Synthesis and Characterization of Paramagnetic Triazenido-complexes of Rhenium(III). The Crystal Structure of $[ReCl_2(p\text{-}MeC_6H_4N\overset{\cdots}{-}N\overset{\cdots}{-}NC_6H_4Me\text{-}p)(PPh_3)_2]$ †

Roberto Rossi,* Adriano Duatti, and Luciano Magon
Istituto di Chimica, Università di Ferrara, Italy
Umberto Casellato
Instituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Padova, Italy
Rodolfo Graziani and Luigi Toniolo
Istituto di Chimica Generale e Chimica Inorganica Industriale, Università di Padova, Italy

The compound $[ReOCl_3(PPh_3)_2]$ reacts with $Li(RN_3R)$ (R = p-MeC_6H_4,Ph, p-FC_6H_4, or p-ClC_6H_4) in boiling tetrahydrofuran to yield new complexes of Re^{III} of the type $[ReCl_2(RN\overset{\cdots}{-}N\overset{\cdots}{-}NR)(PPh_3)_2]$. The i.r. spectra suggest that the organonitrogen ligand acts as a chelating ligand and that the two chlorine ligands are in *cis* position. Magnetic susceptibility measurements on the solids have demonstrated the presence of unpaired electrons, which affect the ^1H n.m.r. spectra, the resonance signals being shifted up- and down-field with respect to $SiMe_4$. The crystal structure of the title compound was determined by the *X*-ray analysis using counter data. The compound crystallizes in the monoclinic system, space group $P2_1/a$, with $a = 14.50(1)$, $b = 24.68(1)$, $c = 12.91(1)$ Å, and $\beta = 108.50(4)°$ for $Z = 4$. The structure was refined to $R = 0.075$. The rhenium atom is in a distorted octahedral co-ordination with two axial PPh_3 groups, two *cis*-chlorine atoms, and the chelate ligand which forms a four-membered ring with the metal.

There is much current interest in the chemistry of pseudo-allyl ligands of the triazenido-, $[RN{=}N{-}NR]^-$, and amidino-, $[RN{-}CR'{=}NR]^-$, types because of their potential reactivity in relation to their several modes of co-ordination.[1,2] A brief up to date outline of the behaviour of such ligands has already appeared.[3,4]

We have recently reported [3,4] the synthesis and characterization of new formamidino- and triazenido-complexes of Re^I of the type $[Re(CO)_2(RN\overset{\cdots}{-}X\overset{\cdots}{-}NR)(PPh_3)_2]$ (X = CH or N) having a pseudo-octahedral geometry with the organonitrogen ligand (acting as chelate) and the CO ligands in the equatorial plane. As an extension of this work, we here report the synthesis and characterization of triazenido-rhenium(III) complexes of the type $[ReCl_2(RN\overset{\cdots}{-}N\overset{\cdots}{-}NR)(PPh_3)_2]$ and the crystal structure of $[ReCl_2(p\text{-}MeC_6H_4N\overset{\cdots}{-}N\overset{\cdots}{-}NC_6H_4Me\text{-}p)(PPh_3)_2]$.

Results and Discussion

The new rhenium(III) complexes $[ReCl_2(RN\overset{\cdots}{-}N\overset{\cdots}{-}NR)(PPh_3)_2]$ (R = p-MeC_6H_4, Ph, p-ClC_6H_4, or p-FC_6H_4) are obtained in satisfactory yields (60—70%) by adding *trans*-$[ReOCl_3(PPh_3)_2]$ and PPh_3 as solids to a boiling tetrahydrofuran (thf) solution of $Li(RN\overset{\cdots}{-}N\overset{\cdots}{-}NR)$ generated *in situ* by treating $RNH{-}N{=}NR$ with $LiBu^n$.

