Crystal Structure of *trans*-Dicarbonylbis(dimethylphenylphosphine)(*N*-phenylsalicylideneaminato)rhenium(I) and *mer*-Trichloro(dimethylphenylphosphine)(*N*-phenylsalicylideneaminato)rhenium(IV).† Comparison of Re$^{\rm I}$, Re$^{\rm III}$, Re$^{\rm IV}$, and Re$^{\rm V}$ Complexes with the Salicylideneaminato Ligand and Reaction Mechanisms

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The crystal structures of *trans*-[Re$^{\rm I}$(CO)$_2$(psal)(PMe$_2$Ph)$_2$] (**1**) (psal = *N*-phenylsalicylideneaminate) and *mer*-[Re$^{\rm IV}$Cl$_3$(psal)(PMe$_2$Ph)] (**2**), have been determined from single-crystal diffractometer data and refined to *R* factors of 0.029 and 0.020. Crystal data are: a = 16.857(3), b = 10.788(3), c = 17.269(5) Å, β = 105.32(2)°, space group $P2_1/n$, Z = 4 for (**1**) and a = 7.981(2), b = 10.868(2), c = 13.917(1) Å, α = 99.63(1), β = 81.23(2), γ = 108.41(2)°, space group $P\bar{1}$, Z = 2 for (**2**). Both compounds display octahedral co-ordination and a general comparison of their bond distances with similar octahedral complexes of rhenium in its Re$^{\rm III}$ and Re$^{\rm V}$ oxidation states has been carried out. Differences are mainly interpreted in terms of *trans* influence and Pearson's hard–soft acid–base theory. Some aspects of the reaction mechanisms of formation of Re$^{\rm V}$, Re$^{\rm IV}$, Re$^{\rm III}$, and Re$^{\rm I}$ complexes with bidentate Schiff bases are also considered on the basis of structural data.

The chemistry of rhenium with Schiff bases has attracted some attention in recent years due to the considerable ability of these ligands to support different electronic configurations of the metal.[1–4] Our investigations on rhenium complexes with Schiff bases showed the possibility for these ligands to bind rhenium in its V, IV, III, and I oxidation states.[2–4] In rhenium(V) oxo complexes an increase in the strength of the bond *trans* to the multiple-bonded oxygen is observed on going through the series from the charged phenolic oxygen, the neutral aldehydic oxygen, the imine nitrogen, and the chlorine atom.[4–5] Further, rhenium-(III) and -(IV) Schiff-base paramagnetic complexes possess sharply resolved ^{1}H n.m.r. spectra.[2a,b] Parallel structural studies on some of these complexes have been carried out.

Previously we reported the crystal structure determinations of a series of octahedral rhenium(V) oxo complexes with Schiff bases such as *N*-phenylsalicylideneaminate (psal) and *N*-methylsalicylideneaminate (msal), *i.e.* [Re$^{\rm V}$OCl(msal)$_2$],[6] *trans*-[Re$^{\rm V}$OBr$_2$(psal)(PPh$_3$)] (monoclinic[7] and triclinic[8] forms), and *trans*- and *cis*-[Re$^{\rm V}$OCl$_2$(msal)(PPh$_3$)],[9] and *N,N'*-ethylenebis(salicylideneiminate) (salen), *i.e.* [Re$^{\rm V}_2$O$_2$Cl$_4$(salen)(PPh$_3$)$_2$].[10] Moreover we reported the structure of an octahedral Re$^{\rm III}$ complex with a salicylideneaminate ligand, namely [Re$^{\rm III}$Cl$_2$(psal)(PMe$_2$Ph)$_2$].[11]

In the present paper we report the crystal structures of two other octahedral salicylideneaminate complexes with rhenium in the I and IV oxidation states, *trans*-[Re$^{\rm I}$(CO)$_2$(psal)(PMe$_2$Ph)$_2$] (**1**) and *mer*-[Re$^{\rm IV}$Cl$_3$(psal)(PMe$_2$Ph)] (**2**), with the aim of determining the effect of metal oxidation state on the bonding interactions between Re and the Schiff base. Some aspects of the reaction mechanisms of complex formation will also be considered in the light of structural data.

