

# New Rhenium(V) Nitrofuryl Semicarbazone Complexes. Crystal Structure of [ReOCl<sub>2</sub>(PPh<sub>3</sub>)(3-(5-Nitrofuryl)acroleine semicarbazone)]

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**Abstract** The synthesis and characterization of the first two Re complexes with semicarbazone ligands is presented. Selected ligands are 5-Nitro-2-furaldehyde semicarbazone (Nitrofurazone) (**L1**) and its derivative 3-(5-Nitrofuryl)acroleine semicarbazone (**L2**). Complexes of general formula [Re<sup>VO</sup>Cl<sub>2</sub>(PPh<sub>3</sub>)L], where **L** = **L1** and **L2**, were prepared in good yields and high purity by reaction of [Re<sup>VO</sup>Cl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] with **L** in ethanol or methanol solutions. The complexes formula and molecular structures were supported by elemental analyses and electronic, FTIR, <sup>1</sup>H-, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopies. In addition, the crystal and molecular structure of [Re<sup>VO</sup>Cl<sub>2</sub>(PPh<sub>3</sub>)**L2**] was determined by X-ray diffraction methods.

[ReOCl<sub>2</sub>(PPh<sub>3</sub>)(3-(5-Nitrofuryl)acroleine semicarbazone)] crystallizes in the space group P-1 with a = 11.2334(2), b = 11.3040(2), c = 12.5040(2) Å, α = 81.861(1), β = 63.555(1), γ = 83.626(1)°, and Z = 2. The Re(V) ion is in a distorted octahedral environment, equatorially coordinated to a deprotonated semicarbazone molecule acting as a bidentate ligand through its carbonylic oxygen and azomethinic nitrogen atoms, to an oxo ligand and a chlorine atom. The six-fold coordination is completed by another chlorine atom and a triphenylphosphine ligand at the axial positions.

**Keywords:** Rhenium; 5-Nitrofurylsemicarbazone complexes

## Neue Rhenium(V)-Nitrofuryl-semicarbazon-Komplexe. Kristallstruktur von [ReOCl<sub>2</sub>(PPh<sub>3</sub>){3-(5-Nitrofuryl)acrolein-semibarbazon}]

**Inhaltsübersicht.** Die Synthese und die Charakterisierung der ersten beiden Re-Komplexe mit Semicarbazon-Liganden wird beschrieben. Die ausgewählten Liganden sind 5-Nitro-2-furaldehyd-semicarbazon (Nitrofurazon) (**L1**) und sein Derivat 3-(5-Nitrofuryl)acrolein-semicarbazon (**L2**). Die Komplexe der allgemeinen Formel [Re<sup>VO</sup>Cl<sub>2</sub>(PPh<sub>3</sub>)L] mit **L** = **L1** und **L2** wurden in guten Ausbeuten und hoher Reinheit durch Reaktion von [Re<sup>VO</sup>Cl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] mit **L** in Ethanol- oder Methanollösungen hergestellt. Die Komplexformeln und die Molekülstrukturen werden durch Elementaranalysen und Elektronen-FTIR-, <sup>1</sup>H-, <sup>13</sup>C- und <sup>31</sup>P-NMR-Spektroskopie gestützt. Zusätzlich wird die Kristall- und Molekülstruktur von

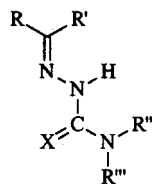
[Re<sup>VO</sup>Cl<sub>2</sub>(PPh<sub>3</sub>)**L2**] durch Röntgenmethoden ermittelt. [ReOCl<sub>2</sub>(PPh<sub>3</sub>){3-(5-Nitrofuryl)acrolein-semicarbazon}] kristallisiert in der Raumgruppe P $\bar{1}$  mit a = 11,2334(2); b = 11,3040(2); c = 12,5040(2) Å; α = 81,861(1); β = 63,555(1); γ = 83,626(1)° und Z = 2. Das Rheniumatom befindet sich in verzerrt oktaedrischer Umgebung, es ist äquatorial durch den deprotonierten, als zwei-zählig fungierenden Semicarbazon-Liganden mittels des Carbonylsauerstoffatoms und des Azomethin-Stickstoffatoms koordiniert sowie durch den Oxo- und einen Chloroliganden. Die Sechsfachkoordination wird durch ein weiteres Chloratom und durch den Triphenylphosphin-Liganden in den Axialpositionen ergänzt.

