

# Reactions of the rhenium fragment $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2$ with chlorinated ethylenes: Coordination and C–Cl bond activation

Rodrigo Arancibia<sup>a</sup>, Fernando Godoy<sup>a</sup>, María Teresa Garland<sup>b</sup>, Andrés Ibáñez<sup>b</sup>, Ricardo Baggio<sup>c</sup>, A. Hugo Klahn<sup>a,\*</sup>

<sup>a</sup> Instituto de Química, P. Universidad Católica de Valparaíso, Casilla 4059, Valparaíso, Chile

<sup>b</sup> CIMAT, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla, 653 Santiago, Chile

<sup>c</sup> Departamento de Física, Comisión Nacional de Energía Atómica, Argentina

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## Abstract

Photochemical reactions of the dinitrogen complex  $\text{Cp}^*\text{Re}(\text{CO})_2\text{N}_2$  with tetrachloroethylene and trichloroethylene yield the coordination complexes  $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-tetrachloroethylene})$  (**1**) and  $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-trichloroethylene})$  (**2**), respectively. Complex **1** reacts thermally in polar organic solvents to produce the C–Cl bond activation product *cis*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{C}_2\text{Cl}_3)\text{Cl}$  (**3**). All complexes were isolated and characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies and mass spectrometry. Complex **3** was also characterized by X-ray crystallography.

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**Keywords:** Coordination; Chloroethylenes; C–Cl bond activation; rhenium; Pentamethylcyclopentadienyl

## 1. Introduction

Tetrachloroethylene (perchloroethylene, PCE) and trichloroethylene (TCE), produced in large quantities and widely used in industrial applications, have received a great deal of attention because they are commonly found as soil and groundwater contaminants [1,2]. Many studies have been undertaken aimed at the dechlorination of these toxic compounds under stoichiometric [3–5] and catalytic [6,7] conditions.

From the stoichiometric point of view, there are several reports dealing with the reactions of low-valent metal complexes with halogenated ethylenes, in which chlorovinyl complexes are formed [5,8–10]. However, most of these reactions are limited to group 10 metals (Ni, Pd and Pt). More recently, cobaloxime complexes have been used as model to study the catalytic dehalogenation of chloroethylenes by vitamin B<sub>12</sub> and metalloporphyrins [11,12].

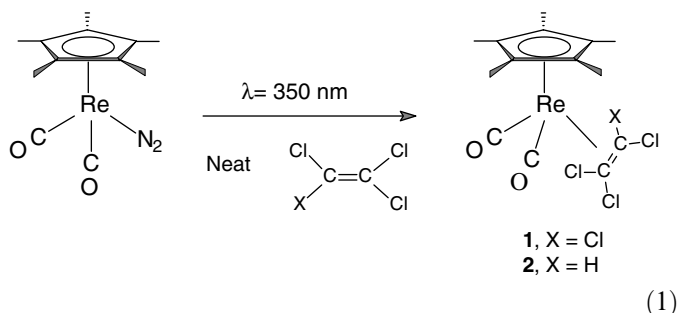
As a part of our continuing interest in the C–Cl bond activation of chlorinated aromatic molecules by rhenium organometallic complexes of the type  $\text{Cp}^*\text{Re}(\text{CO})_2\text{L}$  ( $\text{Cp}^* = (\eta^5\text{-C}_5\text{Me}_5)$ ,  $\text{L} = \text{CO}, \text{N}_2$ ) [13–16] in this paper we would like to report the photochemical reaction of the dinitrogen complex  $\text{Cp}^*\text{Re}(\text{CO})_2\text{N}_2$  with PCE and TCE from which the coordination products  $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-chloroethylene})$  could be isolated and characterized by spectroscopy. Thermal reaction of  $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-C}_2\text{Cl}_4)$  in organic solvents, involves an intramolecular C–Cl bond activation to yield the trichlorovinyl complex *cis*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{C}_2\text{Cl}_3)\text{Cl}$  isolated as an analytically and spectroscopically pure sample. Crystals of this compound allowed us to solve its X-ray structure.

