

Photochemical C–Cl bond activation of trichloroarenes by the rhenium complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$. X-ray structure of *trans*- $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(2\text{-methoxy-4,5-dichlorophenyl})\text{chloride}$

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Abstract

Photochemical reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$, with 2,4,5-trichloroanisole and 3,4,5-trichlorotrifluoromethylbenzene yields $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(\text{C}_6\text{H}_2\text{Cl}_2(\text{MeO}))\text{Cl}$ (**1**) and $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(\text{C}_6\text{H}_2\text{Cl}_2(\text{CF}_3))\text{Cl}$, (**2**) formed by insertion of the fragment $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2$ into the C–Cl bond of the chloroarenes. The C–Cl bond activation of trichloroanisole occurs at the chlorine *ortho* respect to the methoxy group as revealed by the X-ray structure of **1**. In the case of the reaction with $\text{C}_6\text{H}_2\text{Cl}_3(\text{CF}_3)$, ¹H-NMR spectroscopy indicates that only the C–Cl bond *meta* respect to CF_3 group is cleaved. Complex **1** was isolated as the *trans* isomer while **2** was obtained as an isomeric mixture (*trans-2* and *cis-2*). The stereochemistry of these complexes has been assigned by IR and ¹³C-NMR spectroscopies and supported by X-ray crystallography for **1**.

Keywords: C–Cl bond activation; Chloroarenes; Pentamethylcyclopentadienyl; Rhenium

1. Introduction

Chloroarenes are of particular interest because of their negative environmental and health impact [1]. Environmental concerns have driven several research groups to examine practical and effective processes for the transformation of highly toxic chloroarenes into arenes by using transition metal complexes under stoichiometric and catalytic conditions [2]. Unfortunately, the utilization of rhenium complexes into degradation reactions of these persistent environmental pollutants has received little attention. As far as we

know, reports from our laboratory [3,4] and a paper by Sutton and Leiva [5] are the only previous publications related to this work. With regard to photochemical reactions, we and others have demonstrated that cyclopentadienylrheniumtricarbonyl complexes $(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{CO})_3$ (R = H and Me) serve as useful precursors to produce complexes of the type $(\eta^5\text{-C}_5\text{R}_5)\text{Re}(\text{CO})_2\text{L}$, when they are UV-irradiated in the presence of THF [6], PR_3 [7], alkenes [8], etc. These complexes are also appropriate photochemical precursors for studying the coordination [9], C–F and C–H bond activation of fluorinated benzenes [10–12] and C–Cl bond activation of chlorobenzenes [3,4]. As part of our continuing investigation on the C–halogen bond activation by cyclopentadienyl rhenium carbonyl complexes, in this paper we wish to report the photochemical reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ in the presence of 2,4,5-

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trichloroanisole and 3,4,5-trichlorotrifluoromethyl benzene, with the aim to focus on the electronic or steric effects of the methoxy and trifluoromethyl groups on the C–Cl bond activation of the trichlorobenzene ring.

2. Results and discussion

Hexane solutions of 2,4,5-trichloroanisole and 3,4,5-trichlorotrifluoromethylbenzene, in the presence of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$, were UV-irradiated ($\lambda = 350$ nm) at room temperature for 11 and 4 h, respectively. In both cases, the reactions produced one major dicarbonyl product in low conversion yield (Scheme 1), while most of the starting tricarbonyl complex remained unreacted. Longer irradiation times did not increase the yield of the products; instead, significant amounts of the dichloro complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2\text{Cl}_2$ [13] and decomposition products were formed.

The insertion product $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(\text{C}_6\text{H}_2\text{Cl}_2(\text{MeO}))\text{Cl}$ (**1**) was isolated as air stable orange microcrystals after column chromatography on Florisil and crystallization from dichloromethane–hexane. Complex **1** is stable both as a solid and in solution of polar and non-polar organic solvents with regards to the conversion to the *cis* isomer. No isomerization was observed even in boiling benzene or acetonitrile, though the complex does not survive for long at these temperatures. The *trans* stereochemistry of this compound was assigned on the basis of the IR and ^{13}C -NMR spectra. In the former technique, the spectrum exhibited only two $\nu(\text{CO})$ absorptions at 2040 and 1956 cm^{-1} (CH_2Cl_2 solution), being the lower wavenumber band much more intense. Similar patterns of intensities have been observed in several other dicarbonyl rhenium complexes possessing a four-legged piano-stool type of structure