### Introduction

Semicarbazones and thiosemicarbazones have shown a wide range of biological activities. (Figure 1) [1–7]. Some metal thiosemicarbazone complexes have been recently developed as potential bioreductive prodrugs for the selective

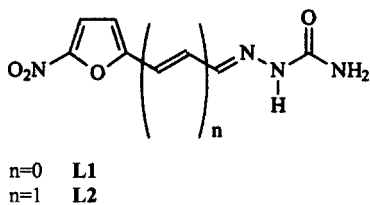
delivery of the metal or the ligand drug in hypoxic solid tumor cells, or for the delivery of a radionuclide for imaging or therapy of cancer [8]. In particular, much effort has been devoted to the development of new <sup>188/186</sup>Re complexes for cancer cytotoxic therapy by selective targeting of these β-emitting radionuclides to the cancer cells and on the application of complexes of the gamma emitting radionuclide <sup>99m</sup>Tc for the imaging, and hence diagnosis, of tumor diseases [9]. The application of rhenium compounds in treatment of cancer has reached a relatively advanced state with compounds in various stages of development ranging from preliminary chemistry to clinical trials and licensed drugs

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R, R', R'', R''' = H or alkyl or aryl group

**Figure 1** General formula of semicarbazones (X = O) and thiosemicarbazones (X = S).



**Figure 2** Ligand formula

[10]. Among the new non radioactive Re complexes, only a very scarce number of Re<sup>I</sup>, Re<sup>III</sup>, and Re<sup>V</sup> complexes with thiosemicarbazone ligands have been prepared [8, 11, 12].

To the best of our knowledge no examples of rhenium complexes with semicarbazone ligands have been yet reported in the literature. So, we decided to investigate the rhenium chemistry of these ligand systems as part of a project dealing with the complexation of 5-nitrofuryl semicarbazones which are bioactive against cancer and Chagas disease [3, 13, 14].

In this work, the synthesis and characterization of the first two Re complexes with semicarbazone ligands is presented. Selected ligands are 5-Nitro-2-furaldehyde semicarbazone (Nitrofurazone) (**L1**) and its derivative 3-(5-Nitrofuryl)acroleine semicarbazone (**L2**). Ligand formula are depicted in Figure 2. Novel complexes of general formulae [Re<sup>V</sup>OCl<sub>2</sub>(PPh<sub>3</sub>)L], where PPh<sub>3</sub> = triphenylphosphine and L = **L1** or **L2**, were prepared and characterized.

## Results and Discussion

Two novel Re<sup>V</sup> 5-nitrofurylsemicarbazone complexes were synthesized and characterized. Complexes of general formula [Re<sup>V</sup>OCl<sub>2</sub>(PPh<sub>3</sub>)L], (**ReL1** and **ReL2**), were prepared from [Re<sup>V</sup>OCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] in good yields and high purity.

Significant vibration bands of the ligands and their metal complexes, useful for determining the ligands mode of coordination,

**Table 1** Selected vibration bands / cm<sup>-1</sup> of the free ligands and their Re complexes

Compound	v(CO)	v(C=N)	v <sub>s</sub> (NO <sub>2</sub> )	v(P-phenyl)	v(ReO)
L1	1716	1583	1350	–	–
L2	1696	1585	1351	–	–
ReL1	1634	1500	1353	1098	971
ReL2	1633	1530	1350	1095	974

v: stretching; s: symmetric

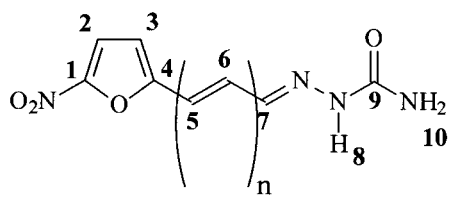
could be tentatively assigned and they are given in Table 1.