## 2. Results and discussion

In previous reports we and others have demonstrated that the dinitrogen complexes  $\text{Cp}^*\text{Re}(\text{CO})(\text{L})\text{N}_2$  ( $\text{L} = \text{CO}$ , phosphines and phosphites) are useful photoprecursors to study the C–H, C–F and C–Cl bond activation of a series

\* Corresponding author. Tel.: +56 32 2273174; fax: +56 32 2273422.  
E-mail address: hklahn@ucv.cl (A. Hugo Klahn).

of partially halogenated arenes [17–19] as well as to achieve the coordination of olefins [20] and halogenated benzenes [19] to the rhenium centre. Now we have found that under similar experimental conditions to those previously used, such as short irradiation time (40 min), wavelength ( $\lambda = 350$  nm), and at room temperature, this complex in the presence of neat PCE or TCE produces the corresponding coordination complex, as shown in Eq. (1).

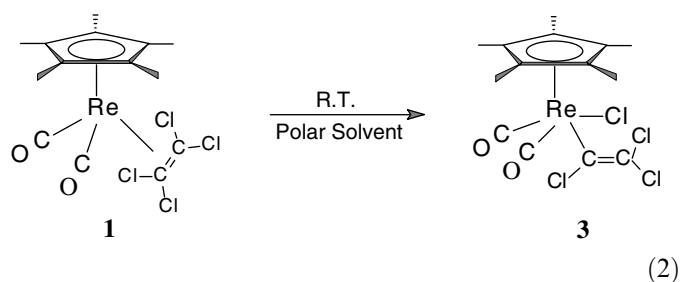


The reactions were easily monitored by IR spectroscopy and were stopped when the IR bands of the starting dinitrogen complex disappeared. Then vacuum evaporation of the chloroethylene from the reaction mixture, yield brown (from PCE) or brown–green (from TCE) solids. Since both products appeared not to be stable in solution of polar organic solvents (see below), we used hexane to extract them from the residual solids, even though, they are moderately soluble in this solvent. This feature may explain, in part, the low yield obtained in these reactions. From the cold concentrated hexane extracts, the complexes were obtained as white solids. Attempts to crystallize them from hexane solution at low temperature were unsuccessful; however, the precipitates exhibited clean IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra but they did not give satisfactory elemental analyses. These compounds are reasonably stable as solids under nitrogen atmosphere at  $-15$  °C, are moderately soluble in non-polar organic solvents such as hexane and benzene and are quite stable under nitrogen at low temperature in solution in dichloromethane or chloroform. The chloroethylene ligand in these complexes is not readily displaced by other ligands. A similar feature was noted for Cp [21] and  $\text{Cp}^*\text{Re}(\text{CO})_2(\text{alkene})$  [20] derivatives. For instance, there was no reaction of **1** and **2** with CO (1 atm) or  $\text{PMe}_3$  in hexane solution.

The IR spectra of complexes **1** and **2** in hexane, show two strong  $\nu(\text{CO})$  absorption bands at about 2020 and  $1950\text{ cm}^{-1}$ . These absorption bands are shifted to higher frequencies when compared with those reported for the ethylene complex  $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-C}_2\text{H}_4)$  ( $\nu(\text{CO})$  1964 and  $1894\text{ cm}^{-1}$ , in hexane) [20] suggesting that stronger d- $\pi$  back-bonding occurs between rhenium and the chlorinated ethylene. The same trend has been observed for the analogous ethene [22] and dibromoethene [23] pentamethylcyclopentadienyl manganese complexes. As expected the  $^1\text{H}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ , shows a single resonance for the protons of the  $\text{Cp}^*$  ligand, whereas the spectrum of **2**,

