η^2 -COORDINATION OF CHLOROBENZENES TO RHENIUM FRAGMENT $\text{Cp}^*\text{Re}(\text{CO})_2$: CHEMICAL AND PHOTOCHEMICAL SYNTHESSES OF $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_{6-n}\text{Cl}_n)$.

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ABSTRACT

The complexes $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_{6-n}\text{Cl}_n)$, $n = 4$, (5,6- η^2 -1,2,3,4- $\text{C}_6\text{H}_2\text{Cl}_4$) **2a**; $n = 3$, (5,6- η^2 -1,2,4- $\text{C}_6\text{H}_3\text{Cl}_3$) **2b**; $n = 2$, (2,3- η^2 -1,4- $\text{C}_6\text{H}_4\text{Cl}_2$) **2c** and (4,5- η^2 -1,3- $\text{C}_6\text{H}_4\text{Cl}_2$) **2d**, have been conveniently prepared by two alternative procedures: Directly, by the photochemical reaction of $\text{Cp}^*\text{Re}(\text{CO})_2(\text{N}_2)$ in neat or saturated hexane solution of the corresponding partially chlorinated benzene or stepwise, by the reaction of the appropriate *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{X}$, $\text{X} = \text{Cl}$, Br (**1a-d**) with LiBHEt_3 followed by protonation with HCl to form the hydrido complexes *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{H}$ which resulted thermally unstable in solution and convert to η^2 -coordination complexes **2a-d**. Due to their low stability as solids and in solution, the new complexes were only characterized by IR and ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectra of the two derivatives containing dichlorobenzene (**2c** and **2d**) indicate that a rapid exchange occurs between the hydrogen atoms on the coordinated carbons and those on the non-coordinated carbons.

1.- INTRODUCTION

Reactions of cyclopentadienyl rhenium complexes with partially halogenated benzenes have been shown to induce both C-H and C-halogen bond activation, as well as, coordination of the aromatic molecule to rhenium center. For instance, we have demonstrated that the photogenerated fragment $[\text{Cp}^*\text{Re}(\text{CO})_2]$ ($\text{Cp}^* = \text{Cp}$ ($\eta^5\text{-C}_5\text{H}_5$), $\text{Cp}^* = (\eta^5\text{-C}_5\text{Me}_5)$) reacts with partially fluorinated benzene C_6HF_5 and 1,2,4,5- $\text{C}_6\text{H}_2\text{F}_4$ to yield only C-H oxidative addition products,¹ but with 1,4- $\text{C}_6\text{H}_4\text{F}_2$ produces a mixture of coordination and C-H activation products.² In contrast, the photochemical reaction of $\text{Cp}^*\text{Re}(\text{CO})_3$ with partially chlorinated arenes lead to the cleavage of C-Cl bond.³⁻⁵ Similar result have been found by Leiva and Sutton in the reaction of several dinitrogen complexes $\text{Cp}^*\text{Re}(\text{CO})(\text{L})\text{N}_2$ ($\text{L} = \text{phosphine}$ and phosphite) with chlorobenzene.⁶ As far as we are aware the η^2 -coordination of chloroarenes to rhenium remains elusive. On this regard, Gladysz has documented the *ligation* of chlorobenzene at low temperature in the cationic complex $[\text{Cp}^*\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}_6\text{H}_5\text{Cl})]^+$.⁷ This species undergo spectroscopic changes on warming, and the formation of a C-Cl oxidative addition products may result, although this could not be conclusively identified. Despite this, cyclopentadienyl rhenium complexes have been shown, in a few cases, to be useful precursors to stabilize the arene coordination in a η^2 -fashion. For instance, $[\text{CpRe}(\text{CO})(\text{NO})(\eta^2\text{-C}_6\text{H}_5(\text{CHPh}_2))]^+$,⁸ $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_6\text{F}_5)$,⁹ $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-arene})$ (arene = benzene, toluene and *tert*-butylbenzene)¹⁰ and $\text{Cp}^*\text{Re}(\text{CO})_2(2,3\text{-}\eta^2\text{-1,4-}\text{C}_6\text{H}_4\text{F}_2)$.²

As part of our continuing interest on the C-Cl bond activation by cyclopentadienyl rhenium carbonyl complexes, in this paper we wish to report the synthesis and spectroscopic characterization of a series of η^2 -chloroarene coordinated to $\text{Cp}^*\text{Re}(\text{CO})_2$ fragment.

