)	2774 (2)	8861 (1)	47 (1)
P(2)	715 (1)	3598 (2)	7109 (1)	43 (1)
O	2339 (4)	1751 (4)	8491 (3)	47 (3)
N	2227 (4)	1632 (5)	7079 (3)	39 (3)
C(1)	2165 (6)	444 (7)	7181 (5)	45 (4)
C(2)	2242 (5)	−142 (6)	7827 (5)	42 (4)
C(3)	2260 (6)	−1467 (7)	7854 (6)	59 (5)
C(4)	2419 (6)	−2088 (7)	8508 (6)	62 (5)
C(5)	2508 (6)	−1435 (8)	9120 (6)	60 (5)
C(6)	2488 (6)	−142 (7)	9114 (5)	49 (4)
C(7)	2353 (5)	514 (6)	8469 (4)	37 (4)
C(8)	2222 (6)	1879 (7)	6395 (5)	51 (4)
C(9)	3030 (7)	1523 (9)	6459 (5)	63 (5)
C(10)	3017 (9)	1723 (11)	5794 (7)	84 (8)
C(11)	2214 (10)	2282 (9)	5078 (7)	82 (8)
C(12)	1452 (11)	2624 (11)	5031 (7)	110 (10)
C(13)	1438 (9)	2408 (11)	5694 (11)	97 (8)
C(14)	4872 (5)	1629 (8)	8647 (5)	49 (4)
C(15)	5417 (6)	1982 (10)	8397 (6)	65 (5)
C(16)	5817 (7)	1064 (11)	8205 (6)	76 (7)
C(17)	5682 (8)	−177 (12)	8255 (6)	83 (7)
C(18)	5126 (8)	−523 (10)	8490 (6)	81 (7)
C(19)	4711 (7)	377 (9)	8684 (6)	66 (6)
C(20)	4691 (7)	2318 (10)	9874 (5)	68 (6)
C(21)	4945 (7)	4210 (9)	9060 (6)	70 (6)
C(22)	−256 (6)	2887 (7)	6114 (5)	50 (4)
C(23)	−481 (6)	1632 (8)	6097 (7)	73 (6)
C(24)	−1241 (10)	1077 (11)	5346 (9)	109 (9)
C(25)	−1757 (9)	1760 (14)	4618 (8)	100 (9)
C(26)	−1530 (8)	2946 (13)	4633 (7)	90 (7)
C(27)	−795 (7)	3535 (10)	5374 (6)	70 (6)
C(28)	327 (6)	3296 (10)	7725 (5)	72 (6)
C(29)	500 (7)	5257 (8)	6898 (7)	79 (6)

Discussion. Final positional and thermal (Hamilton, 1959) parameters are given in Table 1.* A view of the molecule is shown in Fig. 1. Bond distances and angles are reported in Table 2.

The coordination polyhedron is a slightly distorted octahedron with the two chlorines in *cis* and the two P atoms in *trans* positions. Atoms Re, Cl(1), Cl(2), N and O are not far from coplanar [$\sum(\Delta/\sigma)^2 = 34{\cdot}5$] and define an equatorial plane which is an approximate pseudosymmetry mirror plane for the molecule as a whole. Accordingly, the upper and lower halves of the octahedron are almost perfectly symmetrical and the arrangements of the two $\mathrm{PMe_2Ph}$ moieties are very similar. Both P—C(phenyl) bonds almost eclipse the Re—N bond [N—Re—P(1)—C(14) = 2·4 (4) and N—Re—P(2)—C(22) = −5·1 (4)°] and the conformations of the two phenyls are specular [Re—P(1)—C(14)—