in addition to the singlet for the  $\text{Cp}^*$ , also exhibits a sharp singlet at  $\delta$  4.40 assigned to the coordinated TCE proton. Unfortunately, we were unable to find spectroscopic data for other complexes containing TCE coordinated in an  $\eta^2$  fashion. However, this resonance is shifted upfield when compare with free TCE, (from  $\delta$  6.42 in TCE to  $\delta$  4.38 in **2** both in  $\text{CDCl}_3$ ), following the same trend observed for coordinated and uncoordinated olefins [20,24]. Much clearer evidence for the coordination of chloroethylene ligands was obtained by  $^{13}\text{C}$  NMR. The spectrum of **1**, as expected, exhibited a single resonance at  $\delta$  58.3 for the two equivalent carbons, whereas complex **2** showed separated resonances for the two distinct carbon nuclei at  $\delta$  49.5 and 64.6. We assign the high field resonance, which is the more intense of the pair, to the carbon bearing the hydrogen by analogy with the  $^{13}\text{C}$  NMR data reported for mesityl oxide  $\eta^2$ -coordinated to the same rhenium fragment [24]. In the two cases the ethylenic carbon resonances are also shifted upfield compared to free PCE and TCE, respectively. The shift can be explained in term of the Dewar–Chatt–Duncanson model which involves a change in the hybridization of the olefinic carbon from  $\text{sp}^2$  in the free chloroethylene toward an  $\text{sp}^3$ -like carbon in bound chloroethylene [25].

As was mentioned above, complexes **1** and **2** at room temperature, are unstable in polar organic solvents, such as  $\text{CH}_2\text{Cl}_2$  and chloroform. At the present time, we have clear evidence that complex **1** undergoes an oxidative addition process in solution, to form the chlorovinyl-chloro derivative,  $\text{cis-Cp}^*\text{Re}(\text{CO})_2(\text{CCl}=\text{CCl}_2)\text{Cl}$  (**3**) (Eq. (2)).



The above reaction occurs in high yield within 24 h, at room temperature. A small amount of the dichloro complex  $\text{Cp}^*\text{Re}(\text{CO})_2\text{Cl}_2$  is also formed and it was separated by column chromatography in neutral alumina. Complex **3** was obtained as orange crystals, analytically pure, after crystallization from a mixture of  $\text{CH}_2\text{Cl}_2$ /hexane (1:2). By contrast with its precursor, this derivative is stable as a solid and in solution in polar organic solvents. The IR spectrum of **3** in dichloromethane, consists of two  $\nu(\text{CO})$  absorptions at 2033 and  $1961\text{ cm}^{-1}$ . The *cis* orientation of the carbonyl groups was preliminarily assigned on the basis of the relative intensities of the  $\nu(\text{CO})$ , since the higher wavenumber symmetric stretching mode ( $\nu_s$ ) is stronger than the lower wavenumber stretching mode ( $\nu_{as}$ ). A similar pattern of intensities has been observed in other dicarbonyl rhenium complexes possessing a four-legged piano-stool type of structure [13,26]. The appearance

of two resonances for the CO ligands in the  $^{13}\text{C}$  NMR spectrum is additional evidence for the *cis* stereochemistry in this type of molecule. Further confirmation of the lateral orientation of the two CO groups was obtained from an X-ray crystallographic study of **3** (see below).

Evidence for the presence of the trichlorovinyl ligand coordinated to the metal centre was obtained by  $^{13}\text{C}$  NMR. As expected, two resonances at  $\delta$  122.2 and 126.7 were observed and assigned to the terminal carbon and the carbon bound to rhenium, respectively. To confirm the above assignment we recorded the  $^{13}\text{C}$  NMR spectrum of PCE in  $\text{CDCl}_3$ . The only resonance observed occurs at  $\delta$  120.3, close to the one found for the terminal vinylic carbon. Similar assignments have been reported *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{CH}=\text{CHBr})\text{Br}$  [23] as far as we know, the only other vinyl-Re-halide complex described in literature.

The X-ray crystallographic structure of **3** (Fig. 1) confirms cleavage of the C–Cl bond of PCE. Table 1 reports the crystal structure and refinement data and Table 2 shows selected bond distances and angles. In complex **3** the rhenium atom can be considered seven-coordinated, with the  $\text{Cp}^*$  ligand as three-coordinated monoanion, and the overall geometry is comparable to a four-legged piano stool, which is consistent with a Re(III) oxidation state.