2. RESULTS

The preparation of the unreported *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(2,5\text{-}\text{C}_6\text{H}_3\text{Cl}_3)\text{Br}$ (**1c**) was carried out under similar conditions to those established for analogous oxidative addition products.^{3,4} That is by direct photolysis of $\text{Cp}^*\text{Re}(\text{CO})_3$ ($\lambda = 350$ nm, 6 h) in a saturated hexane solution of 2-bromo-1,4-dichlorobenzene at room temperature. Much longer irradiation times produced significant amounts of the dibromo complex $\text{Cp}^*\text{Re}(\text{CO})_2\text{Br}_2$.¹¹ The η^2 -coordination of the 2-bromo-1,4-dichlorobenzene could not be detected by IR spectroscopy. After work up the complex **1c** was isolated as a single isomer, as orange microcrystals. This compound resulted stable at room temperature with respect to isomerization in solution and solid state. Like many other derivatives of general formula $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{X}})(\text{X})$,¹² **1c** exhibit two $\nu(\text{CO})$ absorptions in the IR spectra at about 2036 (s) and 1956 (vs) cm^{-1} (in CH_2Cl_2 solution), pattern which is

characteristic for derivatives with a four-legged piano-stool type of structure possessing two CO ligands in a diagonal or *trans* orientation. The ^1H NMR spectrum of **1c** supports the formation of only one insertion product, since they exhibit a single resonance for the $(\eta^5\text{-C}_5\text{Me}_5)$ group, and the expected resonances for the protons of the dichloro aryl ligands.

2.1. η^2 -Chlorobenzene complexes

The η^2 -Chlorobenzene complexes of general formula $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_{6-n}\text{Cl}_n)$ (**2a-d**) were prepared by two alternative procedures:

a) Chemical reduction of $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{X}$

Chemical reduction of the complexes *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{Cl}$, ($\text{Ar}^{\text{Cl}} = 2,3,4,5\text{-}\text{C}_6\text{HCl}_4$, (**1a**)⁴; $\text{Ar}^{\text{Cl}} = 2,4,5\text{-}\text{C}_6\text{H}_2\text{Cl}_3$, (**1b**), $3,5\text{-}\text{C}_6\text{H}_3\text{Cl}_2$, (**1d**)⁵ and *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(2,5\text{-}\text{C}_6\text{H}_3\text{Cl}_3)\text{Br}$ (**1c**) was carried out by a similar procedure to that used for preparation of fluorophenyl hydride², that is by adding an excess of “super-hydride” at low temperature (-78°C) to a THF solution of the above complexes. The formation of the anionic complexes $[\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})]^-$ was inferred from the presence of two CO absorption bands in the $1850\text{--}1740$ cm^{-1} region of the IR spectra.¹² Further protonation of the anions with HCl at -10°C gave only the corresponding hydride derivative *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{H}$ (Scheme 1).

Scheme 1

The low thermal stability and the extreme air sensitivity of the hydride complexes precluded us in obtaining satisfactory elemental analyses and they could be identified only by IR. These compounds showed two $\nu(\text{CO})$ absorption bands at about 2022 (s) and 1960 (vs) cm^{-1} in hexane solution, with a typical pattern exhibited by other rhenium dicarbonyl complexes possessing a four-legged piano-stool type of structure, with a *trans* stereochemistry. Attempt to get the ^1H NMR spectra of a pure sample of these compounds, in toluene- d_8 , always resulted contaminated with the corresponding η^2 -chlorobenzene, thus we could not assign the aromatic protons. For that reason, we used the high

field region of the ^1H NMR spectra for the identification of these hydride derivatives. In all cases, the spectra showed a singlet at about δ -9.60 (in toluene- d_8 at -10 $^\circ\text{C}$), this resonance occurred at almost the same chemical shift to those reported for the close related complexes *trans*-($\eta^5\text{-C}_5\text{Me}_5$) $\text{Re}(\text{Ar}^F)(\text{CO})_2(\text{H})$ ($\text{Ar}^F = \text{C}_6\text{F}_5$, 2,3,5,6- C_6HF_4 , 2,5- $\text{C}_6\text{H}_3\text{F}_2$)^{1,2,13} and *trans*-($\eta^5\text{-C}_5\text{Me}_5\text{CH}_2\text{PPh}_2$) $\text{Re}(\text{C}_6\text{F}_5)(\text{CO})_2(\text{H})$.¹⁴

