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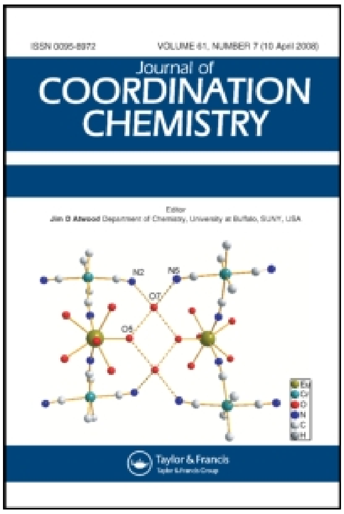

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THE SYNTHESIS, CRYSTAL, MOLECULAR AND ELECTRONIC STRUCTURE OF TRICHLORO(NITROSYL)BIS(TRIPHENYL-PHOSPHINE OXIDE)RHENIUM(II)

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THE SYNTHESIS, CRYSTAL, MOLECULAR AND ELECTRONIC STRUCTURE OF TRICHLORO(NITROSYL)*BIS*(TRIPHENYL-PHOSPHINE OXIDE)RHENIUM(II)

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A new rhenium nitrosyl complex has been synthesized and characterized by IR, electronic and ^{31}P NMR spectroscopy and magnetochemical measurements. Its electronic structure has been determined (Dq = 3333, Ds = −4732 and Dt = 387 cm^{-1}). The crystal and molecular structure of [ReCl$_3$(NO)(OPPh$_3$)$_2$] has been solved by the heavy atom method and refined anisotropically to $R = 0.466$ for 3032 unique observed reflections. The title compound crystallizes in the monoclinic space group $C2/c$, with $a = 13.887(2)$, $b = 13.154(2)$, $c = 19.629(4)$ Å, $\beta = 96.78(2)°$ and $Z = 4$. The Re atom is of six-coordinate distorted octahedral configuration and the linear nitrosyl ligand is *trans* to one of triphenylphosphine oxide molecules. The OPPh$_3$ groups of [ReCl$_3$(NO)(OPPh$_3$)$_2$] are in *cis* positions.

Keywords: Rhenium; nitrosyl; X-ray structure; electronic structure; nitric oxide

INTRODUCTION

For many years the synthesis and characterization of transition metal nitrosyl complexes have been a centre of interest.[1–28] Various methods, *i.e.*, using

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gaseous nitric oxide, nitrosonium salts, organic and inorganic nitroso compounds, inorganic nitrites and hydroxylamine, are available for the synthesis of this group of complexes.[1-22] A most important aspect of research on nitrosyl complexes is the determination of the bonding nature of nitric oxide to metal centres. Terminal NO ligands (NO binds to only one metal centre *via* the N atom) may adopt either linear or bent geometries. In polynuclear complexes, nitric oxide can also act as a bridging ligand between two or three metal centres. In these cases, NO is attached to more than one metal centre either *via* the N atom alone, or *via* the N and O atoms of the same NO group.[23-28] Increasing interest in nitrosyl complexes is connected with their catalytic ability, their use in the production of organonitrogen compounds and their possible application in pollutant control (reduction of NO in exhaust fumes).[29-36] The main aim of our research during the past few years has been the examination of the reactivity of *trans*-oxotrihalogeno*bis*(triphenylphosphine)rhenium(V) complexes towards gaseous NO depending on the solvent.[37-42] The influence of solvents on the mechanisms of chemical reactions and the yields of these reactions is connected to donor–acceptor ability of the solvents. Considering this fact the nitrosylation of $[ReOCl_3(PPh_3)_2]$ by NO in benzene solution is an interesting problem.

Here we present the synthesis, spectroscopic data and electronic, crystal and molecular structure of $[ReCl_3(NO)(OPPh_3)_2]$, obtained by the nitrosylation of a refluxing solution of $[ReOCl_3(PPh_3)_2]$ in benzene by NO.