The absence of any i.r. band in the ν(Re=O) region suggests that the formation of the new complexes occurs *via* reduction of the starting compound. Yields are much lower in the absence of added PPh_3 which probably acts as the reducing agent according to equation (1). The capacity of PPh_3 to interact with the Re=O bond in rhenium(V) complexes and yield rhenium(III) complexes has already been demonstrated.[5] Further substitution of Cl^- does not occur, even when carrying out the reaction in the presence of a large excess of the triazenido-ligand. The new complexes (Table 1) are green, air-stable, soluble in benzene, tetrahydrofuran, dichloromethane, insoluble in pentane, and slightly soluble in ethanol, acetone, and diethyl ether, except for the p-ClC_6H_4 derivative which is not soluble in most common solvents.

$$[ReOCl_3(PPh_3)_2] + PPh_3 + Li(RN\overset{\cdots}{-}N\overset{\cdots}{-}NR) \xrightarrow{thf} [ReCl_2(RN\overset{\cdots}{-}N\overset{\cdots}{-}NR)(PPh_3)_2] + PPh_3O + LiCl \quad (1)$$

The most significant i.r. bands are collected in Table 2. The main stretching bands arising from the organonitrogen ligand appear at *ca.* 1 250 cm^{-1}. The i.r. bands for 1,3-diaryltriazenido-ligands have been classified into two groups.[6] Bands at *ca.* 1 300—1 260 cm^{-1} are indicative of the ligand acting as a chelate; when there are also bands at 1 380—1 360, 1 220, and 1 150 cm^{-1} the ligand is unidentate. The triazenido-complexes reported here do not show any bands at the last frequencies, indicating that the ligand is chelating. With the exception of the phenyl derivative, all the complexes show two bands centred at 300 cm^{-1}, suggesting that the halogens are in a *cis* position. This has been confirmed by the *X*-ray work on the tolyl derivative. The phenyl derivative shows only one band at 300 cm^{-1}. Since this band is rather wide it could be the result of overlapping of two poorly resolved bands and may also indicate a *cis* geometry.

Magnetic susceptibility measurements on the solids have demonstrated the presence of unpaired electrons. The moments found (Table 1) are close to, although generally higher than, those of $[ReCl_3(PR_3)_3]$ complexes,[7,8] suggesting that the triazenido-derivatives may not display temperature-independent paramagnetism but rather Curie–Weiss behaviour. However, we are unable to make the appropriate measurements. The value of 2.8 B.M. for the p-ClC_6H_4 derivative is larger than for the other rhenium(III) complexes, but is

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† [1,3-Bis(p-tolyl)triazenido-N^1N^3]dichlorobis(triphenylphosphine)-rhenium(III).

Supplementary data available (No. SUP 23341, 21 pp.): thermal parameters, H-atom co-ordinates, contact distances and angles, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: B.M. ≈ 9.27×10^{-24} J T^{-1}.

Table 1. General properties, elemental analyses, and magnetic moments of the rhenium(III) triazenido-complexes

Complex	Colour	M.p. (°C)	Yield (%)	Analyses * (%) C	H	N	Cl	$\mu_{eff.}$/B.M.
(1) $[ReCl_2\{N(NC_6H_4CH_3\text{-}p)_2\}(PPh_3)_2]$	Dark green	197	60	59.7	4.9	4.3	7.4	2.15
				(59.7)	(4.4)	(4.2)	(7.1)	
(2) $[ReCl_2\{N(NPh)_2\}(PPh_3)_2]$	Dark green	174	65	57.4	4.3	4.0	7.6	2.21
				(58.9)	(4.1)	(4.2)	(7.2)	
(3) $[ReCl_2\{N(NC_6H_4Cl\text{-}p)_2\}(PPh_3)_2]$	Olive green	212	70	55.2	3.2	3.8	13.6	2.78
				(55.0)	(3.6)	(4.0)	(13.5)	
(4) $[ReCl_2\{N(NC_6H_4F\text{-}p)_2\}(PPh_3)_2]$	Dark green	205	60	57.4	3.6	4.1		2.45
				(56.8)	(3.7)	(4.1)		

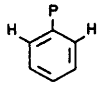
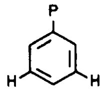
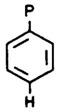
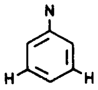
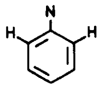
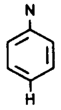
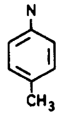
* Calculated values are given in parentheses.

Table 2. I.r. and u.v. spectroscopic data

	I.r. (cm^{-1}), Nujol mull		U.v. absorption	
Complex	$\nu(RN_3R)$ [a]	ν(Re–Cl)	λ/nm	$\varepsilon_{max.}$ [b]
(1)	1 250vs	294—310s	345	14 000
			594	1 560
(2)	1 245vs	300s	340	12 500
			575	1 460
(3)	1 240vs	300—310s		
(4)	1 250s	295—306s	340	12 700
			578	1 320

[a] Only main bands associated with the triazenido-linkages. [b] In CH_2Cl_2; units are dm^3 mol^{-1} cm^{-1}.