When toluene or hexane solutions of these species were stored at room temperature, for about 1 h, both IR and ^1H NMR spectra revealed that they interconvert to the more stable η^2 -chlorobenzene complexes (**2a-d**). Although these compounds resulted moderately stable under nitrogen atmosphere at room temperature in hexane solution, attempts to isolate any of the complexes as analytically pure samples were unsuccessful.

b) Photochemical reactions

Complexes **2** were also prepared by direct photolysis of $\text{Cp}^*\text{Re}(\text{CO})_2\text{N}_2$ ($\lambda = 350$ nm) in the presence of saturated hexane solution of 1,2,3,4-tetrachlorobenzene (**2a**) and neat 1,2,4-trichlorobenzene (**2b**), 1,4-dichlorobenzene (**2c**) and 1,3-dichlorobenzene (**2d**) Scheme 2.

Scheme 2

After 40 min of irradiation pale yellow solutions were produced. An IR spectrum in hexane of an evaporated sample of these solutions showed, in addition to the absorption bands due to the dinitrogen and carbonyl groups of the starting complex, two strong absorptions at about 1970 and 1900 cm^{-1} assigned to the products. An increase in the irradiation time to 90 min. did not improve the yield of products, the solution darkened and the formation of the dichloro complex *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2\text{Cl}_2$ and the corresponding C-Cl activation products could be confirmed by comparing the IR and ^1H -NMR spectra with authentic samples. After work up samples were always contaminated with variable amounts (< 40%) of the dinitrogen precursor.

Products characterization

The IR spectra of **2a-d** exhibited two strong νCO absorptions in the range 1970-1900 cm^{-1} in hexane solution (Table 1). Similar values have been reported for $\text{Cp}^*\text{Re}(\text{CO})_2(2,3\text{-}\eta^2\text{-}1,4\text{-C}_6\text{H}_4\text{F}_2)$ (νCO , hexane: 1970, 1908 cm^{-1})² but much lower wavenumber have been found in the benzene complex $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_6)$ (νCO , benzene: 1938, 1870 cm^{-1})¹⁵ and in the arenes derivatives $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-arene})$, arene = toluene, ethylbenzene and *tert*-butylbenzene (νCO , heptane: 1944, 1881 cm^{-1}).¹⁰

The ^1H NMR spectra of complexes **2**, measured at -10 $^\circ\text{C}$, exhibited the expected resonances for the Cp^* at about δ 1.50, but the resonances for the coordinated arene depend on the number and substitution pattern of the chlorine atoms in the ring. First, the ^1H NMR spectrum of coordinated 1,2,3,4-tetrachlorobenzene **2a** showed a single resonance at δ 2.96 for the protons of the symmetrical coordinated $\text{CH}=\text{CH}$ moiety. As expected, this value resemble to those reported for cyclic conjugated olefin coordinated to $\text{Cp}^*\text{Re}(\text{CO})_2$ fragment.¹⁶ The ^{13}C NMR spectrum of this compound is also in agreement with a symmetrical coordination of the 1,2,3,4- $\text{C}_6\text{H}_2\text{Cl}_4$ (see below). For complex **2b** the ^1H NMR spectrum exhibited one set of three signals which reveal the unsymmetrical η^2 -coordinated 1,2,4-trichlorobenzene to rhenium fragment. (Figure 1)

Figure 1. Proton ^1H NMR spectrum of $\text{Cp}^*\text{Re}(\text{CO})_2(5,6\text{-}\eta^2\text{-}1,2,4\text{-C}_6\text{H}_3\text{Cl}_3)$ (**2b**) in toluene- d_8 at 263 K; $[\text{Re}] = \text{Cp}^*\text{Re}(\text{CO})_2$.