EXPERIMENTAL

Triphenylphosphine and NH_4ReO_4 were purchased from Aldrich Chemical Co. and used without further purification. $[ReOCl_3(PPh_3)_2]$ was synthesized according to a literature method.[43] Gaseous NO, obtained in the reaction: $2NaNO_2 + 3H_2SO_4 + 2FeSO_4 \rightarrow 2NO + 2NaHSO_4 + Fe_2(SO_4)_3 + 2H_2O$, was purified by passing it through concentrated KOH solution and over solid NaOH. Solvents were dried and deoxygenated prior to use in the usual way. The reaction, all preparations and the recrystallization were performed under argon.

Synthesis of $[ReCl_3(NO)(OPPh_3)_2]$

NO was passed through a vigorously stirred, refluxing solution of $[ReOCl_3(PPh_3)_2]$ (0.85 g, 1 mmol) in benzene (40 cm^3). The reaction was carried out for 5–6 h. The colour changed gradually from bright green to dark maroon. Then the resulting solution was evaporated to a volume of 10 cm^3. A green precipitate was formed by an addition of 40 cm^3 of EtOH and after 15 min it was filtered off. The product was washed with cold ether and dried *in vacuo*. Yield: 0.55 g (0.63 mmol) [$ReCl_3(NO)(OPPh_3)_2$]. Crystals suitable for X-ray crystal structure determination were obtained by slow evaporation of an acetonitrile solution of the complex.

Physical Measurements

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the range 4000–400 cm^{-1} with the samples in potassium bromide pellets. Electronic spectra were measured on a Beckman 5240 spectrophotometer in the range 800–220 nm in deoxygenated dichloromethane solution. ^{31}P NMR were obtained at room temperature in $CDCl_3$ solution using a Varian VXR300 spectrometer and chemical shifts are given with reference to external 85% aqueous H_3PO_4 solution. Magnetic susceptibilities were measured at 296 K by the Faraday method.

Crystal Structure Determination and Refinement

Three-dimensional X-ray intensity data were collected on an Kuma KM-4 diffractometer. Details concerning crystal data and refinement are given in Table I. Lorentz polarization and empirical absorption corrections were applied. The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically using full-matrix, least-squares techniques. The hydrogen atom positions of the phenyl rings were found from subsequent difference Fourier syntheses and were treated as riding on the adjacent carbon atom [d(C–H) = 0.96 Å] and refined with individual isotropic temperature factor equal to 1.2 times the value of the equivalent temperature factor of the parent carbon atom. SHELXL97[44] and SHELXTL[45] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs. A final difference electron density residual peak of 1.78 e Å^{-3} and a hole of −1.54 e Å^{-3} were observed within 0.05 and 0.02 Å of the Re(1) atom.

RESULTS AND DISCUSSION

Table II presents atomic coordinates and equivalent isotropic displacement parameters for [$ReCl_3(NO)(OPPh_3)_2$]. Important bond lengths and angles are

TABLE I Crystal data and structure refinement details for [$ReCl_3(NO)(OPPh_3)_2$]

Empirical formula	$C_{36}H_{30}Cl_3NO_3P_2Re$
Formula weight	879.10
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 13.887(2)$ Å $b = 13.154(2)$ Å, $\beta = 96.78(2)°$ $c = 19.629(4)$ Å
Volume	3560.5(10) $Å^3$
Z	4
Density (calculated)	1.640 $mg\,m^{-3}$
Absorption coefficient	3.764 mm^{-1}
$F(000)$	1732
Crystal size	0.16 × 0.13 × 0.05 mm
θ range for data collection	2.09–25.05°
Index ranges	$-16 \leq h \leq 16; -1 \leq k \leq 15; -1 \leq l \leq 22$
Reflections collected	3583
Independent reflections	3032 ($R_{int} = 0.0354$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3011/0/223
Goodness-of-fit on F^2	1.232
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0466$, $wR2 = 0.0840$
R indices (all data)	$R1 = 0.0791$, $wR2 = 0.1064$

