Synthesis, Properties and X-ray Crystal Structure of Schiff Base Organoimido Complexes of Rhenium(V)

R. ROSSI, A. MARCHI, A. DUATTI, L. MAGON*

Istituto Chimico, Università di Ferrara, Ferrara, Italy

U. CASELLATO, R. GRAZIANI

Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R. and Istituto di Chimica Generale, Università di Padova, Padua, Italy

and G. POLIZZOTTI

Istituto di Ingegneria Chimica, Università di Palermo, Palermo, Italy

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$Re(NR)Cl_3(PPh_3)_2$ (R = p-$CH_3C_6H_4$, CH_3) react with polydentate ligands (LH = N-methyl-, N-phenyl-, N-tolyl-salicylideneimine, half N,N'-ethylenebis-, half N,N'-propylenebis-(salicylideneimine), 8-hydroxyquinoline and LH_2 = N-2-hydroxyphenylsalicylideneimine) to yield complexes of the type $Re(NR)Cl_2(L)PPh_3$. With 8-hydroxyquinoline the bisubstituted $Re(NR)Cl(L)_2$ complexes are also obtained. The compounds were characterized by elemental analysis, molecular weight, and i.r. spectra.

The crystal and molecular structures of two arylimido complexes, $Re(p\text{-}CH_3C_6H_4N)Cl_2(RN{=}CH\text{-}C_6H_4O)PPh_3$ with R = C_6H_5 or CH_3, were determined from X-ray crystallography based on diffractometer data. The phenyl compound crystallizes in space group $P2_1/c$ of the monoclinic system, with a = 15.340(5) Å, b = 21.115(6) Å, c = 10.605(5) Å, β = 91.36(5)°, and D_x = 1.59 g cm^{-3} for four formula units in the cell. The structure has been refined by least-squares to the final R factor of 4.7% for the 3931 reflexions above background.

The methyl compound crystallizes in space group $P\bar{1}$ of the triclinic system, with a = 13.457(5) Å, b = 11.795(5) Å, c = 10.997(5) Å, α = 112.16(5)°, β = 108.17(5)°, γ = 86.36(5)°, and D_x = 1.64 g cm^{-3} for two formula units in the cell. The structure has been refined by least-squares to the final R factor of 8.0% for the 4891 reflexions above background. The overall molecular structure is the same for both complexes. The Re atom is in a distorted octahedral configuration with two Cl atoms trans to one another, the arylimido group (bonded to Re via the N atom) trans to the O atom of the bidentate ligand, and the PPh_3 group trans to the N atom of the bidentate ligand. Bond distances and angles in the two molecules agree well. Mean values for some bond distances involving rhenium are: Re–Cl 2.418 Å; Re–P 2.44 Å; Re–O 1.98 Å; Re–N(arylimido) 1.73 Å; Re–N 2.14 Å.

Introduction

The most important class of octahedral rhenium(V) halide compounds includes oxo-, imido- and nitrido-complexes as $ReOX_3(L)_2$, $Re(NR)X_3(L)_2$ and $ReNX_2(L)_3$ (X = halogen, L = tertiary phosphine). The synthesis of the nitrogen–rhenium(V) derivatives involves as starting compound the above mentioned oxo-complex and many appropriate reagents which, in the case of organoimido-derivatives are ArN_2, ArNCO, Ph_3PNAr, ArNHNHCOPh, ArNSO [1].

We have recently studied the reactivity of $ReOCl_3(PPh_3)_2$ with pseudo-ally ligands such as triazenido $[RN{=}N{-}NR]^-$ [2] and formamidino $[RN{=}CH{-}NR]^-$. This latter reagent gives $Re(NR)Cl_3(PPh_3)_2$ (R = C_6H_5, p-$CH_3C_6H_4$, p-ClC_6H_4, p-FC_6H_4) as the main product, which represents a new route to the synthesis of organoimido–rhenium complexes [3].

An analogous behaviour should be expected for oxo and organoimido compounds, based on the strong bonding capability of the imido ligand (NR) and of the isoelectronic oxo and nitrido ligands, as suggested by some structural results [3–5].

We have reported [6] that the reaction of $ReOX_3(PPh_3)_2$ (X = Cl, Br) with some bidentate monoanionic ligands (LH) as Schiff base results in the formation of rhenium(V) complexes of the type $ReOX_2(L)PPh_3$ and $ReOX(L)_2$. In order to compare

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*Author to whom correspondence should be addressed.

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TABLE I. General Properties and Elemental Analyses of the Complexes.