Table 1. Crystal data[a]

Compound	(**1**) [Re$^{\rm I}$(CO)$_2$(psal)(PMe$_2$Ph)$_2$]	(**2**) [Re$^{\rm IV}$Cl$_3$(psal)(PMe$_2$Ph)]
M	714.75	564.9
Crystal size (mm)	0.1 × 0.19 × 0.3	0.05 × 0.12 × 0.27
Space group	$P2_1/n$	$P\bar{1}$
a/Å	16.857(3)	7.981(2)
b/Å	10.788(3)	10.868(2)
c/Å	17.269(5)	13.917(1)
α/°	90	99.63(1)
β/°	105.32(2)	81.23(2)
γ/°	90	108.41(2)
U/Å^3	3 029(1)	1 122.8(4)
Z	4	2
D_c/g cm^{-3}	1.57	1.67
D_m/g cm^{-3}	1.60	1.68
μ(Mo-K_α)/cm^{-1}	41.9	59.2
Standard reflections	3 (stable)	2 (stable)
Independent reflections	6 579	4 884
Reflections with $I > 3\sigma(I)$	4 070	4 003
Variables (last cycle)	343	253
Final R, R'[b]	0.029, 0.031	0.020, 0.025
Final max. shift/error	0.18	0.07
Largest peak (e Å^{-3}) in the final difference map	0.809	0.39
Weighting	$1/w^2 = 1/\sigma^2(I) + 0.03I$	$1/w^2 = 1/\sigma^2(I) + 0.03I$
Error in observation of unit weight	1.1	1.01

[a] Data common to both: Mo-K_α radiation (λ = 0.710 69 Å), graphite monochromator, $\theta_{\rm min.}$—$\theta_{\rm max.}$ range 2—27°, T = 295 K. [b] $R = \Sigma|\Delta F_o|/\Sigma|F_o|$, $R' = (\Sigma_w|\Delta F_o|^2/\Sigma_w|F_o|^2)^{\frac{1}{2}}$.

Experimental

X-Ray Diffraction.—Crystals of (**1**) and (**2**) suitable for *X*-ray analysis were prepared according to the methods given in ref. 2*c* and *d* and recrystallized from CH$_2$Cl$_2$–EtOH. Data for (**1**) and (**2**) (Table 1) were collected on an Enraf–Nonius CAD-4 diffractometer with monochromated Mo-K_α radiation and ω–2θ scan technique. Cell parameters were obtained by least-squares methods from the refined setting angles of 23 reflections for (**1**) and 25 for (**2**) in the range 11 < θ < 14°. Intensities were corrected for Lorentz, polarization and absorption [minimum

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 2. Positional parameters (× 10^4) for (**1**) and (**2**) with e.s.d.s in parentheses