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for [$ReCl_3(NO)(OPPh_3)_2$]. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	U_{eq}
Re(1)	0	3563(1)	2500	32(1)
Cl(1)	1613(1)	3415(2)	3029(1)	50(1)
Cl(2)	−473(7)	4800(7)	3233(5)	53(2)
P(1)	−218(2)	1691(2)	3728(1)	38(1)
O(1)	−344(4)	2410(5)	3136(3)	49(2)
O(2)	−587(23)	5130(23)	3424(15)	88(9)
N(1)	−277(25)	4497(25)	3058(19)	56(8)
C(1)	487(6)	2207(7)	4478(4)	43(2)
C(2)	354(7)	3193(8)	4658(5)	62(3)
C(3)	844(8)	3560(11)	5260(5)	73(3)
C(4)	1482(8)	2980(12)	5664(6)	80(4)
C(5)	1616(8)	1987(11)	5488(6)	74(3)
C(6)	1143(6)	1611(9)	4882(4)	58(3)
C(7)	357(6)	549(7)	3507(4)	45(2)
C(8)	−37(8)	−424(8)	3595(6)	64(3)
C(9)	480(10)	−1269(9)	3448(7)	88(4)
C(10)	1352(10)	−1182(10)	3202(7)	90(4)
C(11)	1746(9)	−230(10)	3107(6)	74(3)
C(12)	1256(7)	619(8)	3269(5)	58(3)
C(13)	−1384(5)	1387(7)	3969(4)	40(2)
C(14)	−2162(6)	1305(8)	3457(5)	54(2)
C(15)	−3077(7)	1044(9)	3625(6)	71(3)
C(16)	−3220(8)	907(9)	4294(7)	80(4)
C(17)	−2461(9)	989(11)	4796(6)	88(4)
C(18)	−1548(7)	1254(9)	4639(5)	66(3)

TABLE III Important bond lengths (Å) and angles (°) for $[ReCl_3(NO)(OPPh_3)_2]$

Bond lengths		*Angles*	
Re(1)-N(1)	1.72(3)	N(1)-Re(1)-O(1)	93.1(13)
Re(1)-O(1)	2.055(6)	O(1)-Re(1)-Cl(2)	92.2(3)
Re(1)-Cl(2)	2.318(8)	N(1)-Re(1)-Cl(1)	92.9(13)
Re(1)-Cl(1)	2.363(2)	O(1)-Re(1)-Cl(1)	87.0(2)
P(1)-O(1)	1.493(6)	Cl(2)-Re(1)-Cl(1)	96.2(2)
P(1)-C(7)	1.778(10)	O(1)-P(1)-C(7)	111.1(4)
P(1)-C(13)	1.786(7)	O(1)-P(1)-C(13)	108.8(4)
P(1)-C(1)	1.801(8)	C(7)-P(1)-C(13)	108.8(4)
O(2)-N(1)	1.21(3)	O(1)-P(1)-C(1)	113.6(4)
C(1)-C(2)	1.363(13)	C(7)-P(1)-C(1)	107.5(4)
C(1)-C(6)	1.379(12)	C(13)-P(1)-C(1)	106.9(4)
C(2)-C(3)	1.380(13)	P(1)-O(1)-Re(1)	157.8(4)
C(3)-C(4)	1.35(2)	O(2)-N(1)-Re(1)	172(4)
C(4)-C(5)	1.37(2)	C(2)-C(1)-C(6)	119.4(9)
C(5)-C(6)	1.380(14)	C(2)-C(1)-P(1)	119.6(7)
C(7)-C(12)	1.387(12)	C(6)-C(1)-P(1)	121.0(8)
C(7)-C(8)	1.410(13)	C(1)-C(2)-C(3)	119.2(11)
		C(4)-C(3)-C(2)	121.8(13)
		C(3)-C(4)-C(5)	119.3(11)
		C(4)-C(5)-C(6)	119.6(11)
		C(1)-C(6)-C(5)	120.5(11)

reported in Table III. The numbering scheme of the $[ReCl_3(NO)(OPPh_3)_2]$ molecule is shown in Figure 1, whereas Figure 2 shows the environment of the Re(1) atom.

The Re(1) atom is octahedrally surrounded by three chlorine atoms, Cl(1), Cl(2) and Cl(1a), a nitrosyl group N(1a)–O(2a), and oxygen O(2) and O(1a) atoms of $(OPPh_3)$ groups. The ^{31}P NMR spectrum for $[ReCl_3(NO)(OPPh_3)_2]$ complex consists of a broad signal at 31.37 ppm. Table IV contains the assignments[46] of characteristic bands in IR range for $[ReCl_3(NO)(OPPh_3)_2]$, which is paramagnetic with a magnetic moment equal to 1.78 BM. The positions and molar absorption coefficients of electronic absorption bands for the complex and the electronic transitions assigned to the bands are shown in Table V.