Complex		M.p.[a]	Colour	Yield %	M.w.	Found (Calcd.) %			
					Found (Calcd.)	C	H	N	Cl
I	$Re(NTo)Cl_2(Me\text{-}Sal)PPh_3$	233	dark-green	80	810(758.4)	51.7(52.2)	3.9(4.0)	3.6(3.7)	10.8(9.3)
II	$Re(NTo)Cl_2(Ph\text{-}Sal)PPh_3$	224	brown-green	70	823(820.5)	55.5(55.6)	3.9(3.9)	3.3(3.4)	8.1(8.6)
III	$Re(NTo)Cl_2(To\text{-}Sal)PPh_3$	209	dark-green	70	825(820.5)	55.8(56.1)	3.9(4.1)	3.1(3.3)	7.8(7.5)
IV	*cis*-$Re(NTo)Cl_2(Oxine)PPh_3$	200	green	20	750(768.4)	52.3(53.1)	4.7(5.0)	3.5(3.6)	8.8(9.2)
V	*trans*-$Re(NTo)Cl_2(Oxine)PPh_3$	228	dark-green	75	761(768.4)	52.8(53.1)	4.9(5.0)	3.5(3.6)	8.6(9.2)
VI	$Re(NTo)Cl(Oxine)_2$	261	brown-green	58	602(615.0)	49.1(48.8)	3.2(3.4)	6.9(6.8)	5.5(5.8)
VII	$Re(NTo)Cl_2(o\text{-}Ph\text{-}SalH)PPh_3$	221	brown-green	80	805(836.8)	54.7(54.5)	3.7(3.8)	3.3(3.3)	8.2(8.5)
VIII	$Re_2(NTo)_2Cl_4(Sal_2en)(PPh_3)_2$	246	green	40	1540(1515)	52.7(52.3)	3.9(3.8)	4.3(3.7)	9.0(9.4)
IX	*cis*-$Re_2(NTo)_2Cl_4(Sal_2prop)(PPh_3)_2$	227	dark-green	65		52.5(52.5)	3.8(4.0)	3.1(3.7)	8.7(9.3)
X	*trans*-$Re_2(NTo)_2Cl_4(Sal_2prop)(PPh_3)_2$	245	light-green	65	1570(1531.5)	51.8(52.5)	3.7(4.0)	3.3(3.7)	8.5(9.3)
XI	$Re(NMe)Cl_2(Me\text{-}Sal)PPh_3$	218	red-brown	40	654(682.6)	46.2(47.5)	3.7(3.8)	4.0(4.1)	9.5(10.4)
XII	$Re(NMe)Cl_2(Ph\text{-}Sal)PPh_3$	244	red-brown	75	716.5(744.4)	51.6(51.6)	3.7(3.8)	3.7(3.7)	9.3(9.5)
XIII	$Re(NMe)Cl_2(To\text{-}Sal)PPh_3$	220	red-brown	65	745(758.7)	52.2(52.2)	4.0(4.0)	3.6(3.7)	8.9(9.3)
XIV	*cis*-$Re(NMe)Cl_2(Oxine)PPh_3$	240	red-brown	20	680(692.3)	47.2(48.6)	3.3(3.5)	3.8(4.0)	9.4(10.2)
XV	*trans*-$Re(NMe)Cl_2(Oxine)PPh_3$	229	red-brown	85	688(692.3)	47.4(48.6)	3.2(3.3)	3.9(4.0)	9.6(10.2)
XVI	$Re(NMe)Cl(Oxine)_2$	217	light-brown	65	525(539.0)	41.8(42.3)	2.6(2.8)	7.7(7.8)	5.8(6.6)
XVII	$Re(NMe)Cl_2(o\text{-}Ph\text{-}SalH)PPh_3$	230	red-brown	80	757(760.7)	50.4(50.5)	3.6(3.7)	3.7(3.7)	9.2(9.3)
XVIII	$Re_2(NMe)_2Cl_4(Sal_2prop)(PPh_3)_2$	219	red-brown	30		47.4(47.9)	3.6(3.8)	3.9(4.1)	10.1(10.3)

[a] M.ps. were determined in capillaries and are uncorrected.

TABLE II. Some Important I.r. Stretching Frequencies (cm^{-1}) of the Complexes.

	Complex	(C=N)	(C–O)	(Re–Cl)	(O–H)
I	$Re(NTo)Cl_2(Me\text{-}Sal)PPh_3$	1600s	1290s	280s	
II	$Re(NTo)Cl_2(Ph\text{-}Sal)PPh_3$	1590s	1300s	290s	
III	$Re(NTo)Cl_2(To\text{-}Sal)PPh_3$	1590s	1310s	295s	
IV	*cis*-$Re(NTo)Cl_2(Oxine)PPh_3$		1270s, 1315s	285m, 320m	
V	*trans*-$Re(NTo)Cl_2(Oxine)PPh_3$		1270s, 1315s	290s	
VI	$Re(NTo)Cl(Oxine)_2$		1270s, 1315s	360s	
VII	$Re(NTo)Cl_2(o\text{-}Ph\text{-}SalH)PPh_3$	1600s	1295s	285s	2220m
VIII	$Re_2(NTo)_2Cl_4(Sal_2en)(PPh_3)_2$	1615s	1300s	295s	
IX	*cis*-$Re_2(NTo)_2Cl_4(Sal_2prop)(PPh_3)_2$	1585s	1305s	290m, 310m	
X	*trans*-$Re_2(NTo)_2Cl_4(Sal_2prop)(PPh_3)_2$	1610s	1275m, 1300s	310m	
XI	$Re(NMe)Cl_2(Me\text{-}Sal)PPh_3$	1600s	1600s	280m	
XII	$Re(NMe)Cl_2(Ph\text{-}Sal)PPh_3$	1590s	1295s	295s	
XIII	$Re(NMe)Cl_2(To\text{-}Sal)PPh_3$	1590s	1290s	290s	
XIV	*cis*-$Re(NMe)Cl_2(Oxine)PPh_3$		1270s, 1320s	315m, 285w	
XV	*trans*-$Re(NMe)Cl_2(Oxine)PPh_3$		1270s, 1320s	295s	
XVI	$Re(NMe)Cl(Oxine)_2$		1270s, 1315s	350s	
XVII	$Re(NMe)Cl_2(o\text{-}Ph\text{-}SalH)PPh_3$	1600s	1295s	285s	2220m
XVIII	$Re_2(NMe)_2Cl_4(Sal_2prop)(PPh_3)_2$	1585s	1295s	285m, 305m	

the chemical behaviour of oxo- and organoimido–rhenium(V) complexes, we have studied the reactivity of $ReNRCl_3(PPh_3)_2$ (R = CH_3, *p*-$CH_3C_6H_4$) towards the Schiff base ligands LH = N-methylsalicylideneimine (Me-SalH); N-phenylsalicylidenimine (Ph-SalH), N-*p*-tolylsalicylideneimine (To-SalH); 8-hydroxyquinoline (Oxine); and LH_2 = N,N′-ethylene-bis(salicylideneimine) $(SalH)_2en$; N,N′-propylene-bis(salicylideneimine) $(SalH)_2prop$; and N-2-hydroxyphenylsalicylideneimine (*o*-Ph-$SalH_2$).