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* The ligand salicylideneaminato is also known as salicylideneiminato.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39075 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Re—Cl(1)	2·383 (3)	C(5)—C(6)	1·39 (1)
Re—Cl(2)	2·468 (2)	C(6)—C(7)	1·40 (1)
Re—P(1)	2·450 (1)	C(8)—C(9)	1·38 (2)
Re—P(2)	2·448 (2)	C(8)—C(13)	1·34 (1)
Re—O	1·990 (7)	C(9)—C(10)	1·40 (2)
Re—N	2·088 (7)	C(10)—C(11)	1·38 (2)
P(1)—C(14)	1·83 (1)	C(11)—C(12)	1·32 (3)
P(1)—C(20)	1·82 (1)	C(12)—C(13)	1·42 (3)
P(1)—C(21)	1·81 (1)	C(14)—C(15)	1·40 (2)
P(2)—C(22)	1·82 (1)	C(14)—C(19)	1·38 (1)
P(2)—C(28)	1·83 (1)	C(15)—C(16)	1·40 (2)
P(2)—C(29)	1·81 (1)	C(16)—C(17)	1·37 (2)
O—C(7)	1·326 (8)	C(17)—C(18)	1·39 (2)
N—C(1)	1·31 (1)	C(18)—C(19)	1·41 (2)
N—C(8)	1·45 (1)	C(22)—C(23)	1·39 (1)
C(1)—C(2)	1·42 (2)	C(22)—C(27)	1·38 (1)
C(2)—C(3)	1·42 (1)	C(23)—C(24)	1·39 (2)
C(2)—C(7)	1·42 (1)	C(24)—C(25)	1·39 (2)
C(3)—C(4)	1·38 (2)	C(25)—C(26)	1·32 (2)
C(4)—C(5)	1·38 (2)	C(26)—C(27)	1·39 (2)

Cl(1)—Re—Cl(2)	91·2 (1)	C(3)—C(2)—C(7)	118 (1)
Cl(1)—Re—P(1)	90·9 (1)	C(2)—C(3)—C(4)	120 (1)
Cl(1)—Re—P(2)	89·6 (1)	C(3)—C(4)—C(5)	121 (1)
Cl(1)—Re—O	177·0 (2)	C(4)—C(5)—C(6)	121 (1)
Cl(1)—Re—N	94·6 (2)	C(5)—C(6)—C(7)	120 (1)
Cl(2)—Re—P(1)	84·2 (1)	O—C(7)—C(2)	122 (1)
Cl(2)—Re—P(2)	84·1 (1)	O—C(7)—C(6)	118 (1)
Cl(2)—Re—O	85·8 (2)	C(2)—C(7)—C(6)	120 (1)
Cl(2)—Re—N	174·1 (2)	N—C(8)—C(9)	119 (1)
P(1)—Re—P(2)	168·3 (1)	N—C(8)—C(13)	121 (1)
P(1)—Re—O	89·5 (2)	C(9)—C(8)—C(13)	119 (1)
P(1)—Re—N	94·8 (2)	C(8)—C(9)—C(10)	120 (1)
P(2)—Re—O	89·5 (2)	C(9)—C(10)—C(11)	121 (2)
P(2)—Re—N	96·9 (2)	C(10)—C(11)—C(12)	119 (2)
O—Re—N	88·3 (3)	C(11)—C(12)—C(13)	121 (1)
Re—P(1)—C(14)	119·7 (2)	C(8)—C(13)—C(12)	120 (2)
Re—P(1)—C(20)	110·4 (4)	P(1)—C(14)—C(15)	122 (1)
Re—P(1)—C(21)	112·9 (3)	P(1)—C(14)—C(19)	118 (1)
C(14)—P(1)—C(20)	104·0 (5)	C(15)—C(14)—C(19)	120 (1)
C(14)—P(1)—C(21)	104·4 (5)	C(14)—C(15)—C(16)	120 (1)
C(20)—P(1)—C(21)	103·9 (5)	C(15)—C(16)—C(17)	121 (1)
Re—P(2)—C(22)	120·8 (4)	C(16)—C(17)—C(18)	119 (1)
Re—P(2)—C(28)	110·9 (3)	C(17)—C(18)—C(19)	121 (1)
Re—P(2)—C(29)	112·2 (4)	C(14)—C(19)—C(18)	119 (1)
C(22)—P(2)—C(28)	104·2 (5)	P(2)—C(22)—C(23)	118 (1)
C(22)—P(2)—C(29)	103·5 (4)	P(2)—C(22)—C(27)	123 (1)
C(28)—P(2)—C(29)	103·5 (6)	C(23)—C(22)—C(27)	119 (1)
Re—O—C(7)	131·2 (7)	C(22)—C(23)—C(24)	119 (1)
Re—N—C(1)	124·5 (7)	C(23)—C(24)—C(25)	120 (1)
Re—N—C(8)	122·3 (5)	C(24)—C(25)—C(26)	120 (1)
N—C(1)—C(2)	128 (1)	C(25)—C(26)—C(27)	121 (1)
C(1)—C(2)—C(3)	118 (1)	C(22)—C(27)—C(26)	121 (1)
C(1)—C(2)—C(7)	124 (1)		