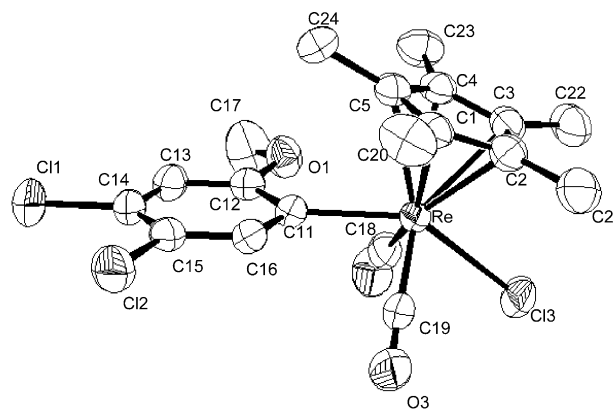
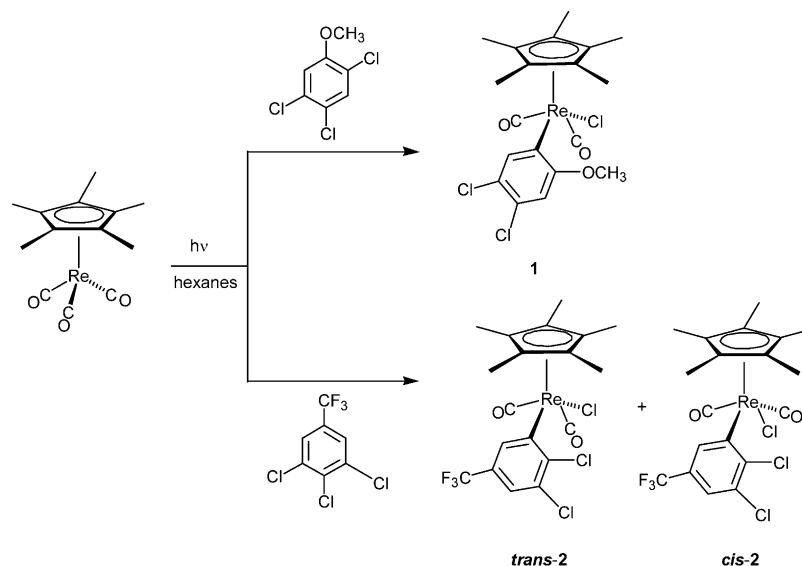


Fig. 1. Perspective view (ORTEP) of *trans*- $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(\text{C}_6\text{H}_2\text{Cl}_2\text{OMe})\text{Cl}$ (**1**) showing the atom numbering scheme. Atoms are represented by thermal ellipsoids at the 50% probability level.

[3,4,13,14]. The appearance of a single resonance for the equivalent CO groups in the ^{13}C -NMR spectra at δ 196.0, is a further evidence for the *trans* orientation of the carbonyl ligands in this type of compounds. Furthermore, the X-ray structure of complex **1** (Fig. 1) confirms the geometry of the isomer and adds to the list of determined structures of related cyclopentadienyl complexes containing the aryl-Re-halogen moiety. These include *trans*- $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(2,3,4,5\text{-C}_6\text{HCl}_5)\text{Cl}$ [3], *trans*- $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(\text{C}_6\text{H}_5)\text{I}$ [15], *trans*- $(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{Br})\text{Re}(\text{CO})_2(\text{C}_6\text{F}_5)\text{Br}$ [16] and *trans*- $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{C}_6\text{HF}_4)\text{Br}$ [17]. Selected bond lengths and angles are presented in Table 1. The Re–C(aryl) bond (2.188 Å) and Re–Cl bond (2.478 Å) compare well with those determined for *trans*- $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(2,3,4,5\text{-C}_6\text{HCl}_5)\text{Cl}$ [3] (2.197 and 2.488 Å, respectively). The interbond angle subtended by the two CO groups at Re (98.9°) is also close to the angles in similar *trans* complexes.



Scheme 1. Products from the irradiation of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ with chloroarenes.