Upon coordination, the v(CO) and the v(C=N) bands of the free semicarbazones, at *ca.* 1700 cm<sup>-1</sup> and *ca.* 1580 cm<sup>-1</sup>, respectively, shift to lower frequencies. These modifications are consistent with bidentate coordination of the semicarbazone ligands through the carbonylic oxygen and the azomethynic nitrogen atoms. v(CO) also decreases as a result of the deprotonation of the ligands due to coordination. In addition, near 1350 cm<sup>-1</sup>, the v<sub>s</sub>(NO<sub>2</sub>) band is detected. The observed ReO stretching frequency lies in the middle of the common reported range for other hexacoordinated Re monoxo complexes (*ca.* 930–1000 cm<sup>-1</sup>) [15]. The v(NH) band at *ca.* 3120–3150 cm<sup>-1</sup> is absent in both complexes, suggesting that, in the solid state, the ligand is deprotonated. The medium strong P-phenyl stretching vibrations at *ca.* 1092 cm<sup>-1</sup>, characteristic of the triphenylphosphine ligand is also observed [16,17]. As previously described, this vibration is not greatly affected by coordination [18]. New bands in the low frequency region can be tentatively assigned to Re-ligand vibrations.

NMR experiments show narrow signals, typical for Re<sup>V</sup> diamagnetic complexes. HETCOR experiments allowed to assign all the signals of the free ligands and the investigated complexes. <sup>1</sup>H NMR integrations and signal multiplicities are in agreement with the proposed formula (Table 2). The attached figure shows the numbering scheme of the free ligands mentioned in the Table 2 and in the text.

The two complexes show similar <sup>1</sup>H and <sup>13</sup>C chemical shifts of the nitrofurylsemicarbazone common portion of their molecules. The chemical shift differences between each complex and the corresponding ligand, expressed as Δδ, are shown in Table 2. When the ligand is coordinated, the deshielding effect of the metal atom is apparent in some protons, causing a downfield shifting of the corresponding <sup>1</sup>H NMR peaks, including those of the triphenylphosphine ligand (free triphenylphosphine δ-H = 7.30 ppm) [15]. Furthermore, in the complexes, largest Δδ are observed for the protons that are located close to the coordinating atoms (azomethynic nitrogen and carbonylic oxygen atom), i.e. protons 6 (complex **ReL2**), and 10 (both complexes).

Upon coordination, the most distinguishing feature of the <sup>1</sup>H NMR spectra is the change in the chemical shifts of the idylenic proton, numbered 7. In both complexes, the signal of proton 7 is significantly displaced (–1.00 ppm for **ReL1** and –0.77 ppm for **ReL2**). The electron delocalization process of the deprotonated ligand, shown in Fig-

**Table 2**  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shift values ( $\delta$ ) in ppm of L and  $[\text{Re}^{\text{V}}\text{OCl}_2(\text{PPh}_3)_n\text{L}]$ , with L = **L1** and **L2**, in  $\text{dms}\text{-}d_6$  at 303 K.