Results and Discussion

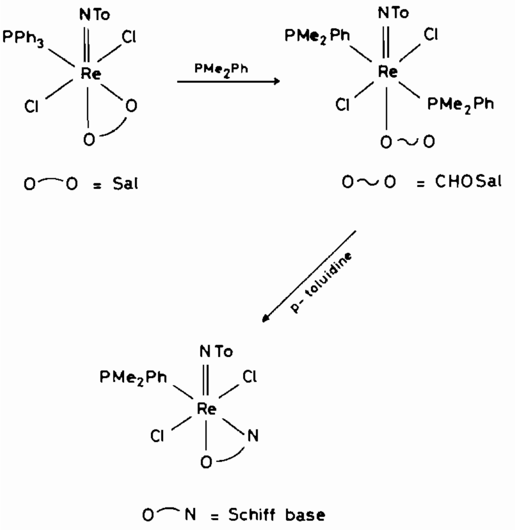
The complexes $Re(NR)Cl_3(PPh_3)_2$ (R = CH_3, *p*-$CH_3C_6H_4$) react with LH and LH_2 to give monosubstituted complexes $Re(NR)Cl_2(L)PPh_3$. With oxine bisubstituted complexes are also obtained. The N-methylsalicylideneimine derivatives are obtained in good yields in boiling PhH, while the N-phenyl-, N-tolyl- and N-2-hydroxy-salicylideneimine ones are obtained in toluene. With half N,N′-propylenebis, *cis* isomers are formed in toluene at room temperature and *trans* isomers under reflux. With oxine in boiling PhH only monosubstituted *trans*-isomers are obtained, whereas in boiling toluene small amounts of *cis*-isomers and of bisubstituted products are also formed. Good yields of the latter products are obtained by using the tallium salt of the ligand.

The general properties and elemental analyses of the new complexes are collected in Table I. The complexes are air stable, soluble in PhH, THF, dichloromethane, insoluble in pentane and slightly soluble in ethanol, acetone and diethylether.

The most significant i.r. bands are reported in Table II. The (C=N) bands for the Schiff bases are at about 1600 cm^{-1}, indicating chelation of the ligands. In the range of metal–chlorine vibrations the monosubstituted complexes show one band at about 300 cm^{-1}, suggesting that the halogens are in *trans* positions. For the ligands $(SalH)_2prop$ and Oxine, *cis*-isomers are also obtained, as may be inferred by the presence of two Re–Cl bands centred at 300 cm^{-1}. The formation of the two bisubstituted oxine complexes $Re(NR)Cl(Oxine)_2$ is proved by the absence of the phosphine band at about 1090 cm^{-1}.

No value has been assigned to the Re=NR stretching frequency, owing to the difficult location of this band. Many authors suggest that most metal–imide vibrations fall in the range 1100–1300 cm^{-1} [1]

The reaction of rhenium nitrene complexes containing substituted phosphines such as $Re(NR)Cl_3(PR'_3)_2$ (PR'_3 = $PMePh_2$, PMe_2Ph, PEt_2Ph and PEt_3) with a Schiff base gives no products. Likewise no phosphine substitution occurs between $Re(NR)Cl_2$ (Schiff base)PPh_3 and PR'_3. A useful route in order to prepare rhenium complexes with a Schiff base and PR'_3 is represented by the reaction of $Re(NR)Cl_2(Sal)PPh_3$ (Sal = salicylaldehyde) with PR'_3 and then with mono-aryl or -alkylamine following the scheme [7]:



The higher reactivity towards PR'_3 of the six-membered chelate ring of the salicylaldehyde compared with that of the analogous ring with the Schiff base may be ascribed to the fact that the aldehydic oxygen is less basic than is the aldiminic nitrogen.

However, the presence of a chelate ring strongly decreases the reactivity of organoimido- as well as of oxo-rhenium(V) complexes. In fact, the reaction of $Re(NTo)Cl_3(PPh_3)_2$ with O_2 in boiling toluene to give $Re(ToNO)Cl_3(OPPh_3)$ [12] does not occur for $Re(NTo)Cl_2$(Schiff base)PPh_3. Similarly the substitution of the oxygen atom of the Re=O group with the organoimido (NTo) ligand occurs easily by reaction of $ReOCl_3(PPh_3)_2$ with $CH_3C_6H_4NSO$ [12], while the corresponding oxo-complexes $ReOCl_2$(Schiff base)PPh_3 do not react.

A comparison of the rhenium(V) oxohalide compounds reveals a higher reactivity of $ReOCl_3(PPh_3)_2$ to give bisubstituted compounds, [6]. For Re(NR)-$Cl_3(PPh_3)_2$ only the bisubstituted Oxine derivatives are obtained. As far as the configuration is concerned, *trans*-$Re(NR)Cl_2$(Schiff base)PPh_3 isomers are prevalently formed, whereas the halogens are in *cis* positions in the corresponding oxo-complexes [6].

The proton N.M.R. data do not reveal any influence of the ligands on the methyl chemical shift in the arylorganoimido group.

In the methyl of alkyl derivatives, the resonance is shifted to lower field. In the starting compound $Re(NCH_3)Cl_3(PPh_3)_2$ the resonance is at δ 0.37 ($CDCl_3$, triplet, J_{PH} = 4 Hz), whereas the resonances in $Re(NCH_3)Cl_2$(Schiff base)PPh_3 occur near δ 1.7 ($CDCl_3$, doublet, J_{PH} = 4 Hz) and in $Re(NCH_3)$-$Cl_2(Sal)PPh_3$ (sal = salicylaldehyde) at δ 2.55 ($CDCl_3$, doublet, J_{PH} = 5 Hz) [7]. For these complexes the observed values of δ increase with increasing electronegativity, *i.e.* $P < N < O$.

X-ray Structure of $ReCl_2(NC_6H_4CH_3)(RN{=}CH{-}C_6H_4O)PPh_3$ $(R = C_6H_5, CH_3)$

The overall molecular configurations of the two compounds are shown in Figs. 1 and 2 together with the adopted numbering scheme. Both structures are composed of closely packed monomeric molecules of $ReCl_2(NC_6H_4CH_3)$-$(RN{=}CH{-}C_6H_4O)PPh_3$ with R = C_6H_5 or CH_3. Although they crystallize in different crystal systems with different packing schemes, the configurations of the two compounds are strikingly similar. In both molecules distortions from ideal octahedral configurations are basically determined by repulsions among the sterically bulky ligands, by a movement of the ligands *cis* to the arylimino group away from the N atom, and by geometrical constraints related to the nature of the bidentate ligand. The formal double Re–N(1) bond [mean 1.73 Å] agrees with 1.726(6) Å observed in $ReCl_3(NC_6H_5)(PPh_3)_2\cdot CH_2Cl_2$ [8] and with 1.72(1) Å in $ReCl_2(NC_6H_4CH_3)$-$(CHOC_6H_4O)PPh_3$ [7], whereas the Re–N(2) distance [mean 2.14 Å] is in good agreement with previous values obtained for Re–N single bonds [9].

