PERGAMON

Polyhedron 18 (1999) 2313–2320

POLYHEDRON

New synthetic routes to some nitrosyl rhenium complexes. Crystal, molecular and electronic structure of [$ReCl_3(NO)(PPh_3)_2$] and [$ReCl_2(CO)(NO)(PPh_3)_2$] complexes

T.J. Bartczak[a,*], W. Czurak[a], J.O. Dzięgielewski[b,1], B. Machura[b], A. Jankowska[b], J. Kusz[c], J. Warczewski[c]

[a] *X-Ray Crystallography Laboratory, Institute of General and Ecological Chemistry, Technical University of Łódź, 116 Żeromski St., 90-924 Łódź, Poland*

[b] *Department of Inorganic and Radiation Chemistry, Institute of Chemistry, University of Silesia, 9 Szkolna St., 40-006 Katowice, Poland*

[c] *Institute of Physics, University of Silesia, 4 Uniwersytecka St., 40-006 Katowice, Poland*

Received 10 December 1998; accepted 21 April 1999

Abstract

The reactions of the nitrosyl rhenium(II) complex [$ReCl_3(NO)(OPPh_3)(PPh_3)$] with triphenylphosphine, $NaBH_4$ in the presence of PPh_3, and CO in the presence of PPh_3 were examined. The rhenium nitrosyl complexes [$ReCl_3(NO)(PPh_3)_2$] (**1**), [$ReCl_2(CO)(NO)(PPh_3)_2$] (**2**) and [$ReH_2(NO)(PPh_3)_3$]$\cdot 1/2C_6H_6$ (**3**) obtained were characterised by IR, UV–Vis, NMR (^1H and ^{31}P) and magnetochemical measurements. For **1** and **2**, the electronic, crystal and molecular structures were determined. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Rhenium; Nitrosyl; X-ray structure; Electronic structure; Nitric oxide

---

1. Introduction

For many years, much attention has been focused on the synthesis and study of a variety of nitrosyl transition metal complexes, due to their catalytic abilities and uses in the production of organonitrogen compounds or in pollutant control [1–36].

In our recent publications, we disclosed very convenient single stage syntheses of some nitrosyl rhenium complexes with phosphine ligands: [$ReX_2(NO)_2(PPh_3)_2$] (X=Cl or Br) [37], [$ReBr_3(Ph)(NO)(PPh_3)$] [38], [$ReBr_3(NO)(MeCN)(PPh_3)$] [39], [$ReCl_3(NO)(OPPh_3)(PPh_3)$] [40] and [$ReCl_3(NO)(OPPh_3)_2$] [41]. They are all products of reductive nitrosylation of oxotrihalogenobis-(triphenylphosphine)rhenium(V) by gaseous nitric oxide. For the unstable dinitrosyl complexes [$ReX_2(NO)_2(PPh_3)_2$], we determined only their electronic structure, but for the others, we presented both electronic and molecular structures.

Here, we describe new synthetic methods for [$ReCl_3(NO)(PPh_3)_2$] (**1**), [$ReCl_2(CO)(NO)(PPh_3)_2$] (**2**) and [$ReH_2(NO)(PPh_3)_3$]$\cdot 1/2C_6H_6$ (**3**), their spectroscopic characterisation, and determination of the electronic, crystal, molecular structures of **1** and **2**. We have observed the formation of the complexes **1**, **2** and **3** in the reaction of [$ReCl_3(NO)(OPPh_3)(PPh_3)$] with triphenylphosphine, with CO in the presence of PPh_3 and with $NaBH_4$ in the presence of PPh_3, respectively. The complexes **1**–**3** are known as rhenium nitrosyl compounds: they have been obtained by various methods so far. Complex **3** is one of the most studied rhenium compounds and is a very useful starting material for the syntheses of a variety of rhenium nitrosyls [42–45]. We used it to test our new preparative method. Its crystal and molecular structure were presented in Ref. [46]. The nitrosyl complex **1** was a product of the following reactions: [$ReCl_2(OMe)(NO)(PPh_3)_2$] with HCl [47], [NEt_4][$ReCl_5(NO)$] with PPh_3 [48] and [$ReO(OEt)Cl_2(PPh_3)_2$] with NO in the presence of [NEt_4N]Cl [49]. Complex **2** was isolated in the reactions of [$ReCl_2(OMe)(NO)(PPh_3)_2$] or [$ReCl_2(NO)(PPh_3)_3$]

---

*Corresponding author. Tel.: +48-42-631-3137; fax: +48-42-631-3103.

E-mail address: tadekbar@cl-sg.p.lodz.pl (T.J. Bartczak)

[1] Corresponding author. This author is also a Senior author.

0277-5387/99/$ – see front matter

PII: S0277-5387(99)00120-5

with CO [47,50]. However, the crystal, molecular and electronic structures of **1** and **2** were determined for the first time in this study.