The doublet of doublet centered at δ 2.85 (J_{HH} 1.3 and 8.9 Hz) can be unequivocally assigned to the proton H5 and the doublet centered δ 3.00 (J_{HH} 8.9 Hz) to the proton H6, whereas the doublet observed at δ 6.06 (J_{HH} 1.3 Hz) is assigned to the CH proton (H3) without bonding interaction with the rhenium atom. Much more interesting are the ^1H NMR spectra of the dichlorobenzenes coordinated to rhenium. First, the symmetrical coordinated 1,4- $\text{C}_6\text{H}_4\text{Cl}_2$ showed, only two broad resonances at δ 3.13 and 5.84. These values are similar to those observed for the closely related complex $\text{Cp}^*\text{Re}(\text{CO})_2(2,3\text{-}\eta^2\text{-}1,4\text{-C}_6\text{H}_4\text{F}_2)$ (δ 3.20 and 5.51, in toluene- d_8)² and suggest a dynamic behaviour where the hydrogen atoms on the coordinated $\text{CH}=\text{CH}$ bond exchange with those on non-coordinated $\text{CH}=\text{CH}$ bond, probably through an unusual [1,4]-metallotropic shift.²

Complex **2d** which possesses η^2 -1,3-dichlorobenzene, exhibited three resonances in its ^1H NMR spectrum. A triplet centered at δ 3.21 and a broad singlet at δ 5.07, with an integration ratio 1:2, which can be explained by assuming a rapid exchange occurring between the hydrogen atoms on the coordinated carbon and those on the non-coordinated carbons, probably via [1,2]-metallotropic shift.² The third resonance observed at δ 6.25 is assigned to the aromatic hydrogen located at the 2-position of the coordinated 1,3-dichlorobenzene.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of η^2 -complexes **2**, showed around δ 50, the presence of one carbon resonance for the symmetrical coordinated chloroarene molecule (**2a,c**), whereas two resonances are observed for the carbon nuclei of the unsymmetrical chloroarene (**2b,d**) coordinated to rhenium fragment. Nevertheless, the carbon atoms without bonding interaction are observed to higher frequency (δ : 110-140). In addition, the chemical shift of the terminal CO groups is also indicative of the symmetrical or unsymmetrical nature of coordinated chloroarenes, since only a single resonance is observed for the formers (**2a,c**), whereas two resonances are observed for the latter's (**2b,d**). Figure 2 shows the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **2b**.

Figure 2. Carbon ^{13}C NMR spectrum of $\text{Cp}^*\text{Re}(\text{CO})_2(5,6\text{-}\eta^2\text{-}1,2,4\text{-C}_6\text{H}_3\text{Cl}_3)$ (**2b**) in toluene- d_8 at 263 K.

Finally, we consider important to point out that like many other η^2 -arenes coordinated to metal fragments, the chlorobenzene ligands in complexes **2** can be easily displaced by other two electron donor ligands, as was evidenced by the reaction of **2a** and **2d** with CO and PMe_3 with formation of the known complexes $\text{Cp}^*\text{Re}(\text{CO})_3$ and $\text{Cp}^*\text{Re}(\text{CO})_2(\text{PMe}_3)$ respectively.^{17,18}

3. DISCUSSION

In previous communications we have demonstrated that the dinitrogen complex $\text{Cp}^*\text{Re}(\text{CO})_2\text{N}_2$ can be an useful photoprecursor to achieve C-H and C-F bond activation as well as η^2 -coordination of partially fluorinated benzenes. We have also demonstrated that the low thermal stability of pentamethylcyclopentadieny dicarbonyl hydrido complexes containing fluoroaryl group bound to rhenium are primary product which decomposed to the more stable η^2 -coordination complex.² In this work we have used the same synthetic approach to form rhenium complexes with chlorobenzenes coordinated in an η^2 -fashion. As far as we are aware, these complexes are the first examples of partially chlorinated benzenes bound to a metal fragment through an η^2 -coordination mode.

Even though η^2 -complexes are too unstable to be isolated as pure samples, they are fairly robust to allow their characterization by spectroscopic techniques. The presence of two IR absorption bands of almost equal intensity at about 1970 and 1905 cm^{-1} suggested the formation of a $\text{Re}(\text{I})$ with an η^2 -bound chlorobenzenes complexes. These values resemble more to those found for the complex $\text{Cp}^*\text{Re}(\text{CO})_2(2,3\text{-}\eta^2\text{-}1,4\text{-C}_6\text{H}_4\text{F}_2)$ than the ones reported for $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_6)$.¹⁵ An interesting trend can be observed when comparing the $\nu(\text{CO})$ frequencies as a function of the number of chlorine substituents in the benzene ring, Table 1.