(**1**)				(**2**)			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	2 055.8(1)	1 962.0(2)	−433.2(1)	Re	2 723.7(2)	2 926.4(1)	2 726.7(1)
P(1)	1 134.6(9)	2 218(2)	412.0(9)	Cl(1)	4 054(1)	1 714.1(9)	1 462.3(7)
P(2)	2 798.2(9)	1 652(1)	−1 429.8(9)	Cl(2)	5 043(1)	4 481.7(9)	2 516.3(7)
O(1)	1 432(2)	3 474(3)	−1 145(2)	Cl(3)	1 355(1)	4 051.9(9)	4 025.9(7)
O(2)	797(2)	125(4)	−1 389(3)	P	4 402(1)	2 340.2(8)	3 844.5(7)
O(3)	2 907(3)	−290(4)	486(3)	O	791(3)	1 308(2)	2 940(2)
N	2 887(3)	3 393(4)	231(3)	N	1 175(4)	3 181(3)	1 682(2)
C(1)	1 284(3)	826(5)	−1 022(3)	C(1)	−30(5)	2 226(3)	1 273(3)
C(2)	2 586(3)	587(5)	151(3)	C(2)	−697(4)	901(3)	1 492(3)
C(3)	2 802(4)	4 571(5)	106(4)	C(3)	−1 902(5)	−9(4)	890(3)
C(4)	2 184(4)	5 235(5)	−486(4)	C(4)	−2 639(5)	−1 271(4)	1 064(3)
C(5)	2 226(4)	6 532(6)	−439(4)	C(5)	−2 200(6)	−1 677(4)	1 859(3)
C(6)	1 656(5)	7 275(5)	−938(4)	C(6)	−1 007(5)	−811(4)	2 478(3)
C(7)	1 016(4)	6 714(6)	−1 493(4)	C(7)	−259(4)	490(3)	2 306(3)
C(8)	948(4)	5 455(6)	−1 566(4)	C(8)	1 538(5)	4 433(3)	1 328(3)
C(9)	1 527(4)	4 647(5)	−1 064(3)	C(9)	890(7)	537(4)	1 878(4)
C(10)	3 536(3)	3 063(6)	926(3)	C(10)	1 267(8)	6 581(5)	1 529(5)
C(11)	4 152(4)	2 286(6)	838(4)	C(11)	2 275(6)	6 794(4)	647(3)
C(12)	4 796(4)	2 025(7)	1 528(4)	C(12)	2 898(9)	5 869(5)	135(4)
C(13)	4 816(4)	2 487(7)	2 258(4)	C(13)	2 528(8)	4 665(4)	465(3)
C(14)	4 191(4)	3 246(6)	2 331(4)	C(14)	3 649(4)	608(3)	3 933(2)
C(15)	3 547(4)	3 537(6)	1 671(4)	C(15)	2 326(5)	124(4)	4 673(3)
C(16)	1 360(4)	3 306(6)	1 552(4)	C(16)	1 675(6)	−1 210(4)	4 723(3)
C(17)	1 621(4)	2 931(7)	2 044(4)	C(17)	2 323(6)	−2 051(4)	4 059(3)
C(18)	1 793(5)	3 806(8)	2 661(4)	C(18)	3 624(7)	−1 593(4)	3 323(4)
C(19)	1 736(5)	5 049(8)	2 487(4)	C(19)	4 293(6)	−260(4)	3 251(3)
C(20)	1 487(5)	5 419(7)	1 715(5)	C(20)	6 727(5)	2 742(5)	3 455(4)
C(21)	1 304(4)	4 565(7)	1 088(4)	C(21)	4 251(6)	3 116(4)	5 096(3)
C(22)	116(4)	2 697(8)	−163(4)				
C(23)	936(4)	772(7)	870(4)				
C(24)	3 768(4)	2 432(7)	−1 364(4)				
C(25)	4 504(5)	1 810(10)	−1 219(5)				
C(26)	5 232(5)	2 410(20)	−1 211(7)				
C(27)	5 161(6)	3 710(10)	−1 291(9)				
C(28)	4 468(6)	4 340(10)	−1 427(8)				
C(29)	3 764(5)	3 699(7)	−1 446(5)				
C(30)	3 035(5)	59(8)	−1 556(5)				
C(31)	2 187(4)	2 030(9)	−2 430(4)				

transmission factor of 79.4% and 71.7% for (**1**) and (**2**) respectively]. Scattering factors and anomalous dispersion parameters were taken from International Tables.[12] The positions of rhenium atoms were found from Patterson synthesis and all other non-H atoms were located in the subsequent Fourier map. After few cycles of isotropic refinement both structures were refined by full-matrix least-squares methods using anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were given calculated positions with C–H bond distances of 0.95 Å and fixed isotropic $B = 5$ Å^2. Weights for the last cycle were applied according to the scheme given in Table 1. The phenyl ring C(24)—C(29) in (**1**) was somewhat disordered as indicated by the unrealistically high values of the vibration parameters for the atoms C(26), C(27), and C(28).

All calculations were done using the SDP system of programs.[13] Final positional parameters[14] are given in Table 2. Relevant bond distances and angles are given in Table 3 for (**1**) and Table 4 for (**2**) and views of the two molecules with the atom labelling are shown in Figures 1 and 2.

Discussion

Crystal Structures of (**1**) *and* (**2**).—In both compounds the co-ordination is nearly octahedral. In (**2**) the three Cl atoms are in meridional positions, the phosphine is axial, the other two vertices being occupied by the bidentate ligand. In (**1**) both carbonyls are *trans* to the ligand N and O^- atoms, the two phosphines being in axial positions. Neither psal ligand is planar. In (**1**) the C(4)—C(9) phenyl ring and the atoms N, C(3), C(4), C(9), and O(1) define two planes making an angle of 3.5(2)°; the Re atom is displaced out of the second plane by −0.12 Å. In (**2**) the atoms O, N, C(8), and Re are displaced from the C(1)—C(7) plane by −0.07, 0.09, −0.03, and 0.57 Å respectively. The conformation of the psal phenyl ring is described by the torsion angles C(3)–N–C(10)–C(11) [−123.2(6)°] in (**1**) and C(1)–N–C(8)–C(9)[103.4(5)°] in (**2**). The PMe_2Ph ligand conformations are such that the P(1),P(2)–C(phenyl) bonds nearly eclipse the Re–N bond [N–Re–P(1)–C(16) −1.9(3), N–Re–P(2)–C(24) 5.1(3)°] in (**1**), while the Re–Cl(3) bond is nearly eclipsed by a P–C(methyl) bond [Cl(3)–Re–P–C(21) −8.3(2)°] in (**2**).