The synthesis methods given in the literature involve a multi-stage process; for $[ReCl_3(NO)(PPh_3)_2]$:

$$[ReOCl_3(PPh_3)_2]\xrightarrow{96\%}[ReCl_2(N_2COPh)(PPh_3)_2]\xrightarrow{86\%}[ReCl_2(OMe)(NO)(PPh_3)_2]\xrightarrow{71\%}[ReCl_3(NO)(PPh_3)_2]\ [47]$$

or

$$[ReOCl_3(PPh_3)_2]\xrightarrow{89\%}[ReO(OEt)Cl_2(PPh_3)_2]\xrightarrow{25\%}(NMe_4)_2[Re(NO)Cl_5]\xrightarrow{60\%}[ReCl_3(NO)(PPh_3)_2]\ [10,45,57]$$

Our method is as follows:

$$[ReOCl_3(PPh_3)_2]\xrightarrow{51\%}[ReCl_3(NO)(OPPh_3)(PPh_3)]\xrightarrow{95\%}[ReCl_3(NO)(PPh_3)_2]$$

In the case of $[ReCl_2(NO)(CO)(PPh_3)_2]$, the methods presented in the literature are:

$$[ReOCl_3(PPh_3)_2]\xrightarrow{96\%}[ReCl_2(N_2COPh)(PPh_3)_2]\xrightarrow{86\%}[ReCl_2(OMe)(NO)(PPh_3)_2]\xrightarrow{55\%}[ReCl_2(NO)(CO)(PPh_3)_2\ [47]$$

or

$$[ReOCl_3(PPh_3)_2]\xrightarrow{96\%}[ReCl_2(N_2COPh)(PPh_3)_2]\xrightarrow{86\%}[ReCl_2(OMe)(NO)(PPh_3)_2]\xrightarrow{91\%}[ReH_2(NO)(PPh_3)_3]\xrightarrow{95\%}[ReCl_2(NO)(PPh_3)_3]\xrightarrow{97\%}[ReCl_2(NO)(CO)(PPh_3)_2]\ [42]$$

Our method is as follows:

$$[ReOCl_3(PPh_3)_2]\xrightarrow{51\%}[ReCl_3(NO)(OPPh_3)(PPh_3)]\xrightarrow{76\%}[ReCl_2(NO)(CO)(PPh_3)_2]$$

Our two-staged preparative procedures have comparable yields to those of the methods described in the literature. Therefore, the aim of our work was to simplify the synthesis of an important group of rhenium compounds, to determine their crystal and electronic structures, and also to characterise their magnetic and spectroscopic properties in the range of electron, infrared and ^{31}P NMR spectroscopies.

2. Experimental

Triphenylphosphine and NH_4ReO_4 were purchased from Aldrich Chemical Co. and used without further purification.

The $[ReOCl_3(PPh_3)_2]$ and $[ReCl_3(NO)(OPPh_3)(PPh_3)]$ complexes were synthesised according to methods described in the literature [40,51]. 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 the washers with concentrated KOH solution and over solid NaOH. Gaseous CO, obtained from HCOOH, was purified by passing it through the washers with 50% KOH and alkaline $Na_2S_2O_4$ solutions and over solid KOH and $CaCl_2$.

Solvents were dried and deoxygenated in the usual way prior to use. The reaction, all preparations and the recrystallisation were performed under an argon atmosphere.

2.1. Preparation of $[ReCl_3(NO)(PPh_3)_2]$

The solution of $[ReCl_3(NO)(OPPh_3)(PPh_3)]$ (0.4 g, 0.46 mmol) and PPh_3 (0.4 g, 1.5 mmol) in CH_2Cl_2 (30cm^3) was refluxed for 2 h. The colour immediately changed from green to dark red. The dark red precipitate was formed by an addition of 100 cm^3 of EtOH and filtered off after 20 min. The product was washed with cold ether and dried in vacuo. Yield: 0.37 g (0.44 mmol) $[ReCl_3(NO)(PPh_3)_2]$.

Crystals suitable for X-ray structure determination were obtained by slow evaporation of an acetonitrile solution of nitrosyl rhenium(II) complex at room temperature.

2.2. Preparation of $[ReCl_2(CO)(NO)(PPh_3)_2]$

(A) CO was passed through a vigorously stirred and refluxing solution of $[ReCl_3(NO)(OPPh_3)(PPh_3)]$ (0.3 g, 0.35 mmol) and PPh_3 (0.3 g, 1.1 mmol) in tetrahydrofuran (THF; 50 cm^3). The reaction was carried out for 6–7 h. The colour changed first from green to dark red and then gradually to yellow. The resulting solution was evaporated to a volume of 10 cm^3. The bright yellow precipitate was formed by the addition of 100 cm^3 of EtOH and, after 20 min, it was filtered off. The product was washed with cold ether and dried in vacuo. Yield: 0.22 g (0.27 mmol) $[ReCl_2(CO)(NO)(PPh_3)_2]$. When the reaction was carried out in the absence of triphenylphosphine, the yields of $[ReCl_2(CO)(NO)(PPh_3)_2]$ dropped to 5% (0.014 g). Crystals suitable for X-ray structure determination were obtained by slow evaporation of an acetonitrile solution of nitrosyl rhenium(I) complex at room temperature.

(B) CO was passed through a vigorously stirred and refluxing solution of $[ReCl_3(NO)(PPh_3)_2]$ (0.3 g, 0.35 mmol) in THF (50 cm^3). The reaction was carried out for 6–7 h. The colour changed gradually from dark red to yellow. The resulting solution was evaporated to a volume of 10 cm^3. A light yellow precipitate was formed on the addition of 100 cm^3 of EtOH and, after 20 min, it was filtered off. The product was washed with cold ether and dried in vacuo. Yield: 0.23 g (0.28 mmol) $[ReCl_2(CO)(NO)(PPh_3)_2]$.