Table 1. IR data of the complexes $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-chlorobenzene})^a$

Complex	Chlorobenzene	$\nu(\text{CO}) \text{ cm}^{-1}$
2a	1,2,3,4- $\text{C}_6\text{H}_2\text{Cl}_4$	1977, 1915
2b	1,2,4- $\text{C}_6\text{H}_3\text{Cl}_3$	1974, 1912
2c	1,4- $\text{C}_6\text{H}_4\text{Cl}_2$	1970, 1908
2d	1,3- $\text{C}_6\text{H}_4\text{Cl}_2$	1964, 1903

^a Values measured in hexane solution.

The fact that the tetrachlorobenzene shift $\nu(\text{CO})$ frequencies at higher energy compared to their trichloro and dichloro analogues suggest an stronger d-p back-bonding occurring between rhenium and the more chlorinated benzene. Similar trend was observed in the IR spectra of the complexes $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-C}_6\text{Cl}_4\text{X})$ X = H, Cl.¹⁹

The NMR data for complexes **2** show unambiguously that the η^2 -coordination of the partially chlorinated benzene ring, occurs at the $\text{CH}=\text{CH}$ bond in preference to the $\text{CH}=\text{CCl}$ bond in agreement with theoretical studies carried out on fluorobenzenes bound to the same metal fragment.²⁰

The above assertion was confirmed experimentally by the short irradiation of $\text{Cp}^*\text{Re}(\text{CO})_2\text{N}_2$ in presence of C_6Cl_6 and C_6HCl_5 . In none of the cases the coordination products could be detected by IR spectroscopy. Longer irradiation times lead to the formation of decomposition products.⁴ Accordingly, only one coordination position is observed for the tetrachloro- and trichlorobenzene derivatives (**2a** and **2b**). Furthermore, based on their coupling constants the coordinated and non-coordinated aromatic CH protons of 1,2,4- $\text{C}_6\text{H}_3\text{Cl}_3$ could be assigned unequivocally. Taking into account the results previously found in the complex $\text{Cp}^*\text{Re}(\text{CO})_2(2,3\text{-}\eta^2\text{-}1,4\text{-C}_6\text{H}_4\text{F}_2)$ and other complexes possessing arenes coordinated in an η^2 -fashion^{21,22} the ^1H NMR spectra of the coordinated dichlorobenzenes allow us to establish that, in the two cases, a fluxional process is occurring probably through successive metallotropic shift.

4. EXPERIMENTAL

4.1 General Methods

All reactions were carried out using the standard Schlenk technique under nitrogen. All solvents were purified and dried by conventional methods, and were distilled under nitrogen prior to use. 1,2,4,5- $\text{C}_6\text{H}_2\text{Cl}_4$, 1,2,4- $\text{C}_6\text{H}_3\text{Cl}_3$, 1,4- $\text{C}_6\text{H}_4\text{Cl}_2$, 1,3- $\text{C}_6\text{H}_4\text{Cl}_2$, hydrogen chloride in diethyl ether 1.0 M, superhydride solution in THF 1.0 M (Aldrich) were used as received. $\text{Cp}^*\text{Re}(\text{CO})_3$ and $\text{Cp}^*\text{Re}(\text{CO})_2\text{N}_2$ were synthesized following literature procedures.^{11,17} Photochemical reactions were carried out at 350 nm with a Rayonet RPR 100 photoreactor in quartz tubes. Infrared spectra were recorded in solution (CaF_2 cell) on a Perkin-Elmer FT-1605 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded at -10°C or at room temperature, on a Bruker AC 400 instrument. All ^1H NMR chemical shifts were referenced using the chemical shifts of residual solvent resonances. ^{13}C NMR chemical shifts were referenced to solvent peaks.

