

## The $(\text{NHEt}_3)[\text{Rh}(\text{C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2]$ complex: an example of the adverse counterion influence in the formation of metallic stacks

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### Abstract

The synthesis and complete characterisation of the chloroanilato anionic rhodium complexes  $(\text{NHEt}_3)[\text{Rh}(\text{C}_6\text{Cl}_2\text{O}_4)(\text{COD})]$  (**1**) and  $(\text{NHEt}_3)[\text{Rh}(\text{C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2]$  (**2**) are reported. In these complexes the chloroanilate dianion chelates the metal through the 1,2 oxygen atoms. The crystal structure of complex  $(\text{NHEt}_3)[\text{Rh}(\text{C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2]$  (**2**) reveals the adverse influence of the counterion in the formation of metal-columnar stacking. Although the molecules exhibit intermetallic interactions between the planar mononuclear units, the presence of secondary hydrogen bonding between  $\text{NHEt}_3^+$  and the anionic rhodium complexes prevents the formation of an infinite stacked structure. © 1999 Published by Elsevier Science S.A. All rights reserved.

**Keywords:** Metal complex stacks; Chloroanilato rhodium complexes; Three-centre hydrogen bond; Packing studies

The current interest devoted to stacked square-planar  $d^8\text{-ML}_4$  complexes and their partially oxidised derivatives is directly associated with the possibility of developing one-dimensional systems showing electrical conductivity [1–6].

Compounds possessing sterically undemanding and/or planar ligands would appear to be favourable to the formation of intermolecular metallic interactions. With this in mind, we have been engaged in the preparation of a variety of metal planar rhodium(I) complexes containing azolate [7,8], acetylacetonate [8–10] or anthraquinonate [11] type ligands. More recently, we have prepared a nearly linear metallic chain in the dithiocarbamate complex  $[\text{Rh}\{\text{S}_2\text{CN}(\text{Me})(\text{Ph})\}(\text{CO})_2]$ , showing short intermetallic distances ( $\text{Rh}\cdots\text{Rh}$  3.2528(7) Å) [12].

In an analogous manner to those neutral metal species, planar ionic complexes can also form stacked supramolecular structures [1–6]. However, the extension of these metallic stacks should be sensitive not only to the nature of the ligands but also to the presence of different counterions. Thus, depending on the bulkiness or on the chemical nature of a particular counterion, the potential formation of alternative intermolecular interactions could make difficult or even avoid

the development of the metallic stacks [13,14]. Furthermore, it has been shown by X-ray crystallography, that the  $[\text{Ir}_2\{\mu\text{-NH}(p\text{-tolyl})\}_2(\text{CO})_4]$  complex presents two polymorphs, one of them displaying an infinite linear array while, in the other, the dimer molecule exhibits short intermetallic contacts in a pairwise fashion [15].

We have previously explored the coordination capability of the chloroanilate dianion  $\text{C}_6\text{Cl}_2\text{O}_4^{2-}$  to induce the formation of metallic stacks. Due to its planarity together with its ability to chelate one or two metal centres through the 1,2 oxygen atoms of the *o*-quinone resonance form (Fig. 1(B)) or through the 1,2 and 4,5 oxygen atoms of the *p*-quinone resonance form (Fig. 1(C)), respectively, it could be a versatile anion for the preparation of mono- or binuclear potentially stacked metal complexes [16–19]. In particular, we have reported a family of neutral binuclear rhodium derivatives where the chloroanilate dianion is bridging both metal centres [19,20].

We now report the synthesis and complete characterisation of the anionic rhodium complexes  $(\text{NHEt}_3)[\text{Rh}(\text{C}_6\text{Cl}_2\text{O}_4)(\text{COD})]$  (**1**) and  $(\text{NHEt}_3)[\text{Rh}(\text{C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2]$  (**2**). In these complexes the chloroanilate dianion chelates the metal atom through the 1,2 oxygen atoms.