Rhenium–carbonyl bond distances of 1.881(6) and 1.879(6) Å are strictly comparable with those found in other rhenium carbonyls, usually in the range 1.88—1.91 Å.[15] The Re^{IV}–Cl distances in (**2**) are on average 2.339(3) Å. This value is at the shortest end of the range for Re^{V}–Cl (2.33—2.43 Å[6–10]). No trend with the changing oxidation number is observed, however, as in *cis*-[$Re^{III}Cl_2(psal)(PMe_2Ph)_2$] where the two Re–Cl distances are 2.383(3) (*trans* to O^-) and 2.468(2) Å (*trans* to N).[11]

Table 3. Selected bond distances (Å) and interatomic angles (°) for (**1**) with e.s.d.s in parentheses

Re–P(1)	2.412(2)	P(1)–C(16)	1.827(6)	O(1)–C(9)	1.278(6)	C(4)–C(5)	1.402(8)
Re–P(2)	2.404(2)	P(1)–C(22)	1.817(7)	O(2)–C(1)	1.172(6)	C(4)–C(9)	1.429(8)
Re–O	2.143(4)	P(1)–C(23)	1.820(7)	O(3)–C(2)	1.165(7)	C(5)–C(6)	1.367(9)
Re–N	2.194(4)	P(2)–C(24)	1.816(7)	N–C(3)	1.290(7)	C(6)–C(7)	1.379(9)
Re–C(1)	1.879(6)	P(2)–C(30)	1.791(8)	N–C(10)	1.438(6)	C(7)–C(8)	1.366(9)
Re–C(2)	1.881(6)	P(2)–C(31)	1.809(7)	C(3)–C(4)	1.442(8)	C(8)–C(9)	1.421(7)
P(1)–Re–P(2)	171.72(5)	N–Re–C(2)	97.3(2)	C(30)–P(2)–C(31)	100.9(5)	C(5)–C(6)–C(7)	118.1(6)
P(1)–Re–O(1)	87.9(1)	C(1)–Re–C(2)	86.5(2)	Re–O(1)–C(9)	131.5(4)	C(6)–C(7)–C(8)	122.1(6)
P(1)–Re–N	91.6(1)	Re–P(1)–C(16)	121.5(2)	Re–N–C(3)	125.3(4)	C(7)–C(8)–C(9)	121.8(6)
P(1)–Re–C(1)	86.4(2)	Re–P(1)–C(22)	111.6(2)	Re–N–C(10)	120.1(4)	O(1)–C(9)–C(4)	124.6(5)
P(1)–Re–C(2)	93.2(2)	Re–P(1)–C(23)	112.8(3)	C(3)–N–C(10)	114.2(5)	O(1)–C(9)–C(8)	119.7(5)
P(2)–Re–O(1)	88.0(1)	C(16)–P(1)–C(22)	102.7(3)	Re–C(1)–O(2)	179.4(5)	C(4)–C(9)–C(8)	115.7(5)
P(2)–Re–N	95.2(1)	C(16)–P(1)–C(23)	103.2(3)	Re–C(2)–O(3)	177.4(5)	N–C(10)–C(11)	119.3(5)
P(2)–Re–C(1)	86.5(2)	C(22)–P(1)–C(23)	103.0(4)	N–C(3)–C(4)	129.5(5)	N–C(10)–C(15)	120.4(5)
P(2)–Re–C(2)	90.6(2)	Re–P(2)–C(24)	121.4(2)	C(3)–C(4)–C(5)	116.1(6)	P(1)–C(16)–C(17)	122.9(6)
O–Re–N	85.0(2)	Re–P(2)–C(30)	113.3(3)	C(3)–C(4)–C(9)	123.7(5)	P(1)–C(16)–C(21)	118.6(5)
O–Re–C(1)	91.3(2)	Re–P(2)–C(31)	112.3(3)	C(5)–C(4)–C(9)	120.1(6)	P(2)–C(24)–C(25)	122.6(7)
O–Re–C(2)	177.4(2)	C(24)–P(2)–C(30)	103.1(4)	C(4)–C(5)–C(6)	122.2(6)	P(2)–C(24)–C(29)	118.3(6)
N–Re–C(1)	175.8(2)	C(24)–P(2)–C(31)	103.4(3)				