4.2 Preparation of $\text{trans-Cp}^*\text{Re}(\text{CO})_2(2,5\text{-C}_6\text{H}_3\text{Cl}_2)\text{Br}$ (**1c**).

$\text{Cp}^*\text{Re}(\text{CO})_3$ (200 mg, 0.494 mmol) was dissolved in 15 mL of a saturated solution of 2-bromo-1,4-dichlorobenzene in hexanes. The resulting solution was bubbled with nitrogen for 10 min and then irradiated for 6 h. The solution turned orange-yellow. The solvent was evaporated under vacuum, and the resulting yellow solid was chromatographed over neutral alumina. Elution with hexanes resulted in a mixture of unreacted $\text{Cp}^*\text{Re}(\text{CO})_3$ and 2-bromo-1,4-dichlorobenzene. Elution with hexanes/ CH_2Cl_2 (1:5) moved an orange band, from which $\text{trans-Cp}^*\text{Re}(\text{CO})_2(2,5\text{-C}_6\text{H}_3\text{Cl}_2)\text{Br}$, **1c** (45 mg, 0.074 mmol), was isolated as a orange solid. Yield: 15%. IR (CH_2Cl_2 , $\nu(\text{CO})$, cm^{-1}): 2036 (s), 1956 (vs). ^1H NMR (CDCl_3) δ : 1.84 (s, 15H, Cp^*), 7.06 (dd, $J = 1.5$; 7.5 Hz, 1H, $\text{C}_6\text{H}_3\text{Cl}_2$), 7.36 (d, $J = 7.5$ Hz, 1H, $\text{C}_6\text{H}_3\text{Cl}_2$), 7.77 (d, $J = 1.5$ Hz, 1H, 2,5- $\text{C}_6\text{H}_3\text{Cl}_2$).

Mass spectrum (EI, based on ^{187}Re , ^{79}Br , ^{35}Cl) m/z : 602 (M^+), 574 ($\text{M}^+ - \text{CO}$), 546 ($\text{M}^+ - 2\text{CO}$). Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{Cl}_2\text{O}_2\text{BrRe}$: C, 35.83; H, 3.01. Found: C, 35.98; H, 3.11.

4.3. Chemical reduction of $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{Cl}$

$\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{Cl}$ 0.100 mmol were dissolved in THF (15 mL) at -78°C under nitrogen and super-hydride solution in THF/ 1.0 M (0.210 mmol) was added. The IR spectrum of the solution showed the complete disappearance of the starting material and new CO absorptions around 1855 (s) and 1738 (s) cm^{-1} . Then HCl solution in diethyl ether (0.150 mmol) was added at -10°C . The IR spectrum of the mixture showed new CO absorptions around 2015 (s) and 1940 (vs) cm^{-1} . The solvent was pumped off and cold hexane (3x10 mL) was added to the solid residue. The solution was filtered through Celite under a nitrogen atmosphere and the solvent was concentrated under reduced pressure. The IR spectra of the complexes $\text{trans-Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})(\text{H})$ exhibited two $\nu(\text{CO})$ absorption bands at about 2022 (s), 1960 (vs) cm^{-1} , in hexane solution. The high field region of the ^1H NMR spectra of these derivatives, measured in toluene- d_8 , at -10°C , showed a singlet at about -9.60 ppm (Re-H).

4.4. Photochemical reactions

$\text{Cp}^*\text{Re}(\text{CO})_2\text{N}_2$ (50 mg, 0.123 mmol) were dissolved in a saturated hexane solution of 1,2,3,4-tetrachlorobenzene (**2a**) or neat 1,2,4-trichlorobenzene (**2b**), 1,4-dichlorobenzene (**2c**) and 1,3-dichlorobenzene (**2d**) and the solutions were purged with N_2 for 10 min and irradiated at $\lambda = 300$ nm for 40 min.

4.4.1 $\text{Cp}^*\text{Re}(\text{CO})_2(5,6\text{-}\eta^2\text{-}1,2,3,4\text{-C}_6\text{H}_2\text{Cl}_4)$ (**2a**)

Complex **2a** was isolated as a pale brown solid, after crystallization from hexane at -18°C , 30 mg (0.051 mmol) yield: 41%. IR (hexane, $\nu(\text{CO})$ cm^{-1}): 1977 (s), 1915 (s). ^1H NMR (toluene- d_8) δ : 1.44 (s, 15 H, C_5Me_5), 2.96 (s, 2H, $\text{C}_6\text{H}_2\text{Cl}_4$). $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8) δ : 9.3 (s, C_5Me_5), 48.0 (s, coordinated,

$C_6H_2Cl_4$), 97.5 (s, C_5Me_5), 115.0 (s, non-coordinated, $C_6H_2Cl_4$), 140.5 (s, non-coordinated, $C_6H_2Cl_4$), 201.1 (s, CO).