$[ReOCl_3(PPh_3)_2]$ reacts with gaseous nitric oxide to give different products, depending on the solvent. The reaction of NO with a solution of $[ReOCl_3(PPh_3)_2]$ in benzene affords green crystals of $[ReCl_3(NO)(OPPh_3)_2]$, whereas the same reaction carried out in methylene chloride gives a mixture of two complexes, $[ReCl_3(NO)(OPPh_3)(PPh_3)]$ (major product) and $[ReCl_4(PPh_3)_2]$. [37,38,40] In benzene solution we observe the oxidation of two triphenylphosphine molecules but, in methylene chloride, only one.

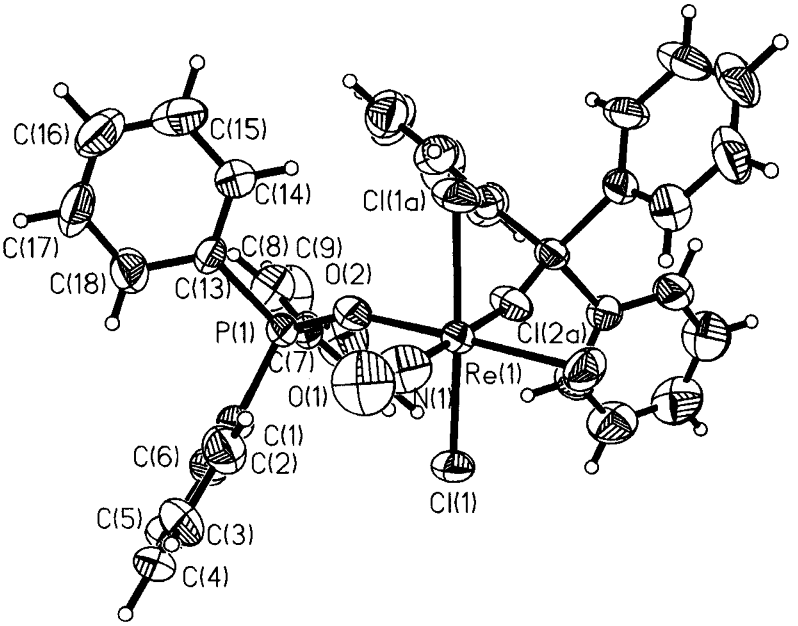


FIGURE 1 Perspective view of the complex showing the atom numbering scheme.

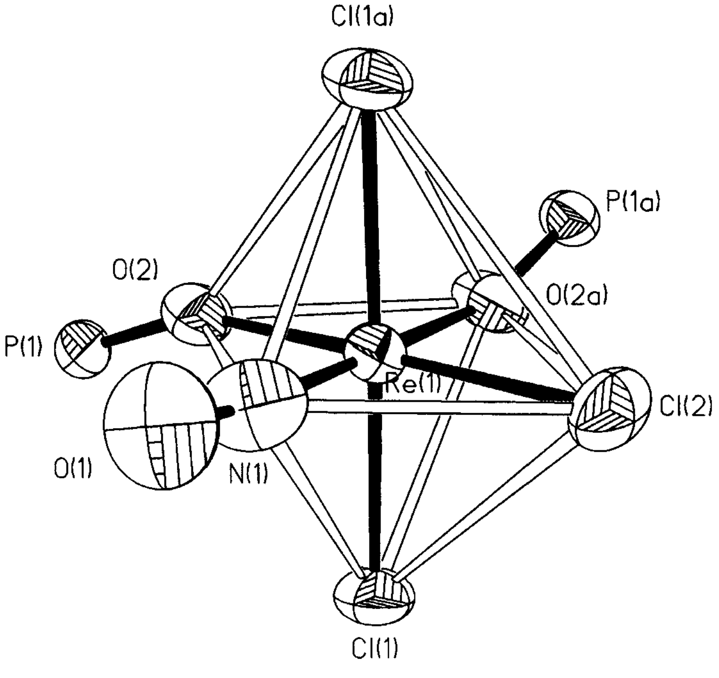


FIGURE 2 Perspective view of the Re environment.