Table 3. Proton n.m.r. spectra of $[ReCl_2(RN \cdots N \cdots NR)(PPh_3)_2]$ in $CDCl_3$, in p.p.m. with respect to $SiMe_4$

	R		
Assignment	Ph	*p*-MeC$_6$H$_4$	*p*-FC$_6$H$_4$
	+12.23 (d)	+12.20 (d)	+12.13 (d)
	+7.90 (t)	+7.95 (t)	+7.95 (t)
	+8.60 (t)	+8.70 (t)	+8.72 (t)
	+11.86 (t)	+12.00 (d)	+11.44 (t)
	−10.00 (d)	−11.11 (d)	−10.4 (d)
	−7.02 (t)		
		+19.95 (s)	

within the expected range for $3d^4$ octahedral systems for which there is no spin–orbit coupling.[9] The unpaired electrons in $[ReCl_2(RN_3R)(PPh_3)_2]$ affect the ^1H n.m.r. spectra (Table 3). The resonance signals are split upfield and downfield with respect to the $SiMe_4$ reference peak (signals are present in the +20 to −11 p.p.m. region). Moreover, the signals appear as sharp bands and only couplings between mutually *ortho*-protons are resolved for phenyl rings. No phosphorus coupling was observed in the proton spectra owing to the rapid ^{31}P relaxation. All these facts are consistent with the behaviour of other rhenium(III) phosphine complexes.[10] The characteristic narrow lines of the spectra permit the assignment of every signal to the corresponding proton. Confirmation of the assignments stems from the decoupling experiments. The singlet due to the methyl groups at +19.9 p.p.m. suggests their equivalence. (*No* low-temperature ^1H n.m.r. spectra were recorded in order to check whether the CH_3 equivalence is due to the molecular geometry found in the solid, or to a fluxional behaviour of the ligand acting in a unidentate manner in solution.[11,12])

X-*Ray Structure of* $[ReCl_2(p\text{-}MeC_6H_4N \cdots N \cdots NC_6H_4\text{-}Me\text{-}p)(PPh_3)_2]$.—The structure consists of discrete molecules of the complex. The Figure shows the conformation of the molecule and the numbering scheme used throughout this paper. Final atomic co-ordinates are listed in Table 4, bond distances and angles in Tables 5 and 6.

Distortions from the idealized octahedral geometry arising from the constraints of the triazenido-group are mainly localized in the base plane where this ligand subtends an angle of only 58° at the metal atom. The Re^{III}–P distances [2.51(1) and 2.50(1) Å] can be compared with 2.47 and 2.48 Å found in octahedral $[ReCl_3(PPh_3)_2(MeCN)]$ [13] and with 2.46 Å found in octahedral *mer*-$[ReCl_3(PMe_2Ph)_3]$.[14] These values are larger than the sum of the covalent radii (2.38 Å) and also than the Re^I–P (*trans* to P) bond distances (mean 2.43 Å) in complexes with very similar configurations.[4,15]

The N–N bond distances [1.30(3) and 1.31(3) Å] are chemically equivalent and compare well with the values found in some complexes of other metal atoms with the same or with a similar ligand, indicating that the N–N distance is influenced little by the nature of the central atom or by the co-ordination mode.

The Re^{III}–N and Re^{III}–P bond distances are respectively shorter and longer than those of the rhenium(I) complex $[Re(CO)_2(p\text{-}MeC_6H_4N \cdots N \cdots NC_6H_4Me\text{-}p)(PPh_3)_2]$ [4] [Re^{III}–N 1.99(3), 2.08(2); Re^I–N 2.21(1), 2.18(1); Re^{III}–P 2.50(1), 2.51(1); Re^I–P 2.42(1), 2.44(1) Å]. This can be understood in terms of Pearson's hard–soft acid–base theory:[16] Re^{III}, a Lewis acid, is harder than Re^I and must form stronger