4.4.2 $Cp^*Re(CO)_2(5,6-\eta^2-1,2,4-C_6H_3Cl_3)$ (**2b**)

Complex **2b** was isolated as a pale brown solid, 31 mg (0.056 mmol) yield: 45%. IR (hexane, $\nu(CO)$ cm^{-1}): 1974 (s), 1912 (s). 1H NMR (toluene- d_6) δ : 1.47 (s, 15 H, C_5Me_5), 2.85 (dd, $J = 1.3$, 8.9 Hz, 1H, $C_6H_3Cl_3$), 3.00 (d, $J = 8.9$ Hz, 1H, $C_6H_3Cl_3$), 6.06 (d, $J = 1.3$, 1H, $C_6H_3Cl_3$). $^{13}C\{^1H\}$ NMR (toluene- d_6) δ : 9.4 (s, C_5Me_5), 48.5 (s, coordinated, $C_6H_3Cl_3$), 50.3 (s, coordinated, $C_6H_3Cl_3$), 97.6 (s, C_5Me_5), 118.0 (s, non-coordinated, $C_6H_3Cl_3$), 120.1 (s, non-coordinated, $C_6H_3Cl_3$), 137.0 (s, non-coordinated, $C_6H_3Cl_3$), 142.8 (s, non-coordinated, $C_6H_3Cl_3$), 201.4 (s, CO), 202.4 (s, CO).

4.4.3 $Cp^*Re(CO)_2(2,3-\eta^2-1,4-C_6H_4Cl_2)$ (**2c**)

Complex **2c** was isolated as a pale brown solid, 21 mg (0.040 mmol) yield: 33%. IR (hexane, $\nu(CO)$ cm^{-1}): 1970 (s), 1908 (s). 1H NMR (toluene- d_6) δ : 1.55 (s, 15 H, C_5Me_5), 3.13 (s, coordinated CH, 2H, $C_6H_4Cl_2$), 5.84 (s, non-coordinated CH, 2H, $C_6H_4Cl_2$). $^{13}C\{^1H\}$ NMR (toluene- d_6) δ : 9.7 (s, C_5Me_5), 51.9 (s, coordinated, $C_6H_4Cl_2$), 95.6 (s, C_5Me_5), 117.0 (s, non-coordinated, $C_6H_4Cl_2$), 140.6 (s, non-coordinated, $C_6H_4Cl_2$), 200.0 (s, CO).

4.4.4 $Cp^*Re(CO)_2(4,5-h^2-1,3-C_6H_4Cl_2)$ (**2d**)

Complex **2d** was isolated as a pale brown solid, 19 mg (0.036 mmol) yield: 29%. IR (hexane, $\nu(CO)$ cm^{-1}): 1964 (s), 1903 (s). 1H NMR (toluene- d_6) δ : 1.53 (s, 15 H, C_5Me_5), 3.21 (t, $J = 7.2$ Hz, 1H, $C_6H_4Cl_2$), 5.07 (broad singlet, 2H, $C_6H_4Cl_2$), 6.25 (s, 1H, $C_6H_4Cl_2$). $^{13}C\{^1H\}$ NMR (toluene- d_6) δ : 9.6 (s, C_5Me_5), 49.0 (s, coordinated, $C_6H_4Cl_2$), 50.9 (s, coordinated, $C_6H_4Cl_2$), 97.7 (s, C_5Me_5), 118.5 (s, non-coordinated, $C_6H_4Cl_2$), 120.7 (s, non-coordinated, $C_6H_4Cl_2$), 137.1 (s, non-coordinated, $C_6H_4Cl_2$), 143.0 (s, non-coordinated, $C_6H_4Cl_2$), 201.2 (s, CO), 202.2 (s, CO).

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