Table 4. Selected bond distances (Å) and interatomic angles (°) for (**2**) with e.s.d.s in parentheses

Re–Cl(1)	2.345(1)	Re–N	2.149(4)	N–C(1)	1.290(4)	C(3)–C(4)	1.358(6)
Re–Cl(2)	2.334(1)	P–C(14)	1.806(3)	N–C(8)	1.452(5)	C(4)–C(5)	1.386(7)
Re–Cl(3)	2.337(1)	P–C(20)	1.793(4)	C(1)–C(2)	1.436(5)	C(5)–C(6)	1.396(6)
Re–P	2.475(1)	P–C(21)	1.808(4)	C(2)–C(3)	1.404(5)	C(6)–C(7)	1.396(5)
Re–O	1.970(2)	O–C(7)	1.328(4)	C(2)–C(7)	1.412(6)		
Cl(1)–Re–Cl(2)	91.94(4)	Cl(3)–Re–O	89.31(8)	C(20)–P–C(21)	104.8(2)	C(3)–C(4)–C(5)	119.3(4)
Cl(1)–Re–Cl(3)	177.39(4)	Cl(3)–Re–N	92.88(10)	Re–O–C(7)	129.1(2)	C(4)–C(5)–C(6)	121.0(4)
Cl(1)–Re–P	86.61(4)	P–Re–O	88.42(7)	Re–N–C(1)	122.8(2)	C(5)–C(6)–C(7)	119.8(4)
Cl(1)–Re–O	88.57(7)	P–Re–N	172.82(9)	Re–N–C(8)	121.3(2)	O–C(7)–C(2)	122.4(3)
Cl(1)–Re–N	88.50(8)	O–Re–N	86.20(12)	C(1)–N–C(8)	115.6(3)	O–C(7)–C(6)	118.4(3)
Cl(2)–Re–Cl(3)	90.13(4)	Re–P–C(14)	111.6(1)	N–C(1)–C(2)	127.9(4)	C(2)–C(7)–C(6)	119.2(3)
Cl(2)–Re–P	90.04(4)	Re–P–C(20)	112.9(2)	C(1)–C(2)–C(3)	118.1(4)	N–C(8)–C(9)	119.5(4)
Cl(2)–Re–O	178.35(8)	Re–P–C(21)	115.5(2)	C(1)–C(2)–C(7)	123.1(3)	N–C(8)–C(13)	120.2(3)
Cl(2)–Re–N	95.38(9)	C(14)–P–C(20)	106.4(2)	C(3)–C(2)–C(7)	118.8(3)	P–C(14)–C(15)	119.6(3)
Cl(3)–Re–P	91.81(4)	C(14)–P–C(21)	105.0(2)	C(2)–C(3)–C(4)	121.8(4)	P–C(14)–C(19)	121.2(3)

The known crystal structures of salicylideneaminate complexes with Re^{V},[6–10] Re^{III},[11] and Re^{I} and Re^{IV} (this work) allow a comparison of the ligand geometries as a function of the oxidation number (Table 5).

In all compounds considered, distances in the phenylene ring are equal within the experimental errors and not significantly different from the standard C–C aromatic distance of 1.392 Å. All C(1)–C(2) and C(1)=N distances are grouped, within two e.s.d.s, around the average values of 1.44(1) and 1.29(1) Å, respectively. The N–R distances are 1.447(3) Å for R = Ph and 1.475(5) Å for R = Me, in agreement with the usual shortening of *ca.* 0.03 Å associated with the sp^3 to sp^2 carbon hybridization change.