With reference to a value of 2.04 Å for a Re^{V}–O single bond derived from the sum of covalent radii [10] a bond order of about 1.16 Å, slightly larger than unity, should be attributed to the Re–O bond [1.98(1) and 1.97(1) Å respectively], probably because of its partial ionic character. The Re–P bond [2.443(4) and 2.446(2) Å] *trans* to Re–N(2) is, as expected, shorter (by *ca.* 0.05 Å) than found in a series of compounds with two phosphine ligands *trans* to one another [11]. A difference of the same order was observed in $ReNCl_2(PMe_2Ph)_3$ between Re–P *trans* to Re–Cl and the two *trans* Re–P bonds [5]. The Re–Cl bond distance [mean 2.418 Å] is normal and needs no comment. The C(32)–N and C–O bond distances [mean 1.30 and 1.34 Å] in the chelating ligand indicate partial double bond character and, by considering the relative shortness of the C(31)–C(32) distance in both compounds, a diffuse delocalization of electron density over the planar moiety of the ligand can be assumed. The C(33)–N(2) bond lengths [1.45 Å in the phenyl compound and 1.48(1) Å in the methyl compound] are normal for aromatic and paraffinic C–N bonds. On the contary, the N–C_6H_4Me distance [1.39 Å in both complexes] is significantly shorter and seems to be characteristic for compounds of this type. In fact the same value was observed in $ReCl_3(NC_6H_5)(PPh_3)_2\cdot$ CH_2Cl_2 and in $ReCl_2(NC_6H_4CH_3)(CHOC_6H_4O)$-$PPh_3$, and very similar values also in $ReCl_3$-$(NC_6H_4OCH_3)(PEt_2Ph)_2$ and in $ReCl_3(NC_6H_4$-$COCH_3)(PEt_2Ph)_2$ [11].

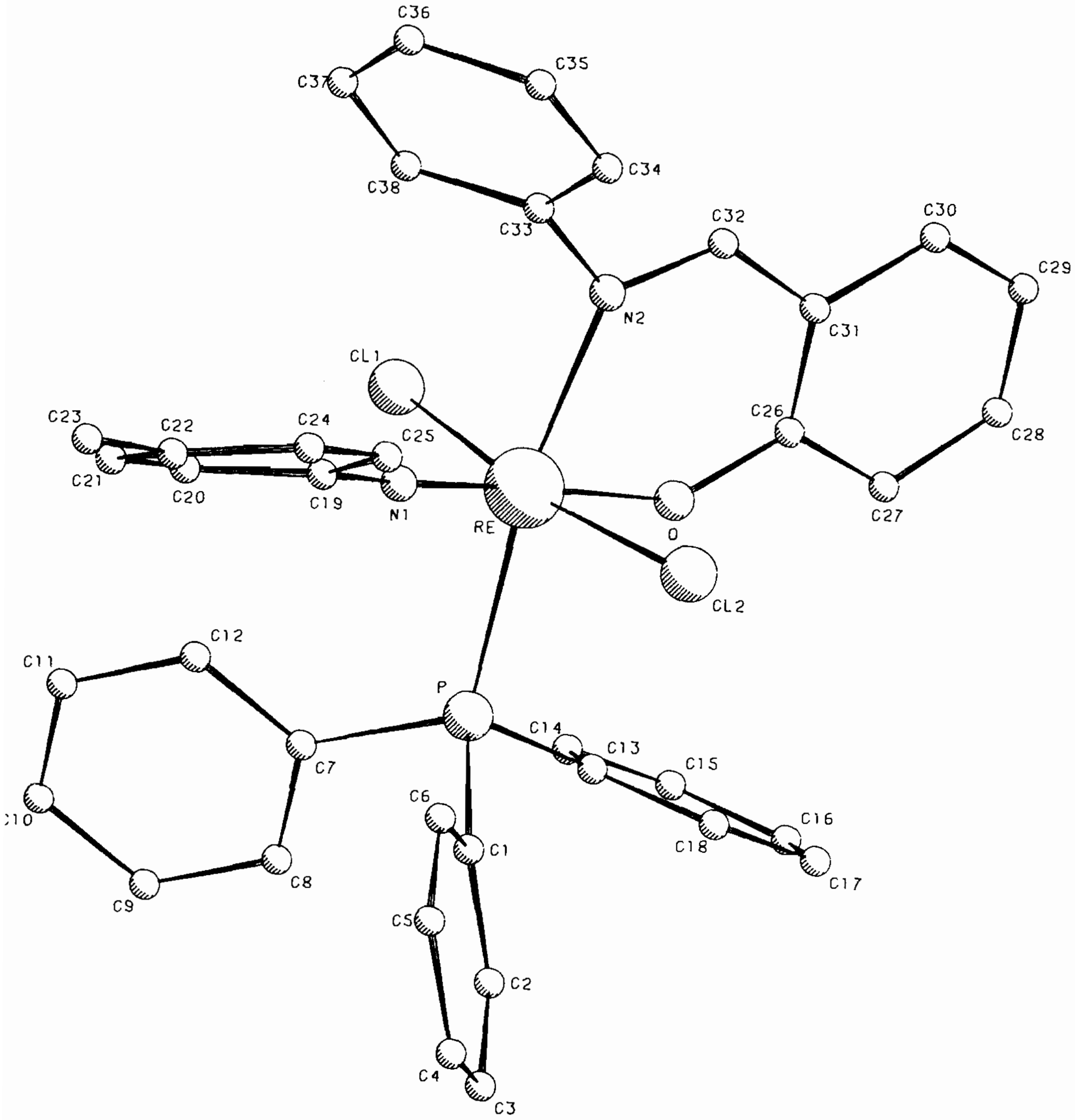


Fig. 1. Crystal structure of $ReCl_2(NC_6H_4CH_3)(PhN{=}CH{-}C_6H_4O)(PPh_3)$ (I).

