Intermolecular C−Cl Activation Reaction of (η⁵-C₅R₅)Re(CO)₃ (R = H, Me) with Pentachlorobenzene: X-ray Structure of *cis*- and *trans*-(η⁵-C₅Me₅)Re(CO)₂(2,3,4,5-C₆HCl₄)Cl and Its Conversion to (η⁶-C₅Me₄CH₂)Re(CO)₂(2,3,4,5-C₆HCl₄)

A. Hugo Klahn,*,† Adriana Toro,† Beatriz Oelckers,† Gonzalo E. Buono-Core,†
Victor Manriquez,‡ and Oscar Wittke‡

*Instituto de Quimica, Universidad Catolica de Valparaiso, Casilla 4059, Valparaiso, Chile,
and Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile*

Photochemical reaction of (η⁵-C₅R₅)Re(CO)₃ (R = H, Me) with pentachlorobenzene (λ = 350 nm, hexane solution) yields *trans*-(η⁵-C₅R₅)Re(CO)₂(2,3,4,5-C₆HCl₄)Cl (*trans*-**1