TABLE IV Infrared data for $[ReCl_3(NO)(OPPh_3)_2]$

Band position (cm^{-1})	*Assignment*
1734	$\nu(NO)$
1485	δ(C–CH in the plane)
1437	$\nu(P–C_6H_5)$
1159	$\nu(P{=}O)$
1136	
1124	δ(C–H in the plane)
1088	
728	δ(C–C out of the plane)
690	δ(C–C in the plane)
536	$\nu(Re–N)$

TABLE V Band positions, molar absorption coefficients and assignments for $[ReCl_3(NO)(OPPh_3)_2]$

Band position (cm^{-1})	*Molar absorption coefficient* ($M^{-1}\,cm^{-1}$)	*Assignment*
15 150	34	$d_{xy} \rightarrow d_{xz}$
16 130	56	$d_{xy} \rightarrow d_{yz}$
23 810	636	$\pi^{o}_{O=P} \rightarrow d_{xy}$
29 410	3 899	$d_{xy} \rightarrow \pi^{*}_{NO}$
33 330	8 747	$d_{xy} \rightarrow d_{x^2-y^2}$
36 360	9 827	$\pi^{b}_{Re-Cl} \rightarrow d_{xz}$
37 313	9 946	$\pi^{b}_{Re-Cl} \rightarrow d_{yz}$
38 460	9 785	$\pi^{o}_{O=P} \rightarrow d_{xz}$ $d_{xz} \rightarrow d_{z^2}$
41 670	10 115	$\pi^{b}_{C_6H_5} \rightarrow 3d_{\mathrm{fosfor}}$

We suggest the course of $[ReCl_3(NO)(OPPh_3)_2]$ formation according to the following scheme.

$$[ReOCl_3(PPh_3)_2] + 4NO + C_6H_6 \rightarrow [ReCl_2(NO)_2(PPh_3)_2] + NOCl \cdot C_6H_6 + NO_2 \qquad (1)$$

$$[ReCl_2(NO)_2(PPh_3)_2] + NOCl \cdot C_6H_6 \rightarrow [ReCl_3(NO)(OPPh_3)(PPh_3)] + C_6H_6 + N_2O \qquad (2)$$

$$[ReCl_3(NO)(OPPh_3)(PPh_3)] + NO^{*} \rightarrow [ReCl_3(NO)(OPPh_3)_2] + N \qquad (3)$$

Reaction times and temperature influence only the yields of the products. Concentration of nitrosyl chloride forming in reaction (1) is higher in benzene because of the formation of the $ClNO \cdot C_6H_6$ complex;[47,48] in dichloromethane solution $ClNO \cdot CH_2Cl_2$ is not formed. Nitrosyl chloride which has not reacted according to reaction (2) undergoes photodissociation under visible light[49] ($n \rightarrow \pi^{*}$ at $\lambda = 460$ nm):

$$NOCl \cdot C_6H_6 \xrightarrow[\text{temp}]{h\nu} NO + Cl + C_6H_6 \qquad (4)$$

Chlorine (as Cl or Cl_2) forms charge-transfer complexes with benzene.

$$Cl(Cl_2) + C_6H_6 \rightarrow C_6H_6 \cdot Cl(C_6H_6 \cdot Cl_2) \tag{5}$$

These complexes absorb light, *e.g.*, $C_6H_6 \cdot Cl$ at 490 and 500 nm,[50–53] transforming into an excited state,

$$C_6H_6 \cdot Cl + h\nu \rightarrow (C_6H_6 \cdot Cl)^* \tag{6}$$

and in intermolecular collisions they transfer excitation energy to nitric oxide molecules.