Thus, the anionic mononuclear complex  $(\text{NHEt}_3)[\text{Rh}(\text{C}_6\text{Cl}_2\text{O}_4)(\text{COD})]$  (**1**) has been prepared by reaction of

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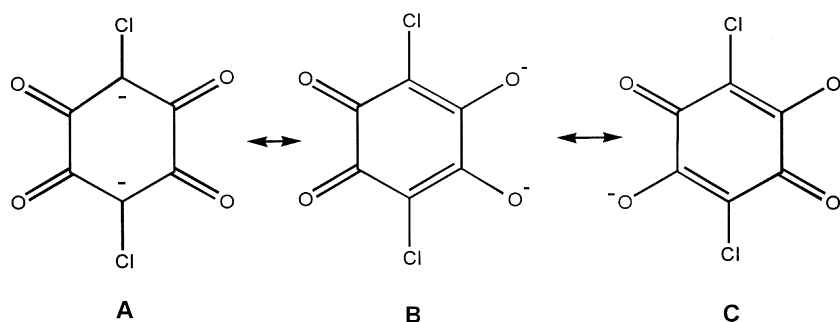


Fig. 1. Resonance forms of  $(C_6Cl_2O_4)^{2-}$ : (A) bis(carbanion), (B) *o*-quinone, (C) *p*-quinone.

$(NHEt_3)_2(C_6Cl_2O_4)$  (obtained by reaction of the chloroanilic acid,  $H_2C_6Cl_2O_4$ , and triethylamine) and the dinuclear compound  $[Rh_2(\mu-Cl)_2(COD)_2]$ , in a 2:1 molar ratio. Compound **1** has been fully characterised by elemental analysis, mass spectrometry and spectroscopic methods. The compound is air stable over long periods as a solid but decomposes rapidly in solution. The IR spectrum of compound **1** shows two strong  $\nu(C=O)$  absorptions at 1641 and  $1627\text{ cm}^{-1}$ . As carbonyl stretching frequencies above  $1600\text{ cm}^{-1}$  are normally associated with localised  $C=O$  groups, these values indicate that the *o*-quinone resonance form contributes significantly to the molecular structure of this mononuclear compound and, consequently, that the chloroanilate group chelates the rhodium centre through the 1,2 oxygen atoms [21].

Slow bubbling of carbon monoxide through a dichloromethane solution of the cyclooctadiene complex **1** rapidly causes the precipitation of fine dark blue dichroic needles. Unfortunately, no analytically pure compound could be isolated by this synthetic method. The carbonyl derivative  $(NHEt_3)[Rh(C_6Cl_2O_4)(CO)_2]$  (**2**) can be straightforwardly obtained as pure dark blue needles, suitable for X-ray diffraction studies, by reaction of  $(NHEt_3)_2(C_6Cl_2O_4)$  and the binuclear tetracarbonyl compound  $[Rh_2(\mu-Cl)_2(CO)_4]$  in a 2:1 molar ratio. In addition to the two  $\nu(C=O)$  bands due to the *o*-quinone form of the chloroanilate group ( $1649$  and  $1618\text{ cm}^{-1}$ ), the IR spectrum of compound **2**, in dichloromethane solutions, exhibits two absorptions of equal intensity typical of a *cis*-dicarbonyl geometry ( $\nu(C\equiv O)$   $2069$  and  $2007\text{ cm}^{-1}$ ). When the spectrum is recorded in the solid state drastic changes are observed in the broadness and intensity of the  $\nu(C\equiv O)$  bands. Furthermore, although the complex gives pale yellow solutions in organic solvents, in the solid state the crystals are dark coloured with a metallic lustre for reflected light. These features have been attributed to a lowering of the local symmetry upon close intermolecular contacts produced by metal–metal interactions [22]. This proposal has been investigated by an X-ray structural determination of complex **2**.

Two crystallographically independent, but geometrically analogous, cation–anion pairs are present in the crystal structure. The rhodium atom in the complex anion exhibits a square-planar coordination environment, with bonds to two

carbonyl groups and to two oxygen atoms of the chloroanilate ligand (Fig. 2). This planar ligand is almost coplanar with the metal coordination plane, with dihedral angles of  $1.21(6)$  and  $4.57(6)^\circ$  in both anions. The rhodium–oxygen bond distances (see Table 1) are significantly shorter than those observed in the related neutral rhodium compound  $[Rh_2(\mu-C_6Cl_2O_4)(COD)_2]$ ,  $2.100(9)$  and  $2.089(8)\text{ \AA}$  [20].