The whole assembly possesses onto a crystallographic symmetry plane which contains the metal center, the  $\text{C}_2\text{Cl}_3$  and one carbonyl group, and bisects the  $\text{Cp}^*$  ligand, thus rendering only half of the molecule crystallographically independent. The remaining carbonyl (C(1)–O(1)) and chloro (Cl(1)) groups appear disordered on both sides of the symmetry plane, sharing the same coordination site with a 50% occupancy each. This peculiar disposition suggested a possible overestimation of the local symmetry, but refinement in non-centrosymmetric space group *Pna2*<sub>1</sub>,

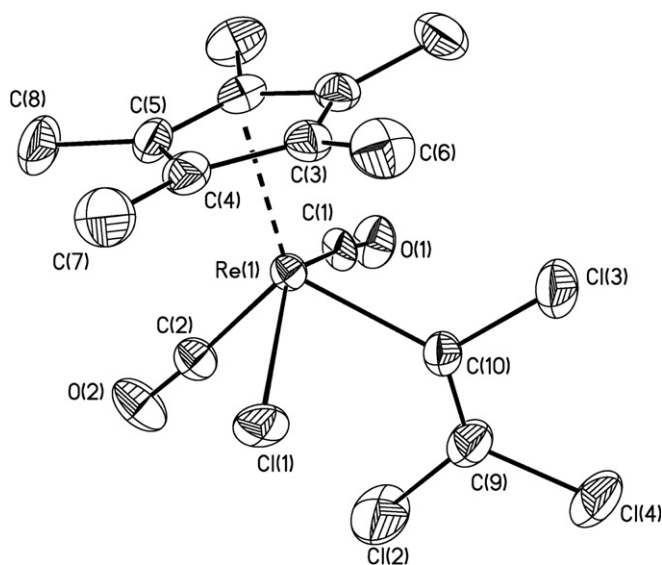


Fig. 1. X-ray structure of *cis*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{C}_2\text{Cl}_3)\text{Cl}$  (**3**) drawn with 40% probability displacement ellipsoids. The hydrogen atoms and disordered fragments have been omitted for clarity (the atomic numbering scheme is shown only in the independent part of the molecule).

Table 1

Crystal data and structure refinement for <i>cis</i> - $\text{Cp}^*\text{Re}(\text{CO})_2(\text{C}_2\text{Cl}_3)\text{Cl}$ ( <b>3</b> )	
Empirical formula	$\text{C}_{14}\text{H}_{15}\text{Cl}_4\text{O}_2\text{Re}$
Formula weight	543.26
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
Unit cell dimensions	$a = 17.4468(17)$ Å $b = 10.7924(11)$ Å $c = 9.1467(9)$ Å
Volume	$1722.3(3)$ Å <sup>3</sup>
Z	4
Density (calculated)	2.095 g/cm <sup>3</sup>
Absorption coefficient	7.675 mm <sup>-1</sup>
<i>F</i> (000)	1032
Crystal size	0.24 × 0.22 × 0.15 mm <sup>3</sup>
$\theta$ Range for data collection	2.33–28.07°
Index ranges	$-21 \leq h \leq 22$ , $-14 \leq k \leq 14$ , $-12 \leq l \leq 11$
Reflections collected	12103
Independent reflections	2094 [ <i>R</i> (int) = 0.0413]
Completeness to $\theta = 28.07^\circ$	94.8%
Absorption correction	Multi-scan
Maximum and minimum transmission	0.3923 and 0.2602
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	2094/0/126
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.843
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	$R_1 = 0.0231$ , $wR_2 = 0.0581$
<i>R</i> indices (all data)	$R_1 = 0.0312$ , $wR_2 = 0.0616$
Largest difference in peak and hole	0.938 and $-0.477$ e Å <sup>-3</sup>

which relaxes the imposed symmetry plane condition, was unsuccessful.

The Re– $\text{Cp}^*$ (centroid) distance of 1.979 Å and the inter-bond angle OC–Re–CO of 80.2° compare well with those determined for other dicarbonyl complexes possessing a *cis* arrangement of the carbonyl ligands [13,26]. The lack of reported Re–C(vinyl) bond distances for similar rhenium complexes precludes any comparison with the one found in **3** (2.148 Å). However, it is quite longer than those reported for  $\text{Ni}(\text{C}_2\text{Cl}_3)(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})(\text{PMe}_2\text{Ph})$ , (1.933 Å) [10], and  $\text{Ni}(\text{C}_2\text{Cl}_3)_2(\text{PMe}_2\text{Ph})_2$ , (1.91 Å) [27] but slightly shorter than those found in complexes containing Re–C(sp<sup>2</sup>) bonds (*cis*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{C}_6\text{HCl}_4)\text{Cl}$ , 2.197 Å [13] and *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{C}_6\text{H}_2\text{Cl}_2(\text{MeO}))\text{Cl}$ , 2.188 Å [15]). The C=C bond distance of the trichlorovinyl ligand of 1.324 Å shows no unusual features compared with the nickel complexes mentioned above [10,27].