Experimental

X-Ray Data

The crystal and experimental data and structure-refinement parameters for $ReCl_2(NC_6H_4CH_3)(PhN{=}CH{-}C_6H_4O)PPh_3$ (I), and for $ReCl_2(NC_6H_4CH_3)(MeN{=}CH{-}C_6H_4O)PPh_3$ (II), are given in Table III. At convergence the shift on the refined parameters was less than 0.2σ. At this point, difference Fourier syntheses were calculated for (I) and (II) to check the correctness of the overall structures. Both maps showed only some residuals around the positions of the Re atoms. Final atomic coordinates and thermal parameters are presented in Tables IV and V, and bond distances and angles are listed in Tables VI and VII.

Compounds

Solvents were purified and dried before use. The starting compounds $Re(p\text{-}CH_3C_6H_4N)Cl_3(PPh_3)_2$ and $Re(NCH_3)Cl_3(PPh_3)_2$ were prepared by the literature methods [12, 13]. Other materials were reagent grade. The syntheses were performed under nitrogen. Molecular weights were measured on a Knauer osmometer; i.r. and ^1H nm.r. spectra were recorded on Perkin-Elmer 577 and on 80-MHz Bruker spectrometers respectively.

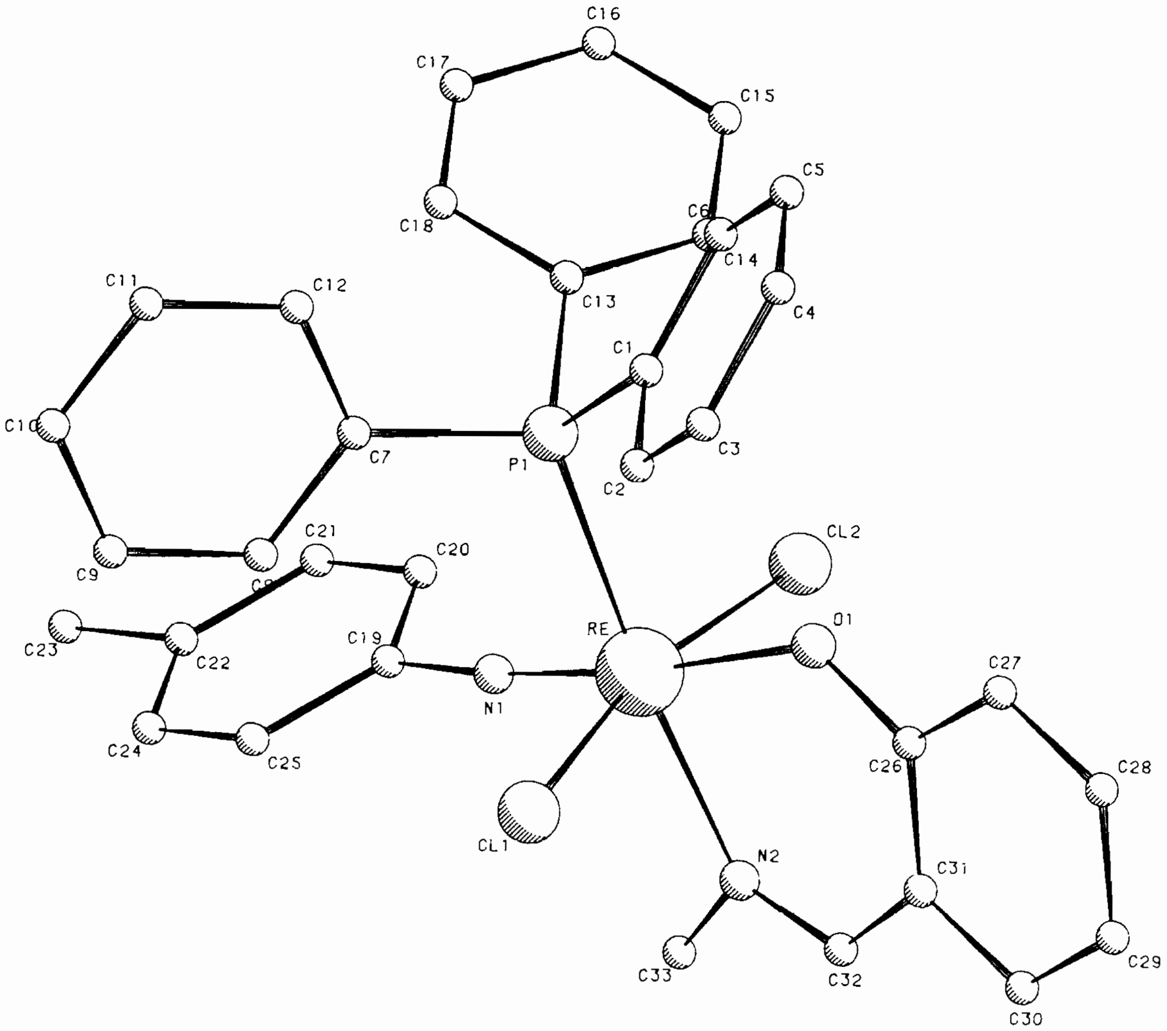


Fig. 2. Crystal structure of $ReCl_2(NC_6H_4CH_3)(MeN{=}CH{-}C_6H_4O)(PPh_3)$ (II).

TABLE III. Crystal and Intensity Data for $ReCl_2(NC_6H_4CH_3)(PhN{=}CH{-}C_6H_4O)(PPh_3)$ (I) and $ReCl_2(NC_6H_4CH_3)(MeN{=}CH{-}C_6H_4O)(PPh_3)$ (II).

Compound	(I): $C_{38}H_{32}Cl_2N_2OPRe$	(II): $C_{33}H_{30}Cl_2N_2OPRe$
FW	820	758
System	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Z	4	2
a (Å)	15.340(5)	13.457(5)
b (Å)	21.115(6)	11.795(5)
c (Å)	10.605(5)	10.997(5)
α (°)		112.16(5)
β (°)	91.36(5)	108.17(5)
γ (°)		86.36(5)
V (Å^3)	3431	1533
D_x (g cm^{-3})	1.59	1.64

(continued on facing page)