Table 4. Positional parameters ($\times 10^4$) for [$ReCl_2(p-MeC_6H_4N \underline{\cdots} N \underline{\cdots} NC_6H_4Me-p)(PPh_3)_2$]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Re	2 568(1)	5 980(0)	8 515(1)	C(22)	−969(13)	6 399(8)	9 762(15)
N(1)	2 008(17)	5 197(10)	8 220(19)	C(23)	−571(13)	6 429(8)	10 602(15)
N(2)	1 137(17)	5 315(10)	7 561(20)	C(24)	360(13)	6 222(8)	10 767(15)
N(3)	1 220(20)	5 837(9)	7 537(22)	C(25)	2 894(13)	6 558(8)	11 290(12)
Cl(1)	4 149(5)	5 791(3)	9 719(6)	C(26)	3 634(13)	6 867(8)	11 109(12)
Cl(2)	2 666(5)	6 947(3)	8 302(6)	C(27)	4 238(13)	7 182(8)	11 949(12)
P(1)	3 200(5)	5 887(3)	6 920(6)	C(28)	4 101(13)	7 189(8)	12 971(12)
P(2)	2 127(5)	6 105(3)	10 222(7)	C(29)	3 361(13)	6 880(8)	13 152(12)
C(1)	2 222(14)	6 076(6)	5 680(16)	C(30)	2 758(13)	6 565(8)	12 312(12)
C(2)	1 555(14)	5 684(6)	5 124(16)	C(31)	2 205(11)	5 444(7)	10 922(16)
C(3)	781(14)	5 828(6)	4 206(16)	C(32)	3 063(11)	5 303(7)	11 736(16)
C(4)	674(14)	6 364(6)	3 845(16)	C(33)	3 141(11)	4 802(7)	12 256(16)
C(5)	1 341(14)	6 756(6)	4 401(16)	C(34)	2 359(11)	4 441(7)	11 962(16)
C(6)	2 115(14)	6 612(6)	5 319(16)	C(35)	1 501(11)	4 582(7)	11 147(16)
C(7)	3 634(13)	5 219(7)	6 649(12)	C(36)	1 423(11)	5 083(7)	10 627(16)
C(8)	3 600(13)	5 055(7)	5 603(12)	C(37)	2 281(17)	4 631(11)	8 389(22)
C(9)	4 004(13)	4 559(7)	5 455(12)	C(38)	1 942(20)	4 258(11)	7 585(24)
C(10)	4 442(13)	4 228(7)	6 352(12)	C(39)	2 252(20)	3 714(12)	7 733(25)
C(11)	4 476(13)	4 392(7)	7 397(12)	C(40)	2 886(19)	3 562(12)	8 664(24)
C(12)	4 071(13)	4 887(7)	7 545(12)	C(41)	3 297(21)	3 918(12)	9 506(25)
C(13)	4 228(13)	6 336(7)	6 903(13)	C(42)	2 987(21)	4 488(12)	9 353(26)
C(14)	4 507(13)	6 356(7)	5 964(13)	C(43)	281(18)	6 101(10)	6 816(22)
C(15)	5 332(13)	6 647(7)	5 968(13)	C(44)	−578(21)	5 788(12)	6 454(24)
C(16)	5 879(13)	6 919(7)	6 910(13)	C(45)	−1 468(22)	6 048(14)	5 798(24)
C(17)	5 600(13)	6 899(7)	7 849(13)	C(46)	−1 465(18)	6 587(10)	5 557(22)
C(18)	4 775(13)	6 608(7)	7 845(13)	C(47)	−602(19)	6 868(11)	5 889(22)
C(19)	892(13)	6 384(8)	10 091(15)	C(48)	278(21)	6 614(12)	6 540(24)
C(20)	494(13)	6 754(8)	9 250(15)	C(49)	−2 411(21)	6 862(13)	4 868(27)
C(21)	−436(13)	6 961(8)	9 086(15)	C(50)	3 278(23)	2 954(13)	8 850(28)