$^1\text{H}$ NMR	<b>L1</b> ( $n=0$ ) <sup>a)</sup>		<b>L2</b> ( $n=1$ ) <sup>b)</sup>		$\Delta\delta$ <sup>c)</sup>	
	$\delta_{\text{Ligand}}$	$\delta_{\text{Complex}}$	$\delta_{\text{Ligand}}$	$\delta_{\text{Complex}}$	$\Delta\delta_{\text{L1}}$	$\Delta\delta_{\text{L2}}$
<b>2</b>	7.75 (d <sup>d)</sup> )	7.98 (d)	7.71 (d)	7.82 (d)	0.23	0.11
<b>3</b>	7.21 (d)	7.36 (d)	6.99 (d)	6.89 (d)	0.15	-0.10
<b>5</b>	—	—	6.88 (d)	6.54 (d)	—	-0.34
<b>6</b>	—	—	6.98 (dd)	7.88 (dd)	—	0.90
<b>7</b>	7.80 (s)	6.80 (s)	7.69 (d)	6.92 (d)	-1.00	-0.77
<b>8</b>	10.76 (bs)	—	10.47 (bs)	—	—	—
<b>10</b>	6.57 (bs)	7.00 (bs)	6.40 (bs)	7.06 (bs)	0.43	0.66
<b>PPh<sub>3</sub></b> <sup>e)</sup>	—	7.41 (m, <i>Hortho</i> )	—	7.43 (m, <i>Hortho</i> )	0.11	0.13
	—	7.46 (m, <i>Hmeta</i> )	—	7.51 (m, <i>Hmeta</i> )	0.16	0.21
	—	7.57 (m, <i>Hpara</i> )	—	7.59 (m, <i>Hpara</i> )	0.27	0.29
	—	—	—	—	—	—

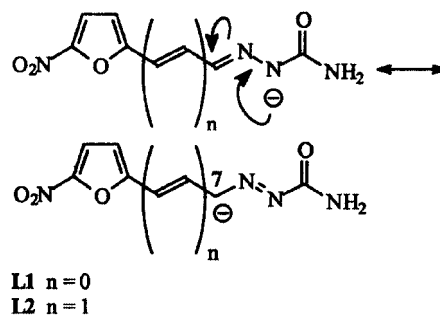
  

$^{13}\text{C}$ NMR	<b>L1</b> ( $n=0$ , R=H)		<b>L2</b> ( $n=1$ , R=H)		$\Delta\delta$ <sup>c)</sup>	
	$\delta_{\text{Ligand}}$	$\delta_{\text{Complex}}$	$\delta_{\text{Ligand}}$	$\delta_{\text{Complex}}$	$\Delta\delta_{\text{L1}}$	$\Delta\delta_{\text{L2}}$
<b>1</b>	152.00	152.46	152.05	153.42	0.46	1.37
<b>2</b>	115.95	114.48	116.35	115.52	-1.47	-0.83
<b>3</b>	112.80	121.96	113.78	117.51	9.16	3.73
<b>4</b>	154.00	147.85	156.04	153.28	-6.15	-2.76
<b>5</b>	—	—	121.53	126.88	—	5.35
<b>6</b>	—	—	131.67	121.27	—	-10.40
<b>7</b>	128.45	130.53	140.53	146.66	2.08	6.13
<b>9</b>	157.00	169.39	157.06	168.10	12.39	11.04
<b>PPh<sub>3</sub></b> <sup>d)</sup>	—	128.67 (C-P) <sup>e)</sup>	—	129.22 (C-P)	-8.53	-7.98
	—	129.93 ( <i>Cmeta</i> )	—	129.86 ( <i>Cmeta</i> )	1.53	1.46
	—	132.97 ( <i>Cpara</i> )	—	132.90 ( <i>Cpara</i> )	4.47	4.40
	—	134.42 ( <i>Cortho</i> )	—	134.50 ( <i>Cortho</i> )	0.82	0.90
	—	—	—	—	—	—