The parameters of the chloroanilate ligand evince an approximate  $C_{2v}$  symmetry and the internal bond distances are indicative of an *ortho*-quinone resonance form (mean bond distances:  $C(3)-C(4)$  and  $C(7)-C(8)$ ,  $1.377(5)$ ;  $C(4)-C(5)$  and  $C(6)-C(7)$ ,  $1.421(5)$ ;  $C(3)-C(8)$ ,  $1.511(5)$  and  $C(5)-C(6)$ ,  $1.559(5)\text{ \AA}$ ) (Fig. 2(a)). This bidentate–chelate coordination mode has been observed in other mononuclear complexes containing this ligand, such as  $[Pd(C_6Cl_2O_4)\{P(C_7H_7)_3\}_2]$  [23] and  $[FeCl(C_6Cl_2O_4)(H_2O)_3]$  [24].

Interestingly, each metal complex is hydrogen bonded to an  $NHEt_3^+$  cation through the non-coordinated oxygen atoms of the chloroanilate ligand and the aminic hydrogen of the

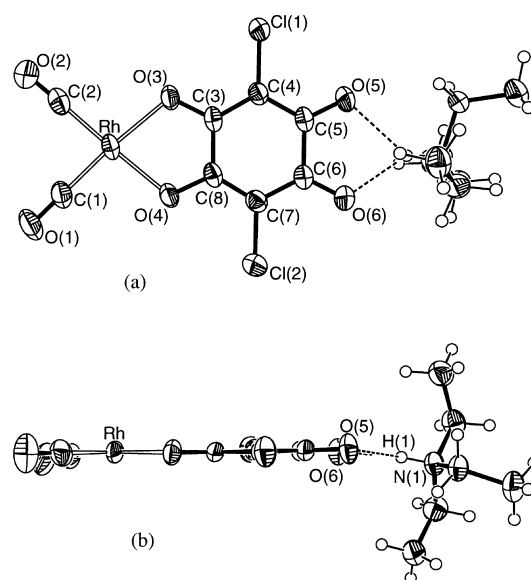


Fig. 2. Molecular representation of  $(NHEt_3)[Rh(C_6Cl_2O_4)(CO)_2]$  (**2**) including the labelling scheme used. The three-centred hydrogen bond between cation and anion is also shown in the drawing; (a) top view, (b) lateral view.

Table 1  
Selected bond lengths (Å), angles (°) and hydrogen bonds for  
(NHEt<sub>3</sub>)[Rh(C<sub>6</sub>Cl<sub>2</sub>O<sub>4</sub>)(CO)<sub>2</sub>] (2)<sup>a</sup>

Rh(1)–C(1)	1.829(4)	1.839(4)	
Rh(1)–C(2)	1.843(4)	1.842(4)	
Rh(1)–O(3)	2.066(2)	2.059(2)	
Rh(1)–O(4)	2.044(3)	2.045(2)	
Cl(1)–C(4)	1.736(4)	1.740(3)	
Cl(2)–C(7)	1.734(4)	1.733(3)	
O(1)–C(1)	1.143(5)	1.142(5)	
O(2)–C(2)	1.136(5)	1.136(5)	
O(3)–C(3)	1.296(4)	1.280(4)	
O(4)–C(8)	1.298(4)	1.294(4)	
O(5)–C(5)	1.231(4)	1.241(4)	
O(6)–C(6)	1.237(4)	1.230(4)	
C(1)–Rh(1)–C(2)	86.22(17)	87.68(17)	
C(1)–Rh(1)–O(3)	173.76(15)	175.88(14)	
C(1)–Rh(1)–O(4)	95.36(15)	96.85(14)	
C(2)–Rh(1)–O(3)	98.62(14)	95.42(13)	
C(2)–Rh(1)–O(4)	178.10(15)	175.40(13)	
O(3)–Rh(1)–O(4)	79.73(10)	80.01(9)	
Rh(1)–C(1)–O(1)	179.3(4)	179.5(4)	
Rh(1)–C(2)–O(2)	178.8(4)	177.1(4)	
Rh(1)–O(3)–C(3)	113.5(2)	113.9(2)	
Rh(1)–O(4)–C(8)	115.0(2)	114.1(2)	
N–H···O <sup>b</sup>	H···O	N···O	<NHO
N(1)–H(1)···O(5)	2.16	2.981(4)	135.6
	1.99	2.902(4)	146.1
N(1)–H(1)···O(6)	1.93	2.813(4)	142.4
	2.15	2.954(4)	133.3

<sup>a</sup> Second value for the second independent molecule.