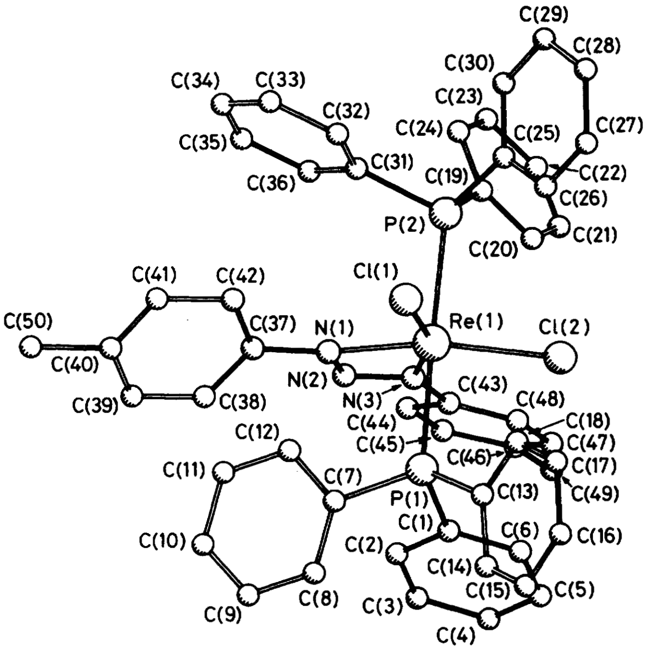


Figure. Molecular structure of [$ReCl_2(p-MeC_6H_4N \underline{\cdots} N \underline{\cdots} NC_6H_4Me-p)(PPh_3)_2$] with the numbering scheme

bonds with a hard nitrogen base, whereas the opposite occurs with the comparatively softer phosphorus base.

Experimental

Solvents were purified and dried before use. The compounds RNH−N=NR [17] and *trans*-[$ReOCl_3(PPh_3)_2$] [18] were prepared following the literature methods. Other materials were reagent grade. All the syntheses were performed under nitrogen. I.r. and ^1H n.m.r. spectra were recorded on Perkin-Elmer 577 and on 80-MHz Bruker spectrometers, respectively. Electronic spectra were obtained on a Cary 219 spectrophotometer. Magnetic susceptibilities were measured by the Gouy method, using a Bruker instrument, Magnet model B-M6.

Table 5. Bond distances (Å)

Re−P(1)	2.51(1)	Re−P(2)	2.50(1)
Re−N(1)	2.08(2)	Re−N(3)	1.99(3)
Re−Cl(1)	2.37(1)	Re−Cl(2)	2.41(1)
N(1)−N(2)	1.31(3)	N(3)−N(2)	1.30(3)
N(1)−C(37)	1.45(3)	N(3)−C(43)	1.53(3)
C(37)−C(38)	1.36(4)	C(43)−C(44)	1.41(4)
C(38)−C(39)	1.41(3)	C(44)−C(45)	1.45(4)
C(39)−C(40)	1.31(4)	C(45)−C(46)	1.37(4)
C(40)−C(41)	1.38(3)	C(46)−C(47)	1.37(4)
C(41)−C(42)	1.47(4)	C(47)−C(48)	1.43(4)
C(42)−C(37)	1.38(4)	C(48)−C(43)	1.31(4)
P(1)−C(1)	1.83(2)	P(2)−C(19)	1.87(2)
P(1)−C(7)	1.84(2)	P(2)−C(25)	1.85(2)
P(1)−C(13)	1.86(2)	P(2)−C(31)	1.85(2)

Preparation of [$ReCl_2(RN \underline{\cdots} N \underline{\cdots} NR)(PPh_3)_2$].—The compounds [$ReOCl_3(PPh_3)_2$] (0.6 mmol) and PPh_3 (*ca.* 2 mmol) were added to a solution of Li(RN_3R) (0.6 mmol) (R = $p-MeC_6H_4$, Ph, $p-ClC_6H_4$, or $p-FC_6H_4$) in dry thf (30 cm^3) at room temperature, under a dinitrogen atmosphere. The solution quickly became deep red. During refluxing it assumed a green colouration and a green solid appeared. After 1 h the mixture was concentrated to one third of its volume. The precipitate was filtered off, and washed with water, EtOH, and Et_2O. From the red mother-liquor, further amounts of the product were obtained upon addition of EtOH.