2.3. Preparation of $[ReH_2(NO)(PPh_3)_3]\cdot 1/2C_6H_6$

A solution of $[ReCl_3(NO)(OPPh_3)(PPh_3)]$ (0.15 g, 0.17

mmol), PPh_3 (0.15 g, 0.57 mmol) and $NaBH_4$ (0.04 g, 0.1 mmol) in ethanol (30 cm^3) was refluxed for 2 h. The colour immediately changed from green to yellow. The yellow precipitate was filtered off. The crude product was solved in CH_2Cl_2. NaCl, which is insoluble in CH_2Cl_2, was filtered off and the precipitate of $[ReH_2(NO)(PPh_3)_3]$ was formed on addition of 100 cm^3 of EtOH. The diamagnetic complex was recrystallised from a mixture of ethanol and benzene. Yield: 0.16 g (0.15 mmol) $[ReH_2(NO)(PPh_3)_3]\cdot 1/2\ C_6H_6$. Anal. calcd.: C, 65.5; H, 4.82; N, 1.34. Found: C, 64.9; H, 4.4; N, 1.31. Infrared spectrum: 1965 cm^{-1} (ν_{Re-H}), 1794 cm^{-1}(ν_{Re-H}), 1630 cm^{-1} (ν_{N-O}). ^{31}P NMR ($CDCl_3$): two singlets at 18.38 and 27.97 ppm. ^1H NMR ($CDCl_3$): two quartets at 1.32 and 2.54 ppm ($J_{PH}=30$ Hz, $J_{HH}=6$ Hz); phenyl multiplets were found between 6.9 and 7.24 ppm). UV–Vis spectroscopy: 29 670 cm^{-1} ($\varepsilon=2432$ dm^3 mol^{-1} cm^{-1}), 37 040 cm^{-1} ($\varepsilon=16\,768$ dm^3 mol^{-1} cm^{-1}), 45 455 cm^{-1} ($\varepsilon=18\,175$ dm^3 mol^{-1} cm^{-1}).

2.4. Physical measurements

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm^{-1}, with the samples in the form of potassium bromide pellets.

Electronic spectra were measured on a Beckman 5240 spectrophotometer in the range 800–220 nm in deoxygenated dichloromethane solution.

^1H and ^{31}P NMR were obtained at room temperature in $CDCl_3$ solution using a Varian VXR300 spectrometer. The sample solutions were prepared using monocrystals of the complex. In the case of the proton resonance, tetramethylsilane (TMS) was used as an internal standard, and for phosphorus resonance, an 85% H_3PO_4 aqueous solution was used.

Magnetic susceptibilities were measured at 296 K by the Faraday method.

2.5. Crystal structure determination and refinement

All of the three-dimensional X-ray intensity data were collected on a Kuma KM-4 diffractometer with graphite monochromated Mo–K_α radiation ($\lambda=0.71073$ Å) at room temperature. Details concerning crystal data and refinement for **1** and **2** are given in Table 1. Lorentz, polarisation and empirical absorption corrections were applied for **1** and **2.** The structures of the complexes were solved by means of the Patterson and Fourier methods. All of the non-hydrogen atoms were refined anisotropically using the full-matrix, least-squares technique. The positions of the hydrogen atoms 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 an individual isotropic temperature factor that was equal to 1.2 times the value of the

Table 1
Crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula	$C_{36}H_{30}Cl_3NOP_2Re$	$C_{37}H_{30}Cl_2NO_2P_2Re$
Formula weight	847.10	827.70
Temperature, K	293(2)	293(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
Unit cell dimensions, Å	$a=25.553(9)$	$a=24.494(4)$
	$b=9.563(4)$	$b=9.500(2)$
	$c=15.890(6)$	$c=15.963(3)$
	$\beta=116.9(3)°$	$\beta=116.030(10)°$
Volume, Å^3	3327(2)	3337(11)
Z	4	4
Density (calculated), Mg/m^3	1.691	1.742
Absorption coefficient, mm^{-1}	4.02	4.01
$F(000)$	1668	1724
Crystal size, mm	0.31×0.21×0.13	0.08×0.09×0.20
θ range for data collection	2.31 to 25.05°	2.34 to 25.05°
Index ranges	$-26\leq h\leq 29$; $-1\leq k\leq 11$;	$-29\leq h\leq 18$; $0\leq k\leq 11$;
	$-18\leq l\leq 1$	$-19\leq l\leq 18$
Reflections collected	3693	3033
Independent reflections	2944 ($R_{int}=0.0285$)	2949 ($R_{int}=0.0214$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2925/0/202	2943/0/215
Goodness-of-fit on F^2	1.06	1.18
Final R indices [$I>2\sigma(I)$]	$R1=0.033$, $wR2=0.087$	$R1=0.028$, $wR2=0.058$
R indices (all data)	$R1=0.055$, $wR2=0.101$	$R1=0.040$, $wR2=0.067$
Largest diff. peak and hole	4.54 and -1.21 eÅ^{-3}	1.50 and -0.73 eÅ^{-3}

equivalent temperature factor of the parent carbon atom. SHELXL97 [52] and SHELXTL [53] programs were used for all of the calculations. Atomic scattering factors were those incorporated in the computer programs.

3. Results and discussion

The [$ReCl_3(NO)(OPPh_3)(PPh_3)$] complex reacts with CO to give [$ReCl_2(CO)(NO)(PPh_3)_2$], but its yield in this synthesis is extremely low (see Section 2). When the reaction of [$ReCl_3(NO)(OPPh_3)(PPh_3)$] with CO is carried out in the presence of triphenylphosphine, the yields of the nitrosyl rhenium (**1**) complex increase considerably. The first step in the reaction of [$ReCl_3(NO)(OPPh_3)(PPh_3)$] with CO, carried out in the presence of PPh_3, involves replacement of the triphenylphosphine oxide molecule by PPh_3 to generate **1**. Complex **1** is then reduced by CO to **2**. In order to confirm this mechanism, we also carried out the reaction of the [$ReCl_3(NO)(OPPh_3)(PPh_3)$] complex with only PPh_3. Then, the product of this reaction, complex **1**, was treated with CO. In this case, nitrosyl complex **2** was isolated also.