<sup>a)</sup> Integration: **ReL1**:  $\text{H}_2:\text{H}_3:\text{H}_7:\text{H}_{10}:\text{H}_{\text{PPh}_3} = 1:1:1:2:15$ ; <sup>b)</sup> Integration: **ReL2**:  $\text{H}_2:\text{H}_3:\text{H}_5:\text{H}_6:\text{H}_7:\text{H}_{10}:\text{H}_{\text{PPh}_3} = 1:1:1:1:1:2:15$ ; <sup>c)</sup>  $\Delta\delta = (\delta_{\text{Complex}} - \delta_{\text{Ligand}})$ ; <sup>d)</sup> multiplicity: d: doublet, s: singlet, dd: doublet doublet, bs: broad singlet; m: multiplet; <sup>e)</sup>  $\delta_{\text{H-PPh}_3} = 7.30$  (*Hortho*, *Hmeta*, *Hpara*) ppm; <sup>f)</sup>  $\delta_{\text{C-PPh}_3} = 137.20$  (C-P), 133.60 (*Cortho*), 128.50 (*Cpara*), 128.40 (*Cmeta*) ppm; <sup>g)</sup> from HETCOR experiments.

ure 3, could explain these results. Moreover, when these ligands are coordinated in the protonated form, a downfield shifting of the corresponding proton is observed [14].

Upon coordination, the most distinguishing feature of the  $^{13}\text{C}$  NMR spectra is the change in the chemical shifts of the carbon atoms numbered 1, 3, 7 and 9 (**ReL1**) and 1, 3, 5, 7 and 9 (**ReL2**). The electron attractive effect of the metal atom is observed in the mentioned carbon atoms. These could be explained through an electron delocalization

**Figure 3** Electron delocalization of the anionic ligand.

process (Figure 4) that would favor an increase in the electronic density of the coordinating atoms. This process would produce an electronic density decrease in the mentioned carbon atoms and hence a deshielding.

Even though the effect of coordination on the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts seems to be opposite and so the proposed electronic delocalization processes, it must be taken into account that the actual electronic distribution of the complexes depends not only on the semicarbazone ligand but also on the metal atom and other ligands' contributions.

$^{31}\text{P}$  NMR experiments show a signal at  $-9.47$  ppm for **ReL1** and at  $-11.49$  ppm for **ReL2**. The presence of a single signal in the  $^{31}\text{P}$  NMR experiments and the integrations observed in the  $^1\text{H}$  NMR experiments for the  $\text{PPh}_3$  protons agree with a 1:1 triphenylphosphine to L ratio, for both complexes. This fact is in agreement with the proposed formula for **ReL1**.

## Structural Results and Discussion

Intra-molecular bond distances and angles around the metal atom are shown in Table 3. Figure 5 is an ORTEP drawing of the molecule [20].

The X-ray diffraction study shows that the complex **ReL2** consists of a discrete monomeric molecule. The  $\text{Re}^{\text{V}}$  ion is in a distorted octahedral environment, coordinated to a 3-(5-Nitrofuryl)acroleine semicarbazone molecule which defines an equatorial plane and acts as a bidentate ligand through its azomethine nitrogen [ $d(\text{Re}-\text{N}3) = 2.132(3)$  Å] and carbonylic oxygen [ $d(\text{Re}-\text{O}1) = 2.037(2)$  Å] atoms. A  $\text{ReO}$  bond [ $d(\text{Re}-\text{O}2) = 1.673(3)$  Å], *trans* to the carbonylic oxygen atom, and a chlorine ligand [ $d(\text{Re}-\text{Cl}2) = 2.3411(9)$  Å] complete the equatorial coordination. The axial positions are occupied by another chlorine atom [ $d(\text{Re}-\text{Cl}1) = 2.3997(8)$  Å] and a triphenylphosphine ligand [ $d(\text{Re}-\text{P}) = 2.4586(9)$  Å]. The  $\text{ReO}$  distance lies within the normal range statistically established for this *core* in other octahedral monoxo complexes (weighted mean value 1.685 Å) [21]. This result is in agreement with the observed  $\text{ReO}$  stretching frequency previously discussed.