TABLE III. *(continued)*

Max. crystal size (mm)	0.2	0.2
Radiation	MoKα	MoKα
μ (cm^{-1})	42.0	40.3
Technique and geometry	Four-circle diffractometer (Philips PN 1100) with graphite-monochromated radiation; $\theta/2\theta$ scan mode; scan rate 2° min^{-1}	
θ_{max} (°)	25	25
Stability	no significant variation	no significant variation
Number of independent reflexions	5148	5397
Number of observed reflexions	3931	4891
Criterion for observed reflexions	$I > 3\sigma(I)$	$1 > 3\sigma(1)$
Corrections applied	Lp, absorption [16]	Lp, absorption [16]
Atomic scattering factors	Re: ref. 14 Cl, P, O, N, C: ref. 15.	Re: ref. 14 Cl, P, O, N, C: ref. 15
Programs used	X-Ray, SHELX: ref. 17, 18	X-ray, SHELX: ref. 17, 18
Correction for anomalous dispersion (Re)	$\Delta f' = -1.598$ $\Delta f'' = 7.232$	$\Delta f' = -1.598$ $\Delta f'' = 7.232$
Solution	Patterson and Fourier methods	Patterson and Fourier methods
Refinement method	Full-matrix least-squares	Full-matrix least-squares
Parameters refined	Scale factor, atomic coordinates, anisotropic temperature factors for Re, Cl, P, N and isotropic temperature factors for C	
Number of reflexions per parameter	22.1	35.7*
Weighting scheme	W = 1	$W = 1/(\sigma^2(F) + 0.0192 F^2)$
R (obs.)	0.047	0.080

*For (II) the ring carbon atoms were refined as rigid bodies.

TABLE IV. Positional Parameters with Esd's for (I).

Atom	*x*	*y*	*z*
Re	0.29972(4)	0.42656(3)	0.31273(6)
Cl(1)	0.2163(2)	0.4728(2)	0.1398(4)
Cl(2)	0.4068(2)	0.3874(2)	0.4649(4)
P	0.2659(2)	0.3192(2)	0.2406(4)
O	0.3969(6)	0.4219(5)	0.1942(10)
N(1)	0.2190(7)	0.4276(7)	0.4261(12)
N(2)	0.3514(7)	0.5188(6)	0.3558(12)
C(1)	0.2678(10)	0.2565(7)	0.3614(15)
C(2)	0.2825(12)	0.1942(9)	0.3283(19)
C(3)	0.2778(13)	0.1457(10)	0.4220(21)
C(4)	0.2584(12)	0.1608(9)	0.5452(19)
C(5)	0.2432(11)	0.2229(9)	0.5783(18)
C(6)	0.2491(10)	0.2711(8)	0.4876(16)
C(7)	0.1587(10)	0.3044(8)	0.1667(16)
C(8)	0.1440(13)	0.2505(9)	0.0918(20)
C(9)	0.0593(15)	0.2379(11)	0.0433(22)
C(10)	−0.0100(14)	0.2773(11)	0.0758(21)
C(11)	0.0036(12)	0.3313(9)	0.1479(19)
C(12)	0.0893(11)	0.3449(8)	0.1935(17)
C(13)	0.3469(10)	0.2952(8)	0.1224(16)
C(14)	0.3305(12)	0.3044(9)	−0.0053(19)
C(15)	0.3976(15)	0.2884(11)	−0.0913(23)

(continued overleaf)

TABLE IV. *(continued)*

Atom	x	y	z
C(16)	0.4728(16)	0.2633(12)	−0.0433(24)
C(17)	0.4921(16)	0.2535(12)	0.0782(25)
C(18)	0.4263(12)	0.2698(10)	0.1687(19)
C(19)	0.1692(10)	0.4315(8)	0.5342(16)
C(20)	0.0806(17)	0.4333(14)	0.5235(26)
C(21)	0.0328(18)	0.4369(14)	0.6358(28)
C(22)	0.0721(14)	0.4398(10)	0.7499(21)
C(23)	0.5172(18)	0.0540(14)	0.3686(28)
C(24)	0.1603(17)	0.4436(13)	0.7571(26)
C(25)	0.2104(15)	0.4399(11)	0.6506(23)
C(26)	0.4705(10)	0.4546(7)	0.1759(16)
C(27)	0.5321(10)	0.4299(8)	0.0933(15)
C(28)	0.6049(11)	0.4655(8)	0.0657(17)
C(29)	0.6205(11)	0.5237(9)	0.1239(18)
C(30)	0.5630(10)	0.5469(8)	0.2079(17)
C(31)	0.4861(10)	0.5131(7)	0.2349(15)
C(32)	0.4262(10)	0.5426(8)	0.3189(16)
C(33)	0.3061(10)	0.5579(7)	0.4455(15)
C(34)	0.3501(11)	0.5773(9)	0.5576(17)
C(35)	0.6942(13)	0.3841(9)	0.3561(20)
C(36)	0.7795(12)	0.3643(9)	0.3823(19)
C(37)	0.8222(11)	0.3846(8)	0.4918(18)
C(38)	0.2198(10)	0.5767(8)	0.4204(16)

Thermal parameters ($\times 10^2$) for **(I)**
Anisotropic thermal parameters are in the form:
$T = \exp[-2\pi^2(U_{11}h^2a^2 + U_{22}k^2b^2 + U_{33}l^2c^2 + U_{12}hkab + U_{13}hlac + U_{23}klbc + U_{23}klbc)]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	1.98(3)	2.21(3)	2.99(4)	−0.2(3)	0.38(2)	−0.15(3)
Cl(1)	3.7(2)	3.2(2)	3.6(2)	−0.1(2)	−0.3(2)	0.4(2)
Cl(2)	3.0(2)	4.0(2)	4.7(3)	0.2(2)	−0.9(2)	0.2(2)
P	2.1(2)	2.1(2)	3.3(2)	−0.4(2)	0.5(2)	−0.2(2)
O	2.4(5)	3.1(6)	4.0(7)	−0.5(5)	1.1(5)	−0.5(6)
N(1)	2.2(6)	4.4(8)	2.3(7)	0.1(6)	0.8(5)	−0.7(7)
N(2)	2.3(6)	3.1(7)	3.2(8)	0.05(6)	0.2(6)	−0.2(6)