The [$ReCl_3(NO)(OPPh_3)(PPh_3)$] reacts with $NaBH_4$ in the presence of PPh_3 to yield [$ReH_2(NO)(PPh_3)_3$]$\cdot 1/2C_6H_6$.

3.1. Molecular structure of trichloronitrosylbis(triphenylphosphine)rhenium(II)

A similar structure of [$ReCl_3(NO)(PMePh_2)_2$] was published previously [58]. However, the compound crystallised in the different crystal system (triclinic), no bond lengths and angles were given and the *R* factor for 4118 diffractometer data was 0.10.

The numbering scheme of **1** is shown in Fig. 1. The Re(1) atom is octahedrally surrounded by three chlorine atoms: Cl(1), Cl2) and Cl(1a), a nitrosyl group, N(1)–O(1), and two phosphorus atoms, P(1) and P(1a). The central ion, Re(1), the nitrosyl group, N(1)–O(1), and one of the chloride ligands, Cl(2), occupy special positions; they all lie on two-fold axis. In the [$ReCl_3(NO)(PPh_3)_2$] complex, in contrast to the starting material [$ReCl_3(NO)(OPPh_3)(PPh_3)$], the phosphine ligands are in a *trans* arrangement.

The most important bond lengths and angles for **1** are reported in Table 2. The Re–NO bond distance of 1.765(9) Å is in good agreement with values previously found by others, for example, 1.76(2) Å in [$ReF(CO)(NO)(PPh_3)_3$][BF_4] [50], 1.749(11) Å in (NEt_4)[$Re(NO)Cl_4(py)$] [54] and 1.77 Å in [$ReH_2(NO)(PPh_3)_3$]$\cdot 1/2\ C_6H_6$ [46]. The N(1)–O(1) bond length of 1.200(11) Å is in the range 1.10–1.25 Å, which is expected for NO^+ [1]. The value of Re–N–O angle, 180.0°, and the bond lengths discussed above confirm the linear co-ordination of the nitrosyl ligand. The Cl(2) ligand is *trans* to the nitrosyl group (π-acceptor ligand) and this is why the bond Re(1)–Cl(2) = 2.398(2) Å is slightly longer than Re(1)–Cl(1) = 2.378(2) Å.

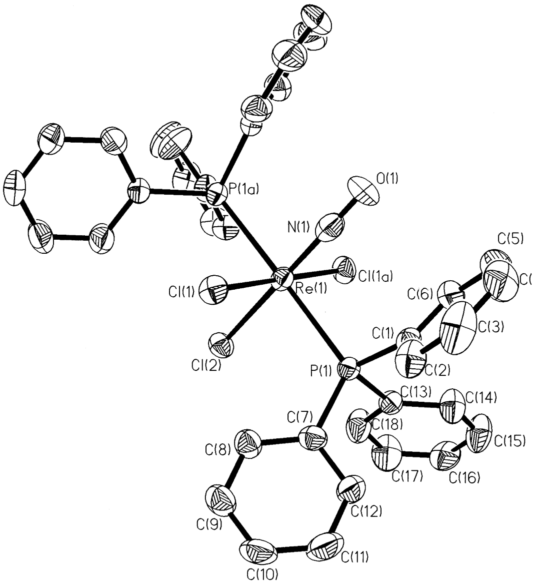

Fig. 1. The molecular structure of **1**.

3.2. Molecular structure of dichloro(carbonyl)(nitrosyl)bis(triphenylphosphine) rhenium(I)

The numbering scheme of **2** is shown in Fig. 2. The Re(1) atom is octahedrally surrounded by two chlorine atoms, Cl(1), Cl(2), a nitrosyl group, N(1)–O(1), a carbonyl group, C(37)–O(2), and two phosphorus atoms, P(1) and P(1a). The central ion, Re(1), the nitrosyl group,

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths		Angles	
Re(1)–N(1)	1.765(9)	N(1)–Re(1)–Cl(1)	90.43(4)
Re(1)–Cl(1)	2.378(2)	N(1)–Re(1)–Cl(2)	180
Re(1)–Cl(2)	2.398(2)	Cl(1)–Re(1)–Cl(2)	89.57(4)
Re(1)–P(1)	2.530(2)	N(1)–Re(1)–P(1)	90.60(4)
P(1)–C(1)	1.819(6)	Cl(1)–Re(1)–P(1)	92.51(6)
P(1)–C(7)	1.822(6)	Cl(2)–Re(1)–P(1)	89.40(4)
P(1)–C(13)	1.826(6)	C(1)–P(1)–C(7)	106.7(3)
N(1)–O(1)	1.200(11)	C(1)–P(1)–C(13)	105.5(3)
		C(7)–P(1)–C(13)	100.8(3)
		C(1)–P(1)–Re(1)	107.0(2)
		C(7)–P(1)–Re(1)	119.1(2)
		C(13)–P(1)–Re(1)	116.8(2)
		O(1)–N(1)–Re(1)	180