The rhenium–ligand co-ordination is such that the N–Re–O angle is in the range 84—88.3° without any trend with Re oxidation number. Re–O and Re–N distances are similar to those in Re^{V} and Re^{IV} compounds, but Re–O distances increase by *ca.* 0.02 Å from Re^{IV} to Re^{III} and *ca.* 0.15 Å from Re^{III} to Re^{I}, while the Re–N distances decrease by *ca.* 0.06 Å going from Re^{IV} to Re^{III} and increase by *ca.* 0.11 Å from Re^{III} to Re^{I}. Differences $\Delta = d(\text{Re–N}) - d(\text{Re–O})$ have a smoother trend being *ca.* 0.17, 0.10, and 0.05 Å for Re^{V} *versus* Re^{IV}, Re^{III}, and Re^{I} respectively. These findings are interpretable in terms of two connected factors. The central atom is an acid which becomes less and less hard while its oxidation number decreases (Pearson's hard–soft acid–base theory [16]) causing a lengthening of the Re–O and a shortening of the Re–N distances (see Δ values), in accordance with the known fact that O^- is a relatively stronger base than imine N. The second factor is the *trans* influence. The effect is very weak for phosphine and Cl^- both on *trans* O^- and N, and also for oxo O in Re^{V} oxo complexes on its natural *trans* O^- substituent,[6–10] while it is remarkable when the *trans* substituent is the carbonyl group as in (**1**). Extrapolation of the scatter plot (not shown here) of the Re–N *versus* Re–O distances suggests that the *trans* influence of carbonyl on both N and O^- atoms is of the order of 0.12 Å. This point of view seems to be supported by the plot given in Figure 3, showing the intercorrelation between Δ values and Re–P bond distances. The soft-base phosphine ligand is more strongly bonded on decreasing the oxidation number [average Re^{V}–P 2.470(3) ≃ Re^{IV}–P 2.475(1) > Re^{III}–P 2.449(1) > Re^{I}–P 2.408(4) Å] while the Δ values decrease for the reasons given above.

Reaction Mechanisms.—The structural results discussed above can be of some usefulness for a better understanding of the observed experimental facts concerning the synthesis of rhenium complexes with bidentate Schiff bases. Generally, the chemistry of rhenium in its various oxidation states is ruled by octahedral geometry, so that synthetic routes concern displacement reactions from mixed phosphine–halogen starting materials such as $[Re^{V}OCl_3(PPh_3)_2]$, $[Re^{IV}Cl_4(PPh_3)_2]$, and $[Re^{I}Cl(CO)_3(PPh_3)_2]$ or $[Re^{I}Cl(CO)_3(PMe_2Ph)_2]$[2–4].

Two synthetic routes have been recognised in rhenium complex formation according to whether free protonated Schiff bases or their lithium salts are employed. In the first case, substitution of a neutral PPh_3 group with the imine nitrogen of the neutral Schiff base (HL) into the corresponding starting complexes gives rise to the compounds $[Re^{V}OCl_3(HL)(PPh_3)]$ (**A**) and $[Re^{IV}Cl_4(HL)(PPh_3)]$ (**B**). To account for this substitution step, it is necessary to refer to the harder basic character of the imine nitrogen in comparison with the softer PPh_3 base. This means that the interaction between the hard Re^{V} and Re^{IV} acids and the imine N is stronger than for the PPh_3[16] favouring the substitution process. With the neutral Schiff bases, there exists another possible mechanism of substitution starting with a first attack of the protonated phenolic oxygen OH and the successive elimination of HCl. However, this step does not take place appreciably, so indicating that the OH is a less strong base than imine N. The formation reactions of Re^{V} and Re^{IV} Schiff-base complexes accomplished by the use of the lithium salt of the ligand lead invariably to the monosubstituted chelate complexes. This is readily explained by observing the increased hardness of the O^- base with respect to the imine N, which causes the first attack of the charged oxygen to be preferred.