*Trans* ligand- $\text{Re}$ -ligand angles are  $(\text{N}3-\text{Re}-\text{Cl}2) = 159.68(9)^\circ$ ,  $(\text{O}2-\text{Re}-\text{O}1) = 162.8(1)^\circ$  and  $(\text{Cl}1-\text{Re}-\text{P}) = 174.68(3)^\circ$  and *cis* ligand- $\text{Re}$ -ligand angles vary in the range

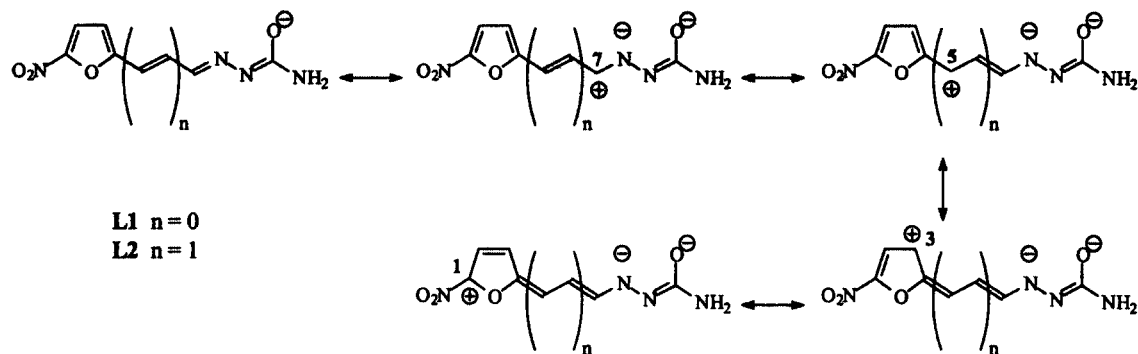


Figure 4 Electron delocalization that favours the ligand coordination form.

Table 3 Interatomic bond distances /Å and angles /° around rhenium in [ReOCl<sub>2</sub>(PPh<sub>3</sub>)(3-(5-Nitrofuryl)acroleine semicarbazone)]

Bond distances	
Re–O(2)	1.673(3)
Re–O(1)	2.037(2)
Re–N(3)	2.132(3)
Re–Cl(2)	2.3411(9)
Re–Cl(1)	2.3997(8)
Re–P	2.4586(9)
Bond angles	
O(2)–Re–O(1)	162.8(1)
O(2)–Re–N(3)	90.8(1)
O(1)–Re–N(3)	73.1(1)
O(2)–Re–Cl(2)	109.37(9)
O(1)–Re–Cl(2)	86.98(7)
N(3)–Re–Cl(2)	159.68(9)
O(2)–Re–Cl(1)	97.58(8)
O(1)–Re–Cl(1)	88.06(7)
N(3)–Re–Cl(1)	87.54(8)
Cl(2)–Re–Cl(1)	87.67(3)
O(2)–Re–P	87.61(8)
O(1)–Re–P	87.30(7)
N(3)–Re–P	93.59(8)
Cl(2)–Re–P	89.50(3)
Cl(1)–Re–P	174.68(3)

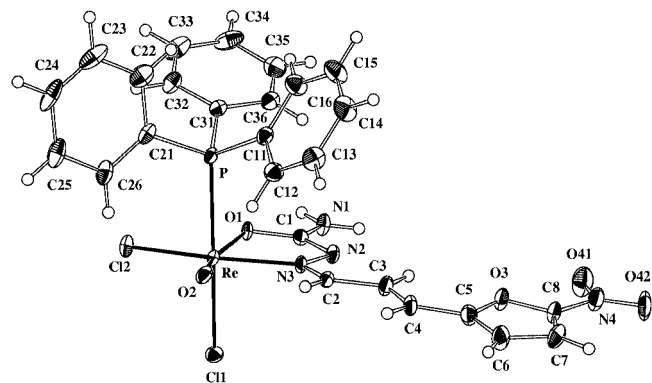


Figure 5 View of [ReOCl<sub>2</sub>(PPh<sub>3</sub>)(3-(5-Nitrofuryl)acroleine semicarbazone)] showing the labeling scheme of the non-H atoms and their displacement ellipsoids at the 50% probability level. Re–ligand bonds are indicated by full lines.