<sup>b</sup> N–H bond distances had been normalised to 1.03 Å.

cation (Fig. 2). This is a good example of a bifurcated three-centred hydrogen bond as defined by Jeffrey [25]. The four atoms involved in each cation–anion couple (N(1), H(1), O(5) and O(6)) are approximately planar; the sum of the three angles around the hydrogen are 359.5(2) and 359.8(2)°. After normalisation of the N–H bonds (Table 1), the H···O separations together with the geometry around the oxygen atoms are in good agreement with those usually observed in N–H···O=C hydrogen bonds [26].

The planar anions are grouped by forming dimers and packed in a stepwise fashion (Fig. 3). The intermetallic separation in these dimers is 3.2130(6) Å, and the metal square-planar environments are almost parallel (dihedral angle

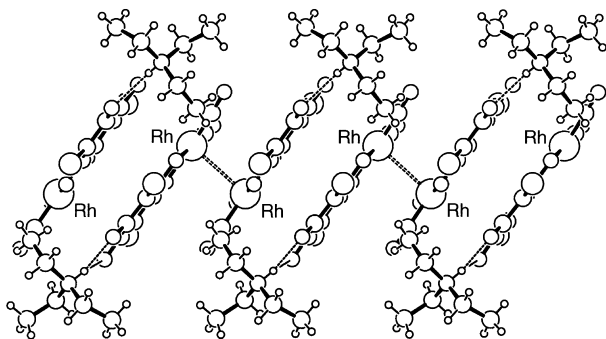


Fig. 3. Stepwise packing of 2 showing the intermetallic interactions.

5.60(10)°) with a staggered conformation (dihedral angle 123.8°), allowing the existence of metal–metal interactions [5].

It is interesting to note that despite the planarity of the anionic metallic complexes, it was not possible to obtain, in the solid state, a stacking arrangement through linear intermetallic interactions. In this case, the presence of secondary hydrogen bonds between anions and cations and their relative positions, as shown in Fig. 3, prevents a linear stacking of the metallic centres.

It should be expected that analogous complex (NMe<sub>4</sub>)-[Rh(C<sub>6</sub>Cl<sub>2</sub>O<sub>4</sub>)(CO)<sub>2</sub>] containing a counterion without aminic hydrogen atoms would allow the existence of supra-molecular networks with extensive stacking arrangement, as previously observed by Bayón and co-workers [6] for the related oxalato complex (NMe<sub>4</sub>)[Rh(C<sub>2</sub>O<sub>4</sub>)(CO)<sub>2</sub>]. However, although the spectroscopic data of the complex (NMe<sub>4</sub>)[Rh(C<sub>6</sub>Cl<sub>2</sub>O<sub>4</sub>)(CO)<sub>2</sub>] clearly indicate the existence of intermetallic interactions (see Experimental Section), all attempts to crystallise the suspected linear metallic chains have been so far unsuccessful.

In conclusion, the planarity of the chloroanilate ligand together with the feeble steric demand of the carbonyl groups and the square-planar coordination of the rhodium centre confer to the anionic metal complex [Rh(C<sub>6</sub>Cl<sub>2</sub>O<sub>4</sub>)(CO)<sub>2</sub>]<sup>−</sup> a reasonable molecular topology suitable for the formation of stacked arrangements with potential intermetallic interactions. However, the presence of NHEt<sub>3</sub><sup>+</sup> as a counterion in complex 2 leads to secondary hydrogen bonding preventing the formation of a linear metal–metal chain, although intermetallic interactions are observed between pairs of metallic planar units.

## Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were purified according to standard literature procedures and distilled under nitrogen prior to use. The chemicals were of reagent grade and were used without further purification. Standard literature procedures were used to prepare the starting material [Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(COD)<sub>2</sub>] [27] and [Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(CO)<sub>4</sub>] [28]. IR spectra were recorded on a Nicolet Magna 550 spectrometer. <sup>1</sup>H NMR spectra were carried out in CDCl<sub>3</sub> solutions at room temperature on a Varian XL 300 spectrometer. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser.

### X-ray structural determination of 2

A summary of the crystallographic data is reported in Table 2. Dark blue prismatic crystals suitable for X-ray were obtained from a CH<sub>2</sub>Cl<sub>2</sub>/pentane solution. Data were collected at 200 K on a Siemens P4 diffractometer, with graphite-monochromated Mo-Kα radiation (ω scans). Three standard

Table 2  
Crystallographic data for  $(\text{NHEt}_3)[\text{Rh}(\text{C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2]$  (**2**)

Chemical formula	$\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{NO}_6\text{Rh}$
FW	468.09
Crystal size (mm)	$0.28 \times 0.48 \times 0.48$
Crystal system, space group	monoclinic, $P2_1/n$ (No. 14)
$a$ (Å)	8.2628(8)
$b$ (Å)	17.6096(15)
$c$ (Å)	25.140(4)
$\beta$ (°)	98.256(10)
$V$ (Å <sup>3</sup> )	3620.1(5)
$Z$	8
$\rho$ (calc) (g cm <sup>-3</sup> )	1.718
$\mu$ (mm <sup>-1</sup> )	1.267
$\theta$ range data collection (°)	2.0–25.0 ( $-1 \leq h \leq 8$ , $-1 \leq k \leq 20$ , $-29 \leq l \leq 29$ )
Collected, unique reflections	8126, 6170 ( $R_{\text{int}} = 0.0255$ )
Transmission factors: max., min.	0.428, 0.494
Data/parameters	6170/437
$R(F)$ [ $F^2 > 2\sigma(F^2)$ ] <sup>a</sup>	0.0265
$wR(F^2)$ [all data] <sup>b</sup>	0.0747

<sup>a</sup>  $R(F) = \sum \|F_o| - |F_c|\| / \sum |F_o|$ , for 4949 observed reflections.

<sup>b</sup>  $wR(F^2) = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2])^{1/2}$ .

reflections were monitored every 97 measured reflections; no variations were observed. Data were corrected for Lorentz, polarisation and absorption effects ( $\psi$  scan, 12 reflections) [29]. The structure was solved by direct methods (SIR92) [30] and Fourier techniques, and refined by full-matrix least-squares on  $F^2$  (SHELXL-97) [31]. After refinement of all non-hydrogen atoms with anisotropic displacement parameters, hydrogen atoms were introduced in calculated positions and refined riding on the corresponding carbon or nitrogen atoms. Residual peaks in the final difference map were 0.47 and  $-0.40 \text{ e } \text{Å}^{-3}$ .

#### Preparation of $(\text{NHEt}_3)_2(\text{C}_6\text{Cl}_2\text{O}_4)$

A solution of  $\text{H}_2\text{C}_6\text{Cl}_2\text{O}_4$  (500 mg, 2.3 mmol) in acetone (15 ml) was treated with  $\text{NEt}_3$  (0.66 ml, 4.7 mmol). The colour of the resulting solution slowly changed from orange to red. After 1 h of stirring the solution was concentrated under reduced pressure to 1 ml. Addition of diethyl ether (20 ml) gave a red solid which was filtered off, washed with diethyl ether and dried under vacuum (yield 908 mg, 92%). *Anal.* Calc. for  $\text{C}_{18}\text{H}_{32}\text{Cl}_2\text{N}_2\text{O}_4$ : C, 52.55; H, 7.78; N, 6.81. Found: C, 52.50; H, 7.33; N, 6.70%. IR (cm<sup>-1</sup> nujol);  $\nu(\text{C}=\text{O})$  1590. <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  7.26 (m, Ph), 3.79 (s, Me), 3.19 (q,  $\text{CH}_2$ , ( $\text{NEt}_3$ ),  $J_{\text{H-H}} = 7.4 \text{ Hz}$ ), 1.32 (t,  $\text{CH}_3$ , ( $\text{NEt}_3$ ),  $J_{\text{H-H}} = 7.4 \text{ Hz}$ ).