Unlike compounds (**A**), which in solution transform into the corresponding chelate complexes $[ReOCl_2(L)(PPh_3)]$ through the replacement of a Cl^- by the charged phenolic oxygen of the Schiff base, compounds (**B**) do not transform easily to $[ReCl_3(L)(PPh_3)]$. Such a reaction occurs quickly with rhenium(v) oxo complexes (**A**) owing to the reactive halogen *trans* to the Re–O group. The formation of the *trans* $O{=}Re^+{-}O^-R$ arrangement can be easily understood by admitting a definite *trans* influence (and therefore a *trans* weakening) caused by the Re=O(oxo) bond, which increases according to the *trans* ligand L, in the order $RO^- < Cl^- < Br^- <$ RN. Shustorovich *et al.*[17] came to the conclusion, based on structural as well as on theoretical arguments on quasi-octahedral $[MXL_5]$ transition-metal complexes, that the *trans* influence generated by the M–X bond increases according to X in the sequence R–N= < O= < N≡ and is greater for neutral (L = H_2O, NR_3, CH_3CN, *etc.*) than for anionic ligands (L = $R{-}O^-$, Cl^-, Br^-, *etc.*). A final point in favour of the idea that the *trans* $O{=}Re^+{-}O^-{-}R$ configuration is preferred since it corresponds to a minimum of *trans* weakening is given by the absence of any *trans* elongation in the Re–O single bond when compared with the small but unquestionable elongation of the Re–Cl bond.[6,17]

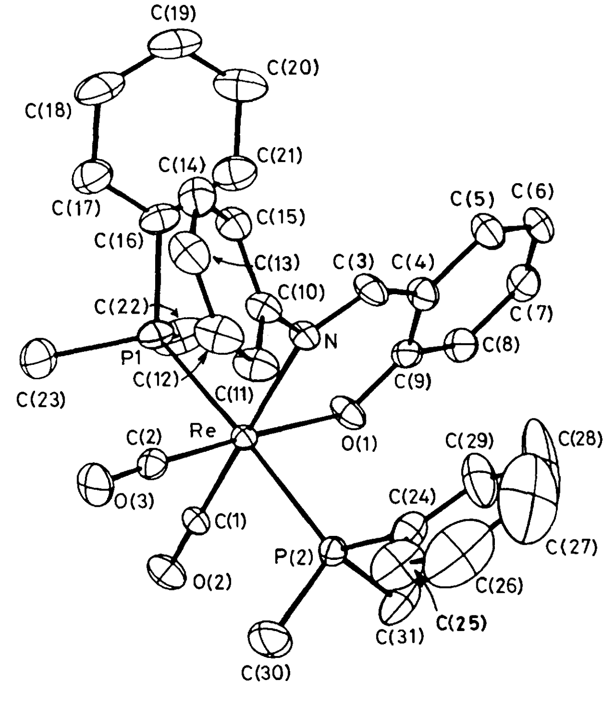

Figure 1. An ORTEP view of the molecule (1) with thermal ellipsoids at the 40% probability level

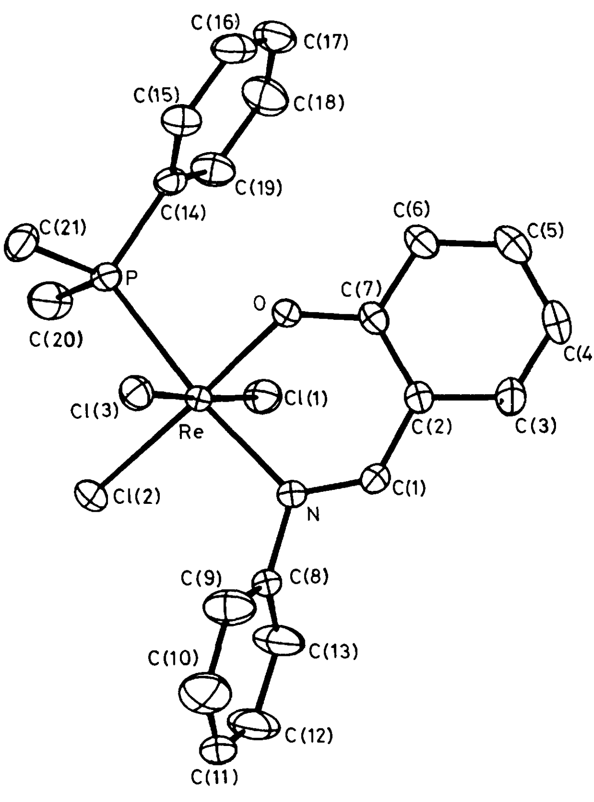

Figure 2. An ORTEP view of the molecule (2) with thermal ellipsoids at the 40% probability level