Table 1
Selected bond lengths (Å) and angles (°) for *trans*-(η^5 -C₅Me₅)Re(CO)₂-(C₆H₂Cl₂OMe)Cl (**1**)

| | |
|---------------------|-----------|
| <i>Bond lengths</i> | |
| Re–C1 | 2.283(4) |
| Re–C2 | 2.251(3) |
| Re–C3 | 2.300(3) |
| Re–C4 | 2.358(3) |
| Re–C5 | 2.284(4) |
| Re–C11 | 2.188(3) |
| Re–C18 | 1.969(4) |
| Re–C19 | 1.916(4) |
| Re–Cl(3) | 2.4784(9) |
| C18–O2 | 1.131(4) |
| C19–O3 | 1.150(4) |
| C12–O1 | 1.368(4) |
| C17–O1 | 1.406(5) |
| <i>Bond angles</i> | |
| C18–Re–C19 | 98.91(16) |
| C11–Re–Cl(3) | 143.2(2) |
| C11–Re–C18 | 79.70(14) |
| C11–Re–C19 | 80.59(13) |
| C18–Re–Cl(3) | 74.98(11) |
| C19–Re–Cl(3) | 77.47(11) |
| O2–C18–Re1 | 175.6(3) |
| O3–C19–Re1 | 176.9(4) |
| C12–O1–C17 | 119.3(3) |

In contrast, the complex (η^5 -C₅Me₅)Re(CO)₂-(C₆H₂Cl₂(CF₃))Cl (**2**) could be separated into the *trans* and *cis* isomeric forms, by column chromatography. Each isomer was characterized by IR and ¹H-NMR spectroscopies. The IR spectrum of *trans*-**2** exhibited similar pattern of the ν (CO) absorption bands (2047 and 1965 cm⁻¹ in CH₂Cl₂ solution) to those observed for complex **1**, whereas *cis*-**2** showed an intensity pattern indicative of a lateral orientation of the two CO groups, that is, the lower wavenumber band is the less intense of the pair [3,13,14]. The ¹H-NMR spectra can also be used to distinguish the two isomers of **2**; the methyl resonances for the (η^5 -C₅Me₅) ligand of *trans*-**2**, observed at δ 1.75, occur at higher field of that found at δ 2.03 for *cis*-**2**, whereas the resonances for the aromatic protons of *trans*-**2** are shifted to lower field when compared with those observed for *cis*-**2**. Unfortunately, after an overnight scanning the ¹³C-NMR spectra of either isomer in CDCl₃, showed resonances for the isomeric mixture (*trans*-**2**:*cis*-**2** ratio of about 0.8) due to the isomerization *trans*-**2** ↔ *cis*-**2** process. A similar isomerization process was observed for the *cis*- and *trans*-(η^5 -C₅Me₅)Re(CO)₂-(2,3,4,5-C₆HCl₄)Cl [3]. Nevertheless, in both cases the spectrum showed three resonances at δ 192.6, 202.6 and 205.1, assigned to the carbonyls of the two products. By comparison with carbonyl chemical shifts found in similar compounds reported from our laboratory [3,4], the higher field resonance is assigned to *trans*-**2** and the lower field resonances to the two inequivalent CO ligands of the complex *cis*-**2**.

Formally, the reactions described above can be viewed as an insertion of the photogenerated fragment [(η^5 -C₅Me₅)Re(CO)₂] into a C–Cl bond of the chlorinated arene molecules, in a similar fashion to the photochemical reactions of (η^5 -C₅Me₅)Re(CO)₃ with several partially fluorinated [10–12] and chlorinated benzenes [3,4], reported previously from our group. Neither coordination nor C–H bond activation products of the chlorinated arenes were observed in these reactions. These results are in good agreement with the lower C–Cl bond strength when compared to that of the C–H bond [18].

An interesting feature associated with the trichloroarenes involved in this work is the possibility they offer to address electronic and/or steric effects of the substituent on the aromatic ring (OMe or CF₃), with respect to the selectivity of the C–Cl bond activation. For 2,4,5-trichloroanisole, the X-ray structure of complex **1** (Fig. 1) reveals that the activation occurs in the position *ortho* with respect to the OMe group. Taking into account the model proposed for the C–H and C–F bonds activation of arenes or fluorinated arenes by transition metal complexes [19], and also the experimental evidence for the coordination of chlorobenzenes to rhenium in the complexes (η^5 -C₅Me₅)Re(CO)₂(5,6- η^2 -1,2,4-C₆H₃Cl₃) and (η^5 -C₅Me₅)Re(CO)₂(5,6- η^2 -1,2,3,4-C₆H₂Cl₄) [20], we have also considered an intermediate with the chloroarene coordinated in an η^2 -fashion, prior to the insertion of the metal fragment into the C–Cl bond. Since the activation occurs at the chlorine *ortho* with respect to the OMe, then two possibilities for the coordination of the unsaturated fragment [(η^5 -C₅Me₅)Re(CO)₂] to 2,4,5-trichloroanisole can be envisaged: coordination through the CCl=C(OMe) or CCl=CH bonds of the molecule. The former can be discarded by considering both experimental results and recent theoretical studies which have demonstrated that the same rhenium fragment coordinate to the less substituted double bond of partially fluorinated [21] and chlorinated [20] benzenes. In the second intermediate, the fragment should coordinate the CCl=CH bond at the 2,3-position of the arene. However, the binding at this position has similar steric environment to the other two distinct CCl=CH bonds present in the chlorinated arene (at 3,4- and 4,5-positions). At this stage we do not have a conclusive answer for the activation of the C–Cl bond *ortho* to the bulky methoxy group, but we suspect that the electron-donor capability of this group plays a still undetermined role.