Atom	U	Atom	U	Atom	U
C(1)	2.9(4)	C(14)	4.9(5)	C(27)	3.3(7)
C(2)	4.8(5)	C(15)	6.9(6)	C(28)	3.9(4)
C(3)	5.7(5)	C(16)	7.6(7)	C(29)	4.4(4)
C(4)	5.0(5)	C(17)	7.5(7)	C(30)	3.7(4)
C(5)	4.5(4)	C(18)	5.2(5)	C(31)	2.9(4)
C(6)	3.5(4)	C(19)	3.4(4)	C(32)	3.3(4)
C(7)	3.4(4)	C(20)	8.7(8)	C(33)	3.0(4)
C(8)	5.2(5)	C(21)	9.3(8)	C(34)	4.1(4)
C(9)	6.7(6)	C(22)	5.9(6)	C(35)	5.3(5)
C(10)	6.1(6)	C(23)	9.3(9)	C(36)	4.9(5)
C(11)	5.1(5)	C(24)	8.5(8)	C(37)	4.3(4)
C(12)	3.9(4)	C(25)	7.3(7)	C(38)	3.6(4)
C(13)	3.4(4)	C(26)	2.9(4)		

Re(NR)Cl$_2$(Me-Sal)PPh$_3$ (R = CH$_3$, p-CH$_3$C$_6$H$_4$)

A stirred suspension of Re(CH$_3$C$_6$H$_4$N)Cl$_3$(PPh$_3$)$_2$ (0.5 g, 0.54 mmol) or Re(NCH$_3$)Cl$_3$(PPh$_3$)$_2$ (0.5 g, 0.59 mmol) and Me-SalH (0.36 g, 2.7 mmol) was refluxed in PhH (100 ml) for 2 h. The solution was concentrated to one third of its volume and a precipitate was obtained upon addition of EtOH. The solid was crystallized from CH$_2$Cl$_2$/EtOH.

TABLE V. Positional Parameters with Esd's for (**II**).

Atom	*x*	*y*	*z*
Re	0.28569(2)	0.16495(3)	0.11500(3)
Cl(1)	0.2099(2)	0.0431(2)	0.1997(3)
Cl(2)	0.3966(2)	0.2637(2)	0.0415(3)
P	0.2202(2)	0.3539(2)	0.2482(2)
O	0.4067(5)	0.1978(6)	0.2836(7)
N(1)	0.1834(6)	0.1539(7)	−0.0295(7)
N(2)	0.3585(6)	0.0012(7)	0.0284(8)
C(1)	0.2865(6)	0.4114(5)	0.4361(7)
C(2)	0.2813(6)	0.3333(5)	0.5030(7)
C(3)	0.3270(6)	0.3714(5)	0.6457(7)
C(4)	0.3779(6)	0.4878(5)	0.7217(7)
C(5)	0.3830(6)	0.5659(5)	0.6549(7)
C(6)	0.3373(6)	0.5278(5)	0.5121(7)
C(7)	0.0830(5)	0.3417(5)	0.2394(6)
C(8)	0.0196(5)	0.2357(5)	0.1493(6)
C(9)	−0.0851(5)	0.2287(5)	0.1429(6)
C(10)	−0.1264(5)	0.3277(5)	0.2267(6)
C(11)	−0.0630(5)	0.4337(5)	0.3168(6)
C(12)	0.0417(5)	0.4407(5)	0.3232(6)
C(13)	0.2300(4)	0.4828(6)	0.1979(7)
C(14)	0.3291(4)	0.5264(6)	0.2137(7)
C(15)	0.3389(4)	0.6230(6)	0.1735(7)
C(16)	0.2496(4)	0.6759(6)	0.1175(7)
C(17)	0.1506(4)	0.6323(6)	0.1017(7)
C(18)	0.1408(4)	0.5358(6)	0.1419(7)
C(19)	0.1094(5)	0.1574(7)	−0.1488(8)
C(20)	0.1308(5)	0.2325(7)	−0.2109(8)
C(21)	0.0588(5)	0.2349(7)	−0.3325(8)
C(22)	−0.0347(5)	0.1621(7)	−0.3920(8)
C(23)	−0.1156(13)	0.1646(15)	−0.5266(18)
C(24)	−0.0561(5)	0.0870(7)	−0.3299(8)
C(25)	0.0160(5)	0.0846(7)	−0.2083(8)
C(26)	0.4753(5)	0.1243(4)	0.3282(6)
C(27)	0.5386(5)	0.1714(4)	0.4659(6)
C(28)	0.6113(5)	0.0985(4)	0.5184(6)
C(29)	0.6208(5)	−0.0214(4)	0.4333(6)
C(30)	0.5576(5)	−0.0685(4)	0.2956(6)
C(31)	0.4849(5)	0.0044(4)	0.2431(6)
C(32)	0.4299(7)	−0.0489(9)	0.0959(10)
C(33)	0.3172(8)	−0.0618(10)	−0.1234(11)

Thermal parameters $(\times 10^2)$ for (**II**)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	2.56(3)	2.56(3)	2.53(3)	0.45(2)	−0.08(2)	−0.07(2)
Cl(1)	4.2(1)	3.7(1)	4.1(1)	1.4(1)	0.7(1)	−0.3(1)
Cl(2)	4.3(1)	3.9(1)	4.7(1)	0.9(1)	1.5(1)	−0.4(1)
P	3.2(1)	2.5(1)	2.7(1)	0.4(1)	0.0(1)	0.2(1)
O	4.0(4)	3.0(3)	3.7(4)	0.2(3)	0.2(3)	0.0(3)
N(1)	3.4(4)	2.9(4)	2.0(4)	−0.2(3)	0.0(3)	−0.3(3)
N(2)	3.6(4)	2.6(4)	2.5(4)	−0.3(3)	0.6(3)	−0.0(3)

Atom	*U*	Atom	*U*	Atom	*U*
C(1)	3.5(2)	C(12)	5.3(2)	C(23)	8.9(4)
C(2)	6.4(3)	C(13)	3.8(2)	C(24)	6.0(3)

(continued overleaf)

TABLE V. *(continued)*

Atom	*U*	Atom	*U*	Atom	*U*
C(3)	6.6(3)	C(14)	4.8(2)	C(25)	4.8(2)
C(4)	6.4(3)	C(15)	5.4(2)	C(26)	3.7(2)
C(5)	6.8(3)	C(16)	7.2(3)	C(27)	4.4(2)
C(6)	5.3(2)	C(17)	7.9(4)	C(28)	5.7(3)
C(7)	4.0(2)	C(18)	5.7(3)	C(29)	5.8(3)
C(8)	4.3(2)	C(19)	4.2(2)	C(30)	4.9(2)
C(9)	5.0(2)	C(20)	6.1(3)	C(31)	4.1(2)
C(10)	5.4(2)	C(21)	7.6(4)	C(32)	3.8(2)
C(11)	5.0(2)	C(22)	5.6(2)	C(33)	4.8(2)

TABLE VI. Bond Distances (Å) with Esd's Referred to the Last Significant Digit.