Table 6. Bond angles (°). The errors are referred to the last digit

(*a*) Co-ordination			
P(1)–Re–P(2)	173.6(3)		
P(1)–Re–N(1)	89(1)	P(2)–Re–N(1)	95(1)
P(1)–Re–N(3)	90(1)	P(2)–Re–N(3)	96(1)
P(1)–Re–Cl(1)	89.5(2)	P(2)–Re–Cl(1)	84.9(3)
P(1)–Re–Cl(2)	87.0(2)	P(2)–Re–Cl(2)	91.1(2)
Cl(1)–Re–Cl(2)	100.9(3)	N(1)–Re–N(3)	58(1)
N(1)–Re–Cl(1)	100(1)	N(3)–Re–Cl(2)	101(1)
N(2)–Re–Cl(2)	158(1)	N(3)–Re–Cl(1)	158(1)
(*b*) Triazenido-ligand			
N(1)–N(2)–N(3)	99(2)		
Re–N(1)–N(2)	99(2)	Re–N(3)–N(2)	104(2)
Re–N(1)–C(37)	143(2)	Re–N(3)–C(43)	144(2)
N(2)–N(1)–C(37)	118(2)	N(2)–N(3)–C(43)	112(2)
N(1)–C(37)–C(38)	122(2)	N(3)–C(43)–C(44)	119(2)
N(1)–C(37)–C(42)	118(2)	N(3)–C(43)–C(48)	120(2)
(*c*) PPh_3			
Re–P(1)–C(1)	108(1)	Re–P(2)–C(19)	118(1)
Re–P(1)–C(7)	118(1)	Re–P(2)–C(25)	118(1)
Re–P(1)–C(13)	117(1)	Re–P(2)–C(31)	109(1)
C(1)–P(1)–C(7)	106(1)	C(19)–P(2)–C(25)	100(1)
C(1)–P(1)–C(13)	104(1)	C(19)–P(2)–C(31)	106(1)
C(7)–P(1)–C(13)	102(1)	C(25)–P(2)–C(31)	104(1)

The solids (except the p-ClC_6H_4 derivative) were crystallized from CH_2Cl_2–EtOH (7 : 3 v/v). Yields 60—70%.

X-Ray Diffractometry.—A well formed fragment of $[ReCl_2(p\text{-}MeC_6H_4N\overset{\cdot\,\cdot}{\text{—}}N\overset{\cdot\,\cdot}{\text{—}}NC_6H_4Me\text{-}p)(PPh_3)_2]$ with approximate dimensions 0.12 × 0.16 × 0.10 mm was mounted on the end of the glass fibre with epoxy-adhesive. Cell dimensions were determined on a Philips PW 1100 automatic diffractometer using graphite-monochromatized Mo-K_α radiation. Unit-cell parameters were obtained by least-squares refinement of 25 medium-angle reflections carefully determined.

Crystal data. $C_{48}H_{40}Cl_2N_3P_2Re$, $M = 977$, Monoclinic, $a = 14.50(1)$, $b = 24.68(1)$, $c = 12.91(1)$ Å, $\beta = 108.50(4)°$, $U = 4\,382$ Å^3, $Z = 4$, $D_c = 1.48$ g cm^{-3}, $F(000) = 1\,952$, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 33.4$ cm^{-1}, space group $P2_1/a$ from systematic absences $h0l$, h odd, and $0k0$, k odd.

Data, up to $\theta = 25°$, were collected by the θ—2θ step-scan method using Mo-K_α radiation, with a scan rate of 2° min^{-1}. Two standard reflections measured at intervals of 100 min were constant within counting statistics. Of the 2 931 independent reflections measured, 2 702 were significantly above background [$I \geqslant 3\sigma(I)$].

Solution of the structure was achieved by standard heavy-atom methods. Refinement of scale-factor, positional, and thermal parameters converged to give a final agreement index R of 0.075, the largest parameter shift in the last cycle being 0.2σ. The structure was refined by full-matrix least squares, minimizing the function $\Sigma w \Delta F^2$ with $w = 1$. The PPh_3 phenyls were refined as rigid bodies with C–C distances of 1.395 Å and C–H distances of 0.95 Å. The hydrogen atoms of the ligand phenyl residues were introduced in calculated positions with C–H distances of 0.95 Å. All hydrogen atoms were assigned fixed thermal parameters of 8 Å^2.

A final difference-Fourier synthesis showed no significant residuals. Scattering factors for Re were from ref. 19, and those for P, Cl, N, C, and H from ref. 20. The rhenium scattering factor was corrected for anomalous dispersion with constant average values $\Delta f' = -1.598$ and $\Delta f'' = 7.232$ for the real and imaginary components.

All calculations were done using the SHELX and *X*-RAY program systems.[21]

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