#### Preparation of $(\text{NHEt}_3)[\text{Rh}(\text{C}_6\text{Cl}_2\text{O}_4)(\text{COD})]$ (**1**)

A solution of  $(\text{NHEt}_3)_2(\text{C}_6\text{Cl}_2\text{O}_4)$  (333 mg, 0.80 mmol) in methanol (5 ml) was added dropwise to a suspension of  $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$  (200 mg, 0.40 mmol) in methanol (10 ml). After 30 min of stirring, a brown solid was formed which was decanted, washed with diethyl ether and dried in

vacuum (yield 66%). *Anal.* Calc. for  $\text{C}_{20}\text{H}_{28}\text{Cl}_2\text{NO}_4\text{Rh}$ : C, 46.15; H, 5.38; N, 2.69. Found: C, 45.86; H, 5.00; N, 2.36%. FAB:  $m/z$  418 (calc. for  $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{O}_4\text{Rh}$ : 418.06). IR (cm<sup>-1</sup> nujol):  $\nu(\text{N-H})$  2721, 2657;  $\nu(\text{C}=\text{O})$  1641, 1627. <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  1.28 (m,  $\text{CH}_3$ ,  $\text{HNEt}_3$ ), 1.70 (d,  $\text{CH}_2$ , COD), 2.40 (m,  $\text{CH}_2$ , COD), 3.10 (m,  $\text{CH}_2$ ,  $\text{HNEt}_3$ ), 4.20 (s,  $\text{CH}=\text{COD}$ ).

#### Preparation of $(\text{NHEt}_3)[\text{Rh}(\text{C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2]$ (**2**)

A solution of  $(\text{NHEt}_3)_2(\text{C}_6\text{Cl}_2\text{O}_4)$  (422 mg, 1.02 mmol) in methanol (5 ml) was added dropwise to a suspension of  $[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4]$  (200 mg, 0.51 mmol) in methanol (10 ml). The resulting dark blue solution was stirred for 30 min. The evaporation of the solvent to 1 ml and addition of diethyl ether (5 ml) gave a dark blue solid which was separated by filtration. The compound was purified by recrystallisation from dichloromethane/diethyl ether (yield: 83%). *Anal.* Calc. for  $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{NO}_6\text{Rh}$ : C, 35.90; H, 3.41; N, 2.99. Found: C, 35.70; H, 3.60; N, 3.12%. FAB:  $m/z$  366 (calc. for  $\text{C}_8\text{Cl}_2\text{O}_6\text{Rh}$ : 365.89). IR (cm<sup>-1</sup>  $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{N-H})$  2666;  $\nu(\text{C}=\text{O})$  1649, 1618;  $\nu(\text{C}\equiv\text{O})$  2069, 2007.

#### Preparation of $(\text{NMe}_4)[\text{Rh}(\text{C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2]$

This complex was prepared similarly to compound **2**, starting from  $(\text{NMe}_4)_2(\text{C}_6\text{Cl}_2\text{O}_4)$  (362 mg, 1.02 mmol) and  $[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4]$  (200 mg, 0.51 mmol). The compound was isolated as a dark blue solid (yield 90%). *Anal.* Calc. for  $\text{C}_{12}\text{H}_{12}\text{Cl}_2\text{NO}_6\text{Rh}$ : C, 32.70; H, 2.70; N, 3.90. Found: C, 32.90; H, 2.60; N, 3.72%. FAB:  $m/z$  365 (calc. for  $\text{C}_8\text{Cl}_2\text{O}_6\text{Rh}$ : 365.89). IR (cm<sup>-1</sup>  $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{C}=\text{O})$  1672, 1618, 1540;  $\nu(\text{C}\equiv\text{O})$  2073, 2003.

### Supplementary material

X-ray data (cif file) for compound **2** have been deposited at the Cambridge Crystallographic Data Centre with registry number CCDC-132210.

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