Table 5. Comparison of selected bond distances (Å) and angles (°) for Re^{V}, Re^{IV}, Re^{III}, and Re^{I} complexes with psal, msal, or salen ligands(L), and the free ligand H_2salen. E.s.d.s are given in parentheses

Compound	Re–O	Re–N	Δ[a]	Re–P	C–O[b]	C=N[b]	N–Re–O	Ref.
$[Re^{V}O_n(L)]$[c]	1.968(8)	2.132(9)	0.16(1)	2.470(3)	1.332(5)	1.290(5)	84(1)	6—10
mer-$[Re^{IV}Cl_3(psal)(PMe_2Ph)]$	1.970(2)	2.149(4)	0.179(3)	2.475(1)	1.328(4)	1.290(4)	86.2(1)	*d*
cis-$[Re^{III}Cl_2(psal)(PMe_2Ph)_2]$	1.990(7)	2.088(7)	0.098(7)	2.449(1)	1.326(8)	1.31(1)	88.3(3)	11
trans-$[Re^{I}(CO)_2(psal)(PMe_2Ph)_2]$	2.143(4)	2.194(4)	0.051(4)	2.408(6)	1.278(6)	1.290(7)	85.0(2)	*d*
H_2salen					1.345(3)	1.270(3)		*e*

[a] Difference between Re–N and Re–O distances. [b] C–O and C=N distances in the Schiff-base ligand. [c] Weighted values on six structures (one salen, two psal, and three msal complexes). [d] This work. [e] N. Bresciani Pahor, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Crystallogr., Sect B*, 1978, **34**, 1360.

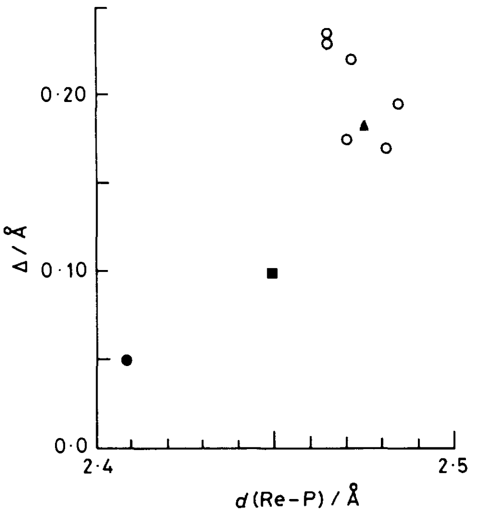

Figure 3. Intercorrelation of Re–P distances *versus* the differences, Δ, between Re–N and Re–O distances for the compounds in Table 5. (●) *trans*-[$Re^I(CO)_2(psal)(PMe_2Ph)_2$], (■) *cis*-[$Re^{III}Cl_2(psal)(PMe_2Ph)_2$], (▲) *mer*-[$Re^{IV}Cl_3(psal)(PMe_2Ph)$], (○) Re^V complexes

On considering the substitution on the rhenium(I) starting material, [$ReCl(CO)_3(PPh_3)_2$], it is found that the replacement of a PPh_3 group with the imine nitrogen of the Schiff base with the formation of [$ReCl(CO)_3(HL)(PPh_3)$] does not occur. The strong soft–soft acid–base interaction between Re^I and phosphine (see bond lengths) makes difficult the displacement of this latter group. Instead, the monosubstituted chelate complexes [$Re(CO)_2(L)(PPh_3)_2$] are obtained in high yield when the salt of the ligand is used. In this case, the first step of the process involves the breaking of the Re–Cl bond with the replacement of Cl^- with the deprotonated phenolic oxygen of the Schiff base. Such a hypothesis is in agreement with the known labilization of a M–Cl bond by a *trans* carbonyl group.[18,19]

A decrease of reactivity was observed with the complex [$Re^{III}Cl_3(PMe_2Ph)_3$]. All rhenium(III) Schiff-base complexes were prepared by reduction of the corresponding monosubstituted oxo complexes of Re^V.[5] No substitution of phosphine or chlorine was achieved by reacting the ligand in its neutral or deprotonated form and this can be related to the increased strength of the interaction between the softer Re^{III} acid and the soft PMe_2Ph base not correspondingly balanced by a decrease in the Re–Cl bond strength (see structural data). The rhenium(III) oxidation state, thus, can be considered as corresponding to a minimum of reactivity concerning the type of displacement reactions discussed here.

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