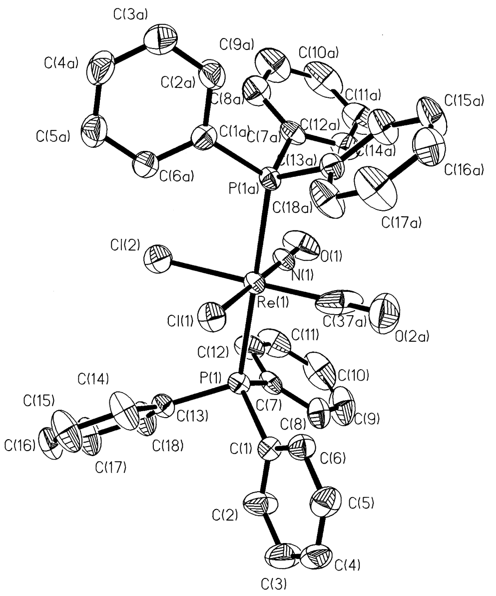

Fig. 2. The molecular structure of **2**.

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths		Angles	
Re(1)–N(1)	1.829(6)	N(1)–Re(1)–C(37)	86.8(9)
Re(1)–C(37)	1.93(2)	N(1)–Re(1)–Cl(2)	88.4(1)
Re(1)–Cl(1)	2.428(2)	N(1)–Re(1)–Cl(1)	180
Re(1)–Cl(2)	2.410(6)	C(37)–Re(1)–Cl(1)	93.2(9)
Re(1)–P(1)	2.492 (1)	Cl(2)–Re(1)–Cl(1)	91.6(1)
C(37)–O(2)	1.16(2)	N(1)–Re(1) –P(1)	90.62(3)
N(1)–O(1)	1.157(8)	C(37)–Re(1)–P(1)	92.5(8)
P(1)–C(1)	1.822(5)	Cl(2)–Re(1)–P(1)	92.3(2)
P(1)–C(13)	1.831(5)	Cl(1)–Re(1)–P(1)	89.4(3)
P(1)–C(7)	1.826(5)	C(1)–P(1)–C(7)	105.5(2)
		C(1)–P(1)–C(13)	101.3(2)
		C(13)–P(1)–C(7)	104.9(2)
		C(1)–P(1)–Re(1)	118.8(2)
		C(7)–P(1)–Re(1)	108.3(1)
		C(13)–P(1)–Re(1)	116.8(2)
		O(2)–C(37)–Re(1)	168.0(3)
		O(1)–N(1)–Re(1)	180

N(1)–O(1), and one of the chloride ligands, Cl(1), occupy special positions as they all lie on a two-fold axis [59]. Therefore, the C(37)–O(2) group and Cl(2) are disordered and were treated during refinement with site occupation factors equal to 0.5. This affected the accuracy of the associated bond lengths and angles. ESDs of the bonds involved in the disorder are, on average, 0.05 Å, compared to 0.001–0.002 Å for the bonds of Re(1) with other atoms. The most important bond lengths and angles for **2** are reported in Table 3. The value of the Re(1)–N(1)–O(1) angle, 180.0°, and the bond lengths for Re(1)–N(1), 1.829(6) Å, and N(1)–O(1), 1.157(8) Å, confirm the linear co-ordination of the nitrosyl ligand.

3.3. Spectroscopic characterisation of the [ReCl$_3$(NO)(PPh$_3$)$_2$] complex

The *trans* geometry of phosphine ligands in **1** was clearly established by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of **1** consists of one singlet at 29.65 ppm.

The ^{1}H NMR spectrum of **1** shows only phenyl multiplets between 7.44 and 7.87 ppm.

A strong band, corresponding to the stretching vibration of the nitrosyl group, appears at 1734 cm^{-1}. Table 4 contains the assignments of characteristic bands in the IR range for **1** [55].

[ReCl$_3$(NO)(PPh$_3$)$_2$] is a paramagnetic compound with a magnetic moment equal to 1.8 BM, corresponding to one unpaired electron.

The positions and molar absorption coefficients of electronic bands for **1** and the electronic transitions assigned to the bands are shown in Table 5. The first two absorption bands in the electronic spectrum of **1** correspond to the electron transitions between *d* orbitals split in a ligand field of C$_{2v}$ symmetry. The band at 26 180 cm^{-1} is a result of two transitions: $d_{xy} \rightarrow \pi^*_{NO}$ and $d_{xy} \rightarrow d_{x^2-y^2}$. The band at 36 360 cm^{-1} is a *charge transfer* transition as it corresponds to transition of π^{b}_{Re-Cl} electrons to the suitable *d* orbitals of rhenium. The band of the highest energy is a result of an electronic transition in the

Table 4
Infrared spectral data for **1** and **2**

Band position (cm^{-1})		Assignment
[ReCl$_3$(NO)(PPh$_3$)$_2$]	[ReCl$_2$(CO)(NO)(PPh$_3$)$_2$]	
	1990	ν(CO)
1734	1722	ν(NO)
1431	1433	ν(P–C$_6$H$_5$)
1482	1479	δ(C–CH in the plane)
1093	1093 and 1026	δ(C–H in the plane)
750 and 725	746	δ(C–C out of the plane)
690	694	δ(C–C in the plane)
534	524	ν(Re–N)

Table 5
Band positions, molar absorption coefficients and assignments for **1** and **2**