### 3. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques.  $\text{Cp}^*\text{Re}(\text{CO})_2\text{N}_2$  was prepared according to a procedure described in the literature [26]. Trichloroethylene (TCE) and perchloroethylene (PCE) (Aldrich) were used as received. Photochemical reactions were carried out using a Rayonet RPR 100 photoreactor. Infrared spectra were recorded in solution (CaF<sub>2</sub> cell) on a Perkin–Elmer FT-1605 spectrophotometer, and <sup>1</sup>H and

Table 2  
Selected bond lengths (Å) and angles (°) for *cis*-Cp\*Re(CO)<sub>2</sub>(C<sub>2</sub>Cl<sub>3</sub>)Cl (**3**)

Bond lengths	
Re(1)–C(2)	1.911(6)
Re(1)–C(1)	1.914(12)
Re(1)–C(10)	2.149(5)
Re(1)–C(4)	2.314(4)
Re(1)–C(3)	2.323(4)
Re(1)–C(5)	2.329(5)
Re(1)–Cl(1)	2.436(4)
Re–Cp*(centre)	1.979(2)
C(9)–C(10)	1.323(8)
Bond angles	
C(1)–Re(1)–C(2)	80.2(6)
C(10)–Re(1)–Cl(1)	76.63(10)
Cl(3)–C(10)–Re(1)	116.3(3)
O(1)–C(1)–Re(1)	174(2)
O(2)–C(2)–Re(1)	176.9(5)
Cl(4)–C(9)–Cl(2)	111.7(3)

<sup>13</sup>C NMR spectra on a Bruker AVANCE 400 spectrometer. <sup>1</sup>H NMR chemical shifts were referenced using the chemical shifts of residual solvent resonances, and <sup>13</sup>C chemical shifts to solvent peaks. Mass spectra were obtained at the Laboratorio de Servicios Analíticos, Universidad Católica de Valparaíso. Elemental analyses were obtained at the Centro de Instrumentación, P. Universidad Católica de Chile, Santiago, Chile.

### 3.1. Cp\*Re(CO)<sub>2</sub>(η<sup>2</sup>-C<sub>2</sub>Cl<sub>4</sub>) (**1**)

Cp\*Re(CO)<sub>2</sub>N<sub>2</sub> (30 mg, 0.074 mmol) was dissolved in 10 mL of PCE and the solution was bubbled with N<sub>2</sub> for 10 min and then irradiated at λ = 350 nm for 40 min. The solution colour changed from light to dark yellow after irradiation and an IR spectrum showed almost the complete disappearance of the starting dinitrogen complex and two prominent absorption bands at 2020 and 1950 cm<sup>-1</sup>. In addition small amount of the complexes Cp\*Re(CO)<sub>2</sub>Cl<sub>2</sub> and Cp\*Re(CO)<sub>2</sub>(CCl=CCl<sub>2</sub>)Cl were also detected in the IR spectrum of the reaction mixture. PCE was pumped off and the brown residue was extracted three times with 10 mL of hexane. After evaporation of hexane under vacuum a grey solid was obtained. Crystallization from hexane at -18 °C yield a white–grey solid (13 mg, 32% yield based on Cp\*Re(CO)<sub>2</sub>N<sub>2</sub>).

IR (hexane, ν(CO), cm<sup>-1</sup>): 2024s, 1954s; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.51 (Cp\*); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 9.9 (C<sub>5</sub>Me<sub>5</sub>), 58.3 (C<sub>2</sub>Cl<sub>4</sub>), 104.8 (C<sub>5</sub>Me<sub>5</sub>), 200.9 (CO). Mass spectrum (based on <sup>187</sup>Re/<sup>35</sup>Cl) *m/z*: 542 M<sup>+</sup>, 514 M<sup>+</sup>–CO, 486 M<sup>+</sup>–2CO.