The same model can be assumed to account for the observed insertion product of 3,4,5-trifluoromethylbenzene, but in this case, the CF₃ group seems to play a minor role on the selectivity of activation. The ¹H-NMR spectrum of **2** shows that the C–Cl bond *meta* with respect to the CF₃ group has been cleaved, since each isomer exhibited two resonances for the aromatic

protons (vide infra). The activation of one of the chlorine atoms located at the *meta* position appears to follow the same pattern of substitution observed previously in the reaction of several polychlorinated benzenes with transition metal complexes, under thermal [22] or photochemical [3] conditions, wherein most of the cases, the C–Cl bond activation occurs at the less hindered position.

As we pointed out above, complex **2** was obtained as an isomeric mixture, but complex **1** was isolated as a single isomer, so an obvious question arises: why the difference? The *cis* ↔ *trans* isomerization is quite a common process observed both in solution [23] and in confined environments [24] in complexes of the type CpML₂L₂. According to the results found previously in our laboratory on the insertion products of several partially chlorinated benzenes, of the general formula (η⁵-C₅Me₅)Re(CO)₂(C₆H_nCl_{5-n})Cl (*n* = 1, 2 and 3), the *trans* to *cis* isomerization only occurs for complexes with *n* = 1 and 2 and it is a solvent-dependent process (*trans* isomers are favored in nonpolar organic solvents, whereas the *cis* forms are the most stable species in polar solvents) [3,4]. By considering now the reluctance of **1** to interconvert to the *cis* isomer and the fact that complex **2**, which possesses the electron withdrawing CF₃ substituent on the dichloroaryl ligand, behaves similarly to their tetra (*n* = 1) and trichloroaryl (*n* = 2) analogues, we suggest that the electronic effects on the aryl ligand also play an important role in the thermal isomerization of this type of compound.

Clearly much work is required to establish unequivocally the above statement as well as the factors influencing the selectivity of C–Cl bond activation of chloroarenes by the photogenerated rhenium fragment [(η⁵-C₅Me₅)Re(CO)₂]. Studies on a more complete series of complexes possessing electron-donating and electron-withdrawing substituents on the chlorophenyl ligands are currently underway to further evaluate these issues.

3. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. (η⁵-C₅Me₅)Re(CO)₃ was prepared according to a procedure described in the literature [25]. 2,4,5-Trichlorophenol, and 3,4,5-trichlorotrifluoromethylbenzene from Aldrich were used as received. 2,4,5-Trichloroanisole was prepared in 85% yield from the corresponding phenol by a Williamson synthesis. Solutions were irradiated using a Rayonet RPR 100 photoreactor. Infrared spectra were recorded in solution (CaF₂ cell) on a Perkin–Elmer FT-1605 spectrophotometer, ¹H- and ¹³C-NMR spectra on Bruker ADVANCE 400. ¹H-NMR chemical shifts were referenced using the chemical shifts of residual solvent resonances, ¹³C chemical shifts to solvent peaks.

Mass spectra were obtained at the Laboratorio de Servicios Analíticos, Universidad Católica de Valparaíso, and the Chemistry Department at University of York. Elemental analyses were obtained at the Centro de Instrumentación, Pontificia Universidad Católica de Chile, Santiago, Chile.