from 86.98(7) to 109.37(9)°. The 3-(5-Nitrofuryl)acroleine semicarbazone ligand is deprotonated. It is interesting to note that during the formation of the five-membered chelate ring, the semicarbazone ligand suffers a stereochemical change around the C=N bond, relative to the free ligand structure. So, although the free ligand exists as the isomeric form *E*, upon coordination the ligand adopts the isomeric form *Z* [14, 22, 23]. The semicarbazone ligand is nearly planar (rms deviation of ligand atoms from the least-squares plane equal to 0.077 Å) with the metal atom laying close to this plane (at 0.045 Å).

The complex is further stabilized by a pair of medium-strength intermolecular N–H···O bonds, involving the terminal NH<sub>2</sub> group of a given ligand molecule and the carbonylic oxygen atom [d(N1···O1') = 3.003 Å, (N1–H2N···O1') = 172.9°] and one of the nitro oxygen atom [d(N1···O42'') = 3.001 Å, (N1–H1N···O42'') = 156.7°] of neighboring ligand molecules.

## Experimental Part

All common laboratory chemicals were purchased from commercial sources and used without further purification. 5-Nitro-2-furaldehyde semicarbazone (Nitrofurazone) was commercially available. 3-(5-Nitrofuryl)acroleine semicarbazone and [Re<sup>V</sup>OCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] were prepared according to literature procedures [14,24].

### Syntheses of the complexes [Re<sup>V</sup>OCl<sub>2</sub>(PPh<sub>3</sub>)L]

[Re<sup>V</sup>OCl<sub>2</sub>(PPh<sub>3</sub>)L1]. [Re<sup>V</sup>OCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] (150 mg, 0.18 mmol) and L1 (73 mg, 0.37 mmol) were heated under reflux in 10 mL ethanol during 8 hours, after which a solid precipitated. The solid was filtered off and recrystallized from acetone / ethanol (10:1) by slow evaporation at room temperature. Yield: 65 mg, 49%. Anal. for [Re<sup>V</sup>OCl<sub>2</sub>(PPh<sub>3</sub>)L1] (732.2); C 40.0 (calc. 39.4); H 3.08 (2.75); N 7.34 (7.65)%. λ<sub>max</sub> (acetone): 331,4 nm.

[Re<sup>V</sup>OCl<sub>2</sub>(PPh<sub>3</sub>)L2]. [Re<sup>V</sup>OCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] (100 mg, 0.12 mmol) and L2 (40 mg, 0.20 mmol) were heated under reflux in 10 mL methanol during 24 hours, after which a solid precipitated. The solid was filtered off. Single brown crystals, suitable for X-ray analysis were obtained by slow evaporation at room temperature of an acetone solution. Yield: 45 mg, 33%. Anal. for [Re<sup>V</sup>OCl<sub>2</sub>(PPh<sub>3</sub>)L2] (758.2); C 41.6 (calc. 41.2); H 3.20 (2.87); N 7.39 (7.38)%. λ<sub>max</sub> (acetone): 332,4 nm.



**Characterization**

C, H, N and S analyses were performed with a Carlo Erba Model EA1108 elemental analyzer. FTIR spectra (4000–400 cm<sup>-1</sup> and 500–200 cm<sup>-1</sup>) of the complexes and the free ligands were measured either as KBr or CsI pellets with a Bomen FTIR model M102 instrument. Electronic spectra were recorded on a Spectronic 3000 spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the free ligands and of the complexes were recorded on a Bruker DPX-400 instrument (at 400 MHz and 100 MHz, respectively). Experiments were performed at 303 K in dmsO-d<sub>6</sub> (stability of the complex in such medium was previously stated). Heteronuclear correlation experiments (2D-HETCOR), HMQC (multiple quantum) and HMBC (multiple bond), were performed with the same instrument. <sup>31</sup>P NMR experiments for the complexes were performed on a Bruker Avance – 500 instrument at 303 K in dmsO-d<sub>6</sub> (at 202 MHz).