$[ReCl_3(NO)(PPh_3)_2]$			$[ReCl_2(CO)(NO)(PPh_3)_2]$		
Band positions (cm^{-1})	Molar absorption coefficients ($dm^3\ mol^{-1}\ cm^{-1}$)	Assignments	Band position (cm^{-1})	Molar absorption coefficient ($dm^3\ mol^{-1}\ cm^{-1}$)	Assignment
15 040	34	$d_{xy} \rightarrow d_{yz}$	14 700	10	$d_{yz} \rightarrow d_{x^2-y^2}$ $d_{yz} \rightarrow \pi^*_{NO}$ [a]
18 760	2800	$d_{xy} \rightarrow d_{xz}$	15 385	13	$d_{xy} \rightarrow d_{xz}$
26 180	3920	$d_{xy} \rightarrow \pi^*_{NO}$ $d_{xy} \rightarrow d_{x^2-y^2}$	36 365	7360	$d_{xy} \rightarrow d_{x^2-y^2}$ $d_{yz} \rightarrow d_{z^2}$ $d_{xy} \rightarrow \pi^*_{NO}$
36 360	16 858	$\pi^{b}_{Re-Cl} \rightarrow d_{yz}$	38 460	16 453	$d_{xy} \rightarrow \pi^*_{CO}$ $d_{yz} \rightarrow d_{z^2}$
41 220	17 220	$\pi^{b}_{C_6H_5} \rightarrow 3d_{fosfor}$	41 670	18 123	$\pi^{b}_{C6H5} \rightarrow 3d_{fosfor}$

[a] Transition forbidden because of symmetry.

phosphine ligand molecule. Based on the data in Table 5, the values of the ligand field parameters Dq, Ds and Dt have been defined and the energies of molecular orbitals for **1** have been estimated. The values of ligand field parameters are shown in Table 6; Fig. 3 presents a simplified molecular orbital (MO) diagram for complex **1**.

A relatively high π^*_{NO} energy level has also been defined by other authors [56].

In the nitrosyl complex, the Re ion is present in the +2 oxidation state, and its electronic configuration, considering splitting of *d* orbitals in C_{2v} symmetry, is as follows: $(d_{xy})^2(d_{yz})^2(d_{xz})^1$.

3.4. Spectroscopic characterisation of the $[ReCl_2(CO)(NO)(PPh_3)_2]$ complex

Table 4 contains the assignments of characteristic bands in the IR range for **2** [55]. Strong bands corresponding to the stretching vibrations of nitrosyl and carbonyl groups appear at 1722 and 1990 cm^{-1}, respectively.

$[ReCl_2(CO)(NO)(PPh_3)_2]$ is a diamagnetic compound.

The positions and molar absorption coefficients of electronic bands for **2** and the electronic transitions assigned to the bands are shown in Table 5. Transition of d_{yz} electrons to π^*_{NO}, which is partially responsible for the origination of the smallest energy band, is forbidden because of symmetry. This fact explains why the intensity of the band is so low. The next absorption band in the electronic spectrum of **2** corresponds to the electron transitions between *d* orbitals split in a ligand field of C_2 symmetry. Its intensity is typical for *d*–*d* transitions. The relatively high intensity of the bands at 36 365 and 38 460 cm^{-1} results from a partial contribution of the transitions $d_{xy} \rightarrow \pi^*_{NO}$ and $d_{xy} \rightarrow \pi^*_{CO}$, respectively. The band of the highest energy is a result of an electronic transition in the phosphine ligand molecule. Based on the data of Table 5, the values of the ligand field parameters, Dq, Ds and Dt, have been defined and the energies of molecular orbitals for **2** have been estimated. The values of the ligand field parameters are shown in Table 6; Fig. 4 presents a simplified MO diagram for **2.**

In the nitrosyl complex, the Re ion is present in a +1 oxidation state, and its electronic configuration, considering splitting of *d* orbitals in C_2 symmetry, is as follows $(d_{xy})^2(d_{xz})^2(d_{yz})^2$.

4. Conclusion

In the light of the results presented above, the simplified synthesis of the rhenium compounds examined has a distinct advantage in comparison to previously used pre-

Table 6
Values of ligand field parameters for **1** and **2**

Ligand field parameter	Value (cm^{-1})	
	$[ReCl_3(NO)(PPh_3)_2]$	$[ReCl_2(CO)(NO)(PPh_3)_2]$
Dq	2617	3636
Ds	−5537	−5282
Dt	430	−93