3.1. *trans*-(η⁵-C₅Me₅)Re(CO)₂(C₆H₂(OMe)Cl₂)Cl (**1**)

(η⁵-C₅Me₅)Re(CO)₃ (100 mg, 0.247 mmol) is dissolved in 20 ml of a saturated solution of 2,4,5-trichloroanisole, in hexanes, in a Pyrex tube (25 cm, 1.5 cm external diameter). The solution is irradiated at 350 nm for 11 h. The solution turned yellow, and red crystals are formed on the walls of the tube. Solvent was transferred under vacuum and the yellow residue and the crystals were chromatographed on Florisil. Elution with hexanes–CH₂Cl₂ (10:1) moved a mixture of unchanged (η⁵-C₅Me₅)Re(CO)₃ and 2,4,5-trichloroanisole. Dichloromethane moved orange *trans*-(η⁵-C₅Me₅)Re(CO)₂(C₆H₂(OCH₃)Cl₂)Cl (**1**) which was obtained as orange crystals by layering a concentrated CH₂Cl₂ solution of the orange solid with hexanes (yield 55 mg, 0.093 mmol, 38% conversion).

IR (CH₂Cl₂, ν(CO)/cm⁻¹): 2040s and 1956vs; ¹H-NMR (CDCl₃) δ 1.70 (s, 15H), 3.80 (s, 3H), 6.84 (s, 1H), 7.68 (s, 1H); ¹³C{¹H}-NMR (CDCl₃) δ 10.82 (C₅Me₅), 57.00 (OCH₃), 105.06 (C₅Me₅); 112.27 (C₆H₃(CH₃)Cl), 119.41 (C₆H₃(CH₃)Cl), 125.35 (C₆H₃(CH₃)Cl), 131.39 (C₆H₃(CH₃)Cl), 147.81 (C₆H₃(CH₃)Cl), 164.35 (C₆H₃-(CH₃)Cl), 196.50 (CO); mass spectrum (based on ¹⁸⁷Re/³⁵Cl) *m/z* 588 [M]⁺, 560 [M – CO]⁺, 532 [M – 2CO]⁺, 356 [M – 2CO – C₆H₂(OCH₃)Cl₂]⁺ (Found: C, 38.51; H, 2.99. Calc. for C₁₉H₂₀Cl₃O₃Re: C, 38.77; H, 3.39%).

3.2. (η⁵-C₅Me₅)Re(CO)₂(C₆H₃(CF₃)Cl₂)Cl (**2**)

Four Pyrex tubes containing (η⁵-C₅Me₅)Re(CO)₃ (100 mg, 0.247 mmol) dissolved in a mixture of 3,4,5-trichlorotrifluoromethylbenzene (1 ml) and hexanes (19 ml) each one, were irradiated at 350 nm for 4 h. The resulting yellow solutions are mixed and the solvent was pumped off. The brown oily residue was chromatographed on a silica gel column. Elution with hexanes moved a mixture of unreacted (η⁵-C₅Me₅)Re(CO)₃ and 3,4,5-trichlorotrifluoromethylbenzene. Hexanes–CH₂Cl₂ (10:1) moved orange *trans*-(η⁵-C₅Me₅)Re(CO)₂(C₆H₃(CF₃)Cl₂)Cl (*trans*-**2**) (10 mg, 0.016 mmol). Hexanes–CH₂Cl₂ (5:1) moved red *cis*-(η⁵-C₅Me₅)Re(CO)₂(C₆H₃(CF₃)Cl₂)Cl (*cis*-**2**) (12 mg, 0.019 mmol).

3.2.1. *trans*-**2**

IR (CH₂Cl₂, ν(CO)/cm⁻¹): 2048s and 1967vs; ¹H-NMR (CDCl₃) δ 1.75 (s, 15H), 7.53 (d, 1H, *J* = 1.6 Hz),

7.93 (d, 1H, $J = 1.6$ Hz); $^{13}\text{C}-\{^1\text{H}\}$ -NMR (CDCl_3) δ 9.60 (C_5Me_5), 192.60 (CO), aromatic carbons cannot be assigned due to the isomerization to the *cis* isomer. Mass spectrum (based on $^{187}\text{Re}/^{35}\text{Cl}$) m/z : 626 $[\text{M}]^+$, 598 $[\text{M} - \text{CO}]^+$, 570 $[\text{M} - 2\text{CO}]^+$, 356 $[\text{M} - 2\text{CO} - \text{C}_6\text{H}_2(\text{CF}_3)\text{Cl}_2]^+$ (Found: C, 36.36; H, 2.54. Calc. for $\text{C}_{19}\text{H}_{17}\text{Cl}_3\text{F}_3\text{O}_2\text{Re}$: C, 36.42; H, 2.71%).