C(19) = −69·2 (9) and Re—P(2)—C(22)—C(23) = 70·7 (9)°]. The C(2)–C(7) phenyl plane $[\sum(\Delta/\sigma)^2 = 3{\cdot}9]$ makes an angle of 12·1 (3)° with the equatorial plane and O, C(1), N and Re atoms are displaced from it by −0·009 (7), −0·09 (1), −0·244 (7) and −0·408 (2) Å, respectively. The Re—O and Re—N distances of 1·990 (7) and 2·088 (7) Å, respectively, are to be compared with the corresponding distances in Re$^{\rm V}$ complexes with the same (*N*-sal) or similar (Ph-sal and salen) ligands (see Bertolasi *et al.*, 1984, and references therein). The observed variation ranges in Re$^{\rm V}$ complexes are 1·92–2·01 Å for Re—O and 2·10–2·17 Å for Re—N, the present values being one of the highest for Re—O and the lowest ever observed for Re—N. This can be interpreted in terms of Pearson's hard–soft acid–base theory (Pearson, 1963). Re$^{\rm V}$ is a hard Lewis acid which must form stronger and shorter bonds with the hard base *R*—O$^-$ than with the softer base $\geqslant$N:. Re$^{\rm III}$ is a less-hard Lewis acid and would bond comparatively better with nitrogen and worse with oxygen, which obviously accounts for the observed variations in internuclear distances. This simple acid–base model seems to be supported also by the comparison between the present Re—Cl and Re—P distances and those observed in Re$^{\rm V}$ complexes (Bertolasi *et al.*, 1984). The average Re—Cl(1)/Re—Cl(2) distance of 2·44 (4) Å is larger than the corresponding weighted average in Re$^{\rm V}$ compounds, *i.e.* 2·38 (1) Å, and, at the same time, the Re—Cl(2) bond *trans* to N is far longer than the Re—Cl(1) bond *trans* to O [2·468 (2) against 2·383 (3) Å], indicating both a possible weakening of the bond between Re$^{\rm III}$ and the hard base Cl$^-$ and a definite *trans* influence exerted by the strong Re$^{\rm III}$—N bond on the Re$^{\rm III}$—Cl bond. As far as Re—P(1) and Re—P(2) distances are concerned, they are statistically indistinguishable [2·450 (1) and 2·448 (2) Å, $\Delta/\sigma = 0{\cdot}89$] and shorter than the weighted average Re$^{\rm V}$—P distance of 2·470 (4) Å, suggesting a stronger interaction between Re$^{\rm III}$ and the soft base PMe$_2$Ph. On the other hand, the shortening of the Re—P bond in Re$^{\rm III}$ complexes is confirmed by the other structural data indicating that the Re$^{\rm III}$—P distance in the absence of *trans* P—Re—P weakening should lie in the range 2·37–2·43 Å (Hahn, Nimry, Robinson, Salmon & Walton, 1978; Jaecker, Robinson & Walton, 1975).

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