### 3.2. Cp\*Re(CO)<sub>2</sub>(η<sup>2</sup>-C<sub>2</sub>HCl<sub>3</sub>) (**2**)

The photochemical reaction was carried out in a similar manner to that described above for complex **1** but using TCE. From the dark yellow solution obtained after irradiation a dark brown–green solid could be isolated. Extraction with hexane followed by crystallization in the same solvent gave white solid in 42% yield.

IR (hexane, ν(CO), cm<sup>-1</sup>): 2014s, 1944s; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.43 (s, 15H, Cp\*), 4.40 (s, 1H, C<sub>2</sub>HCl<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 9.4 (C<sub>5</sub>Me<sub>5</sub>), 49.5 (C<sub>2</sub>HCl<sub>3</sub>), 64.6 (C<sub>2</sub>HCl<sub>3</sub>), 101.4 (C<sub>5</sub>Me<sub>5</sub>), CO resonances were not observed. Mass spectrum (based on <sup>187</sup>Re/<sup>35</sup>Cl) *m/z*: 508 M<sup>+</sup>, 480 M<sup>+</sup>–CO, 452 M<sup>+</sup>–2CO.

### 3.3. *cis*-Cp\*Re(CO)<sub>2</sub>(C<sub>2</sub>Cl<sub>3</sub>)Cl (**3**)

Complex **1** (25 mg, 0.047 mmol) was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred at room temperature. The IR spectrum of the reaction mixture showed the slow disappearance of the absorption bands of the coordination complex (ν(CO): 2021 and 1952 cm<sup>-1</sup>, in CH<sub>2</sub>Cl<sub>2</sub>). After 24 h only two absorptions at 2033 and 1961 cm<sup>-1</sup> were observed. Evaporation of the solvent yielded an orange solid which was chromatographed on an alumina column (prepared in hexane). The column was washed with hexane and the product eluted with CH<sub>2</sub>Cl<sub>2</sub> as an orange band. Complex **3** was isolated as orange crystals in almost quantitative yield (95%) after crystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:5) at -18 °C.

IR (CH<sub>2</sub>Cl<sub>2</sub>, ν(CO), cm<sup>-1</sup>): 2033vs, 1961s; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.00 (Cp\*); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 10.6 (C<sub>5</sub>Me<sub>5</sub>), 108.9 (C<sub>5</sub>Me<sub>5</sub>), 122.2 (C<sub>2</sub>Cl<sub>3</sub>), 126.7 2 (C<sub>2</sub>Cl<sub>3</sub>), 200.6 (CO), 202.6 (CO). Mass spectrum (based on <sup>187</sup>Re/<sup>35</sup>Cl) *m/z*: 542 M<sup>+</sup>, 514 M<sup>+</sup>–CO, 486 M<sup>+</sup>–2CO, 451 M<sup>+</sup>–2CO–Cl. Anal. Calc. for C<sub>14</sub>H<sub>15</sub>Cl<sub>4</sub>O<sub>2</sub>Re: C, 30.93; H, 2.76. Found: C, 30.89; H, 2.56%.

## 4. Crystal structure determination

Orange single crystals suitable for X-Ray diffraction studies were grown in a CH<sub>2</sub>Cl<sub>2</sub>/hexane mixture. One of these crystals was glued on a glass fiber in a random orientation and mounted on a Bruker Smart Apex diffractometer equipped with a CCD area detector. The highly redundant data collection was performed at room temperature using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) with separations of 0.3° between frames and 10 s for frame. Data integration was made using SAINT [28] and a multi-scan absorption correction was applied using SADABS [29]. The structure was solved using XS in SHELXTL-PC [30] by direct methods and completed (non-H atoms) by difference Fourier techniques. Refinement until convergence was obtained by full-matrix least-squares on *F*<sup>2</sup> using SHELXL97 [31]. Hydrogen atoms of the methyl groups were positioned at their expected values and allowed to ride in coordinates (C–H = 0.96) as well in displacements factors (1.5 times their hosts).

## 5. Supplementary material

CCDC 620264 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data

Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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