3.2.2. *cis*-2

IR (CH_2Cl_2 , $\nu(\text{CO})/\text{cm}^{-1}$): 2027vs and 1956vs; ^1H -NMR (CDCl_3) δ 2.03 (s, 15H), 7.16 (d, 1H, $J = 1.5$ Hz), 7.40 (d, 1H, $J = 1.5$ Hz); $^{13}\text{C}-\{^1\text{H}\}$ -NMR (CDCl_3) δ 10.30 (C_5Me_5), 202.60 (CO), 205.10 (CO), aromatic carbons cannot be assigned due to the isomerization to the *trans* isomer. Mass spectrum (based on $^{187}\text{Re}/^{35}\text{Cl}$) m/z : 626 $[\text{M}]^+$, 598 $[\text{M} - \text{CO}]^+$, 570 $[\text{M} - 2\text{CO}]^+$, 356 $[\text{M} - 2\text{CO} - \text{C}_6\text{H}_2(\text{CF}_3)\text{Cl}_2]^+$ (Found: C, 36.06; H, 2.64. Calc. for $\text{C}_{19}\text{H}_{17}\text{Cl}_3\text{F}_3\text{O}_2\text{Re}$: C, 36.42; H, 2.71%).

3.3. Crystal structure determination

X-ray quality crystals of **1** were obtained by recrystallization from hexanes solutions by slow cooling to -10°C . A summary of crystal data, data collection, and refinement parameters for the structural analyses is

Table 2
Crystal data and structure refinement for *trans*-($\eta^5\text{-C}_5\text{Me}_5$) $\text{Re}(\text{CO})_2$ -($\text{C}_6\text{H}_2\text{Cl}_2(\text{OCH}_3)$)Cl (**1**)

| | |
|---|--|
| Empirical formula | $\text{C}_{19}\text{H}_{20}\text{Cl}_3\text{O}_3\text{Re}$ |
| Formula weight | 588.90 |
| Temperature | 297(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, $P2(1)/c$ |
| Unit cell dimensions | |
| a (Å) | 15.4018(11) |
| b (Å) | 9.9530(7) |
| c (Å) | 14.9010(11) |
| α (°) | 90 |
| β (°) | 115.8070(10) |
| γ (°) | 90 |
| V (Å ³) | 2056.4(3) |
| Z | 4 |
| D_{calc} (g cm ⁻³) | 1.902 |
| Absorption coefficient (mm ⁻¹) | 6.314 |
| $F(000)$ | 1136 |
| Crystal size (mm) | 0.32 × 0.22 × 0.10 |
| θ range for data collection (°) | 2.52–27.94 |
| Limiting indices | $-20 \leq h \leq 20$, $-12 \leq k \leq 12$, $-19 \leq l \leq 19$ |
| Reflections collected/unique | 14653/4606 [$R_{\text{int}} = 0.0249$] |
| Completeness to $\theta = 26.00$ | 99.9% |
| Max/min transmission | 1.0, 0.694538 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data/restraints/parameters | 4606/0/241 |
| Goodness-of-fit on F^2 | 1.036 |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0252$, $wR_2 = 0.0559$ |
| R indices (all data) | $R_1 = 0.0314$, $wR_2 = 0.0584$ |
| Largest difference peak and hole (e Å ⁻³) | 0.787 and -0.536 |

given in Table 2. A red crystal of **1** was glued to a glass fiber and mounted on Bruker SMART APEX diffractometer, equipped with a CCD area detector. Data was collected using graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å). Cell constants for **1** were obtained from the least-squares refinement of three-dimensional centroids of 995 reflections in the range $5.04 \leq 2\theta \leq 55.40$. Data were measured through the use of CCD recording of ω rotation frames (0.3° each). All data were corrected for Lorentz and polarization effects. Absorption corrections were applied using the SADABS routine [26]. Both data were integrated with the Bruker SAINT-PLUS program [27].

The structure was solved by Patterson, completed by difference Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL-97) [28] with initial isotropic, but subsequent anisotropic thermal parameters. Hydrogens in **1** were included in calculated positions and refined riding on carbon atoms with free isotropic displacement parameters. Atomic scattering factors were used as implemented in the program [28].

4. Supplementary material

Crystallographic data for complex **1** have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 214452. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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