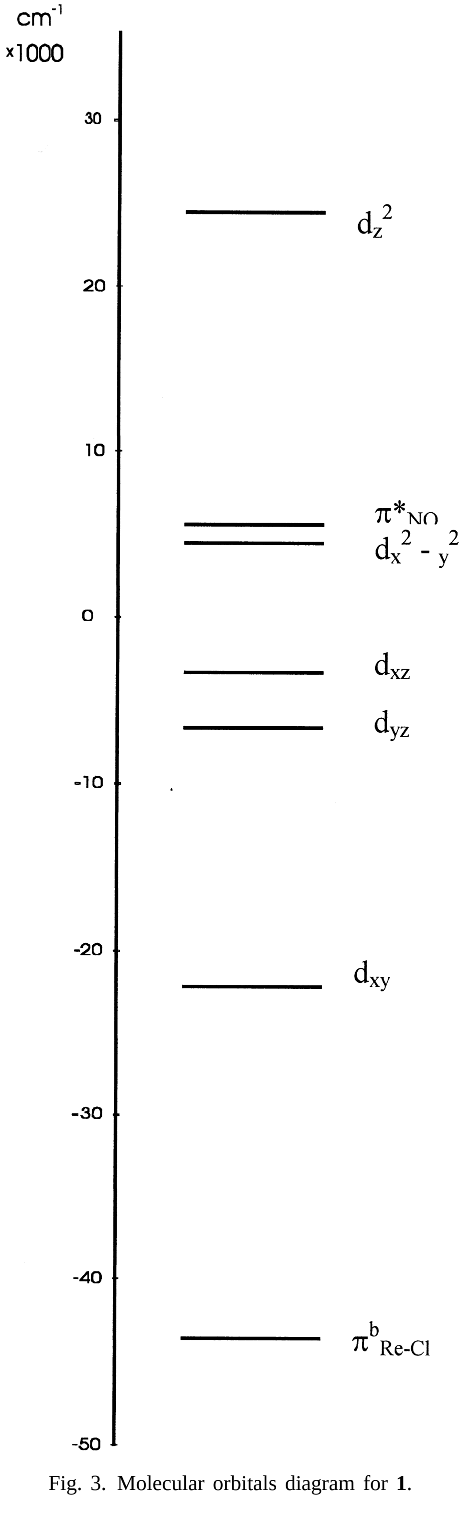

Fig. 3. Molecular orbitals diagram for **1**.

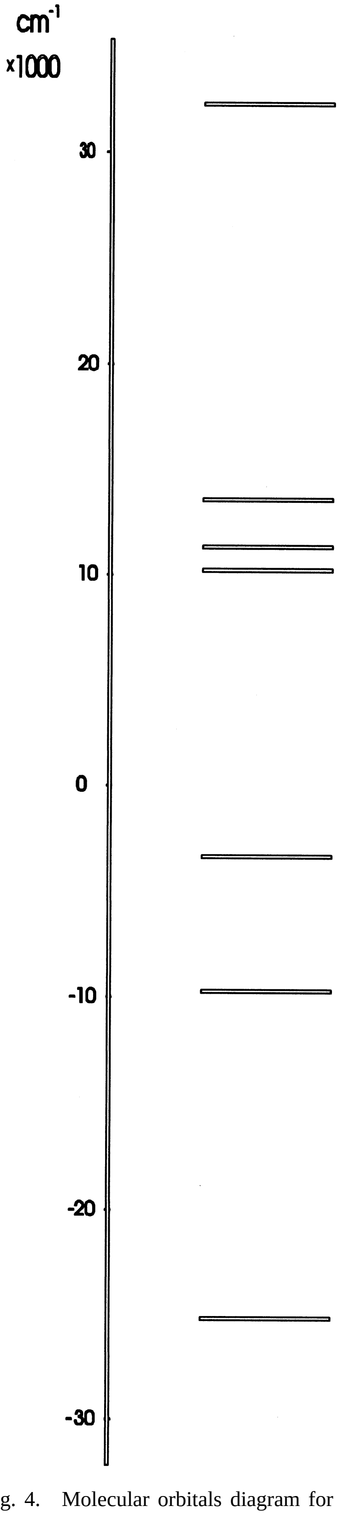

Fig. 4. Molecular orbitals diagram for **2**.

parative methods. It is less labour- and material-consuming and it provides a purer product with a comparable yield. The presented results also allowed for the determination of the crystal and electronic structures of [$ReCl_3(NO)(PPh_3)_2$] and [$ReCl_2(CO)(NO)(PPh_3)_2$], and their spectroscopic characteristics.

Supplementary data

Supplementary data for (**1**) are available from Fachinformationszentrum Karlsruhe (FIZ), Germany, on request, quoting the deposition number CSD 410525 and for (**2**) from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, quoting number 104993.

Acknowledgements

This work was supported financially by the Polish State Committee for Scientific Research (KBN), contract no. PB 1218/T09/97/12, which is gratefully acknowledged.