	(I)	(II)
Re–Cl(1)	2.417(4)	2.401(3)
Re–Cl(2)	2.421(4)	2.433(3)
Re–P	2.443(4)	2.446(2)
Re–O	1.98(1)	1.97(1)
Re–N(1)	1.75(1)	1.71(1)
Re–N(2)	2.15(1)	2.13(1)
N(1)–C(19)	1.39(2)	1.39(1)
C(22)–C(23)	1.54(4)	1.55(2)
O–C(26)	1.34(2)	1.33(1)
C(31)–C(32)	1.44(2)	1.45(1)
C(32)–N(2)	1.32(2)	1.28(1)
N(2)–C(33)	1.45(2)	1.48(1)
P–C(1)	1.84(2)	1.83(1)
P–C(7)	1.83(2)	1.84(1)
P–C(14)	1.86(2)	1.83(1)

For (**I**) the mean of the C–C bonds in the rings is 1.393 Å; for (**II**) the ring carbon atoms were refined as rigid bodies with a fixed C–C bond distance of 1.395 Å.

$Re(NR)Cl_2(L)PPh_3$ ($R = CH_3$, $p\text{-}CH_3C_6H_4$; L = Ph-Sal, To-Sal, o-Ph-SalH)

A stirred suspension of $Re(CH_3C_6H_4N)Cl_3(PPh_3)_2$ (0.5 g, 0.54 mmol) or $Re(NCH_3)Cl_3(PPh_3)_2$ (0.5 g, 0.59 mmol) with an excess of the appropriate ligand (2.7 mmol) was refluxed in toluene (100 ml) for 2 h. The solution was then concentrated to one third of its volume and a precipitate was obtained upon addition of EtOH. The solid was crystallized from CH_2Cl_2/EtOH.

$Re(NR)Cl_2(Oxine)PPh_3$ ($R = CH_3$, $p\text{-}CH_3C_6H_4$)

$Re(CH_3C_6H_4N)Cl_3(PPh_3)_2$ (0.5 g, 0.54 mmol) or $Re(NCH_3)Cl_3(PPh_3)_2$ (0.5 g, 0.59 mmol) and Oxine (0.39 g, 2.7 mmol) were allowed to react under the conditions described above to give the products. When the reaction was carried out in boiling toluene (6 h) small amounts of *cis*-isomer and bisubstituted product were also obtained.

TABLE VII. Bond Angles (Deg) with Esd's Referred to the Last Significant Digit.

	(I)	(II)
Cl(1)–Re–Cl(2)	169.2(1)	167.3(1)
P–Re–N(2)	169.1(3)	171.3(2)
O–Re–N(1)	175.5(5)	173.2(4)
Cl(1)–Re–P	91.8(1)	92.6(1)
Cl(1)–Re–O	86.1(3)	86.1(3)
Cl(1)–Re–N(1)	98.4(4)	99.4(3)
Cl(1)–Re–N(2)	88.9(3)	84.4(3)
Cl(2)–Re–P	91.6(1)	96.1(1)
Cl(2)–Re–O	84.1(3)	85.3(3)
Cl(2)–Re–N(1)	91.5(4)	89.8(3)
Cl(2)–Re–N(2)	85.8(3)	85.7(3)
P–Re–O	85.0(3)	85.9(2)
P–Re–N(1)	94.5(5)	89.9(3)
O–Re–N(2)	84.3(4)	85.7(3)
N(1)–Re–N(2)	96.1(6)	98.6(3)
Re–N(1)–C(19)	168(1)	171(1)
Re–N(2)–C(32)	127(1)	126(1)
Re–N(2)–C(33)	118(1)	116(1)
C(32)–N(2)–C(33)	114(1)	118(1)
Re–O–C(26)	136(1)	132(1)
N(2)–C(32)–C(31)	126(1)	126(1)
Re–P–C(1)	117(1)	115(1)
Re–P–C(7)	118(1)	115(1)
Re–P–C(13)	110(1)	114(1)
C(1)–P–C(13)	106(1)	105(1)
C(7)–P–C(13)	106(1)	102(1)
C(1)–P–C(7)	100(1)	105(1)

$Re(NR)Cl(Oxine)_2$ ($R = CH_3$, $p\text{-}CH_3C_6H_4$)

A stirred suspension of $Re(CH_3C_6H_4N)Cl_3(PPh_3)_2$ (0.5 g, 0.54 mmol) or $Re(NCH_3)Cl_3(PPh_3)_2$ (0.5 g, 0.59 mmol) and OxineTl (0.94 g, 2.7 mmol) was refluxed in toluene (100 ml, 1 h). The solution was concentrated to one third of its volume and a precipitate was obtained upon addition of EtOH. The solid was crystallized from CH_2Cl_2/EtOH.

$Re_2(NTo)_2Cl_4(Sal_2en)(PPh_3)_2$

$Re(CH_3C_6H_4N)Cl_3(PPh_3)_2$ (0.5 g, 0.54 mmol) and $(SalH)_2en$ (0.72 g, 2.7 mmol) were refluxed in toluene (100 ml, 1 h). The solution was concentrated to one third of its volume and a precipitate was obtained upon addition of EtOH. The solid was crystallized from CH_2Cl_2/EtOH.

trans- and cis-$Re_2(NR)_2Cl_4(Sal_2prop)(PPh_3)_2$ (R = CH_3, p-$CH_3C_6H_4$)

$Re(CH_3C_6H_4N)Cl_3(PPh_3)_2$ (0.5 g, 0.54 mmol) or $Re(NCH_3)Cl_3(PPh_3)_2$ (0.5 g, 0.59 mmol) and $(SalH)_2prop$ (0.76 g, 2.7 mmol) were allowed to react under the conditions described above to give the *trans*-isomer. When the reaction was carried out at r.t. with a larger excess of ligand (5.00 mmol), the *cis*-isomer was obtained.

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