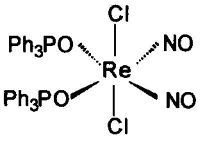
$$(C_6H_6 \cdot Cl)^* + NO \rightarrow C_6H_6 \cdot Cl + NO^* \tag{7}$$

Excited NO^* molecules are able to effectively oxidize the phosphine, according to reaction (3); N atoms, forming in this process, react with NO molecules[54,55]

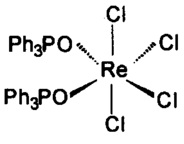
$$NO + N \rightarrow O + N_2 \tag{8}$$

generating O atoms, which also are able to effectively oxidize the phosphine in $[ReCl_3(NO)(OPPh_3)(PPh_3)]$.

The occupancy factor for the atoms Cl(2), N(1), O(2) and Cl(2a), N(1a), O(2a) is 0.5, so we must consider two possible structure (see Figure 1). First, crystals of the examined complex may consist of two kinds of **1A** and **1B** molecules in mol ratio 1 : 1.

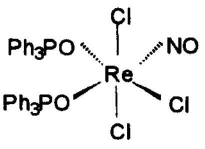


1A



1B

Alternatively, crystals of the complex consists of only **2A** molecules for which NO and Cl are disordered.



2A

This problem can be solved by IR spectroscopy. For the dinitrosyl complex (**1A**) with *cis* configuration of NO groups we should observe two strong bands while, for the **2A** complex, one band in the range specific for the nitrosyl group. The spectrum obtained for the examined compound shows a single strong band at 1734 cm^{-1}, which confirms the presence only of $[ReCl_3(NO)(OPPh_3)_2]$ molecules in the structure.

The above considerations are indeed supported by the results of the X-ray crystal structure analysis. The Re atom occupies special position *e* of the space group $C2/c$ with multiplicity 4 and site symmetry 2.[56] Re(1) is octahedrally surrounded by Cl(1) and O(2) (of $OPPh_3$ group) atoms with site occupation factors 1.0 and by the nitrosyl group N(1)–O(1) and Cl(2) atom occupying statistically common positions with site occupation factors of 0.5. The sum of electrons of the nitrosyl group (16) is only one electron less than of a Cl atom.

The octahedron is slightly elongated along Cl(1)–Re(1)–Cl(1a); Re(1)–Cl(1) = 2.364(2) while Re(1)–Cl(2) = 2.320(8) Å. This last bond length is identical as found by us in the reference structure of $[ReCl_4(PPh_3)_2]$ for this group of complexes.[37] Remaining bond lengths are in good agreement with values found previously by others.

One broad signal in ^{31}P NMR spectrum of the $[ReCl_3(NO)(OPPh_3)_2]$ complex indicate the presence only of one kind of phosphine ligands, $OPPh_3$, in the coordination sphere. The value of magnetic moment for $[ReCl_3(NO)(OPPh_3)_2]$ corresponds to one unpaired electron. Low values of molar absorption coefficients for the bands at 15150 and 16130 cm^{-1} indicate that these are effected by spin–orbital coupling. However, the elimination of the degeneracy of the t_2 level at C_s complex symmetry (basic term $^2B_1$) excludes the assignment of these bands to spin–orbital coupling. Intensities are typical for *d–d* transitions. The band at 29410 cm^{-1} is a *charge-transfer* transition connected with transition of d_{xy} electrons to π^*_{NO}. Relatively high intensity of the band at 33 330 cm^{-1} results from a partial contribution of the $d_{xy} \rightarrow \pi^*_{NO}$ transition. The band of highest energy is a result of an electronic transition in a phosphine ligand. Bands at 23 810, 36 360, 37 313 and 38 460 cm^{-1} are *charge-transfer* transitions connected with transition of $\pi^{o}_{O=P}$ or π^{b}_{Re-Cl} electrons to suitable *d* orbitals of rhenium (see Table V). Based on the data of Table V, values of ligand field parameters Dq, Ds and Dt have been defined and the energies of molecular orbitals for $[ReCl_3(NO)(OPPh_3)_2]$ complex have been estimated. The values of ligand field parameters are Dq = 3333, Ds = −4732 and Dt = 387 cm^{-1}. A relatively high π^*_{NO} energy level (above b_1) is defined found, as by other authors.[57]

Supplementary Material

Full list of bond lengths and angles, atomic coordinates, anisotropic thermal parameters, H-atom parameters and structure factors are available from TBJ on request.

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