References

[1] N.G. Connelly, Inorg. Chim. Acta Rev. 6 (1972) 47.
[2] K.G. Caulton, Coord. Chem. Rev. 14 (1975) 317.
[3] W.L. Gladfelter, Adv. Organomet. Chem. 24 (1985) 41.
[4] D.E. Wigley, R.A. Walton, Organometallics 1 (1982) 1323.
[5] R.G. Bhattacharyya, A.M. Saha, Inorg. Chim. Acta 77 (1984) L81.
[6] A.R. Middleton, G. Wilkinson, J. Chem. Soc., Dalton Trans. (1981) 1898.
[7] B. Hussain-Bates, M.B. Hursthouse, Polyhedron 9 (1990) 2081.
[8] B.S. McGilligan, J. Arnold, G. Wilkinson, B. Hussain-Bates, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1990) 2465.
[9] S. Rakshit, B.K. Sen, P. Bandyopadhyay, Z. Anorg. Allg. Chem. 401 (1973) 212.
[10] D. Giusto, G. Cova, Gazz. Chim. Ital. 102 (1972) 265.
[11] D.K. Hait, B.K. Sen, P. Bandyopadhyay, P.B. Sarkar, Z. Anorg. Allg. Chem. 387 (1972) 265.
[12] D.K. Hait, B.K. Sen, P. Bandyopadhyay, Z. Anorg. Allg. Chem. 388 (1972) 189.
[13] C.M.T. Hayward, J.P. Folkers, J.R. Shapley, Inorg. Chem. 27 (1988) 3685.
[14] A.T. Patton, C.E. Strouse, C.B. Knobler, J.A. Gladysz, J. Am. Chem. Soc. 105 (1983) 5804.
[15] B.W. Hames, B.W.S. Kolthammer, P. Legzdins, Inorg. Chem. 20 (1981) 650.
[16] F. Zingales, A. Trovali, F. Cariati, P. Uguagliati, Inorg. Chem. 10 (1971) 507.
[17] G. Monica, M. Freni, S. Cenini, J. Organomet. Chem. 71 (1974) 57.
[18] R. Colton, R.D. Peacock, G. Wilkinson, J. Chem. Soc. (1960) 1375.
[19] M. Freni, D. Giusto, V. Valenti, Gazz. Chim. Ital. 94 (1964) 797.
[20] J.A. Casey, R.K. Murmann, J. Am. Chem. Soc. 92 (1970) 78.
[21] N. Mronga, U. Müller, K. Dehnicke, Z. Anorg. Allg. Chem. 482 (1981) 95.
[22] R. Bhattacharyya, J. Chem. Soc., Dalton Trans. (1988) 794.
[23] G.B. Richter-Addo, P. Legzdins, Metal Nitrosyls, Oxford University Press, Oxford, 1992.
[24] T. Moeller, J. Chem. Educ. (1946) 542.
[25] J.B. Raynor, Inorg. Chim. Acta 6 (1972) 347.
[26] W.P. Griffith, J. Lewis, G. Wilkinson, J. Inorg. Nucl. Chem. 7 (1958) 38.
[27] J. Lewis, R.J. Irving, G. Wilkinson, J. Inorg. Nucl. Chem. 7 (1958) 32.
[28] T. Beringhelli, G. Ciani, G. D'Alfonso, H. Molinari, A. Sironi, M. Freni, J. Chem. Soc., Chem. Commun. (1984) 1327.
[29] E.A. Zuech, J. Chem. Soc., Chem. Commun. (1968) 1182.
[30] W.B. Hughes, J. Am. Chem. Soc. 92 (1970) 532.
[31] R.H. Grubbs, C.R. Hoppin, J. Chem. Soc., Chem. Commun. (1977) 634.
[32] M. Leconte, Y.B. Taarit, J.L. Bilhou, J.M. Basset, J. Mol. Catal. 8 (1980) 263.
[33] A. Sen, Acc. Chem. Res. 21 (1988) 421.
[34] D. Ballivet-Tkatchenko, C. Bremard, J. Chem. Soc., Dalton Trans (1983) 1143.
[35] D. Ballivet-Tkatchenko, C. Esselin, J. Goulon, J. Phys. C8 (1986) 343.
[36] P. Legzdins, B. Wassink, F.W.P. Einstein, A.C. Willis, J. Am. Chem. Soc. 108 (1986) 317.
[37] J.O. Dzięgielewski, K. Filipek, B. Machura, Polyhedron 14 (1995) 555.
[38] J.O. Dzięgielewski, B. Machura, J. Marek, Polyhedron 15 (1996) 3713.
[39] T.J. Bartczak, W. Czurak, J.O. Dzięgielewski, B. Machura, Polish J. Chem. 72 (1998) 633.
[40] J.O. Dzięgielewski, T. Bartczak, B. Machura, W. Czurak, Polish J. Chem. 72 (1998) 1009.
[41] J.O. Dzięgielewski, B. Machura, T. Bartczak, W. Czurak, J. Kusz, J. Warczewski, unpublished results.
[42] T.S. Cameron, K.R. Grundy, K.N. Robertson, Inorg. Chem. 21 (1982) 4149.
[43] J.Y. Chen, K.R. Grundy, K.N. Robertson, Can. J. Chem. 67 (1989) 1187.
[44] K.L. Leighton, K.R. Grundy, K.N. Robertson, J. Organomet. Chem. 371 (1989) 321.
[45] D. Giusto, G. Ciani, M. Manassero, J. Organomet. Chem. 105 (1976) 91.
[46] G. Ciani, D. Giusto, M. Manassero, A. Albinati, J. Chem. Soc., Dalton Trans. (1976) 1943.
[47] R.W. Adams, J. Chatt, N.E. Hooper, G.J. Leigh, J. Chem. Soc., Dalton Trans. (1974) 1075.
[48] G. Ciani, D. Giusto, M. Manassero, M. Sansoni, J. Chem. Soc., Dalton Trans. (1975) 2157.
[49] D. Giusto, G. Cova, Gazz. Chim. Ital. 102 (1972) 265.
[50] T.S. Cameron, K.R. Grundy, K.W. Robertson, Inorg. Chem. 21 (1982) 4149.
[51] G. Rouschias, G.J. Wilkinson, Chem. Soc. A (1966) 465.
[52] G.M. Sheldrick, SHELXL97. Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Göttingen, 1997.
[53] G.M. Sheldrick, SHELXTL: release 4.1 for Siemens Crystallographic Research Systems, Siemens, Karlsruhe, Germany, 1990.
[54] G. Ciani, D. Giusto, M. Manassero, M. Sansoni, J. Chem. Soc., Dalton Trans. (1978) 798.
[55] J.O. Dziêgielewski, B. Jeżowska-Trzebiatowska, R. Gil-Bortnowska, R. Grzybek, Polyhedron 5 (1986) 833.
[56] D. Wester, R.C. Edwards, D.H. Busch, Inorg. Chem. 16 (1977) 1055.
[57] N.P. Johnson, C.J.L. Lock, G. Wilkinson, J. Chem. Soc. (1964) 1054.
[58] K.W. Muir, R. Walker, Acta Crystallogr., Sect. A (1975) S132.
[59] Wyckoff letter *e*, site symmetry 2, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, Vol. C, Kluwer Academic Publishers, Dodrecht, 1992, p. 183.