**Table 4** Crystal data and structure solution methods and refinement results for [ReOCl<sub>2</sub>(PPh<sub>3</sub>)(3-(5-Nitrofuryl)acroleine semicarbazone)]

Empirical formula	C <sub>26</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>5</sub> PRE
Formula weight	758.54
Temperature /K	120(2)
Low-temperature device	Oxford Cryosystems
Cooling rate	200 K/h
Crystal system	triclinic
Space group	P1
Unit cell dimensions <sup>a)</sup>	
a /Å	11.2334(2)
b /Å	11.3040(2)
c /Å	12.5040(2)
α /°	81.861(1)
β /°	63.555(1)
γ /°	83.626(1)
Volume/Å <sup>3</sup>	1405.26(4)
Z	2
Calculated density / (Mg/m <sup>3</sup> )	1.793
Absorption coefficient μ /mm <sup>-1</sup>	4.614
F(000)	740
Crystal size /mm <sup>3</sup>	0.10 x 0.05 x 0.02
Crystal color/shape	brown/prismatic
Diffraction/scan	KappaCCD/φ and ω
Radiation / graphite monochromator	MoKα /λ = 0.71073 Å
θ range for data collection	2.44 to 26.00°
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected/unique	19487/5520 [R(int) = 0.084]
Completeness	99.8% (to θ = 26.00°)
Reflections observed [I > 2σ(I)]	5170
Absorption correction	PLATON <sup>25</sup>
Max. and min. transm.	0.836 and 0.514
Data reduction and correction <sup>b)</sup> and structure solution <sup>c)</sup> and refinement <sup>d)</sup> programs	DENZO and SCALEPACK <sup>26</sup> SHELXS-97 <sup>27</sup> SHELXL-97 <sup>28</sup>
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Weights, w	[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> ) + (0.03P) <sup>2</sup> + 0.48P] <sup>-1</sup> P = [Max(F <sub>o</sub> <sup>2</sup> , 0) + 2F <sub>c</sub> <sup>2</sup> ]/3
Data/restraints/param.	5520/0/354
Goodness-of-fit on F <sup>2</sup>	1.050
Final R indices [I > 2σ(I)]	R1 = 0.0282, wR2 = 0.0698
R indices (all data) <sup>e)</sup>	R1 = 0.0309, wR2 = 0.0717
Largest peak and hole /e.Å <sup>-3</sup>	1.11 and -1.78

<sup>a)</sup> Least-squares refinement of the angular settings for 19487 reflections in the 2.44 < θ < 26.00° range.

<sup>b)</sup> Corrections: Lorentz, polarization and absorption.

<sup>c)</sup> Neutral scattering factors and anomalous dispersion corrections.

<sup>d)</sup> Structure solved by Patterson and Fourier methods. The final molecular model obtained by anisotropic full-matrix least-squares refinement of the non-hydrogen atoms.

<sup>e)</sup> R indices defined as:  $R1 = \sum |F_o| - |F_c| / \sum |F_o|$ ,  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^{1/2}]^{1/2}$

**X-ray diffraction data and crystal structure determination and refinement**

Crystal data, data collection procedure, structure determination methods and refinement results for **ReL2** are summarized in Table 4.

The hydrogen atoms were included in the molecular model at stereo chemical positions and refined with the riding model.

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**Supplementary material available:** Listings of full bond distances and angles (Table S4), atomic anisotropic thermal parameters (Table S5), hydrogen atoms positions (Table S6), and calculated and observed structure factor amplitudes (Table S7). Crystallographic data for [Re<sup>VO</sup>Cl<sub>2</sub>(PPh<sub>3</sub>)L2] have been deposited with the Cambridge Crystallographic Data Centre, CCDC 195159. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK (Fax: int code +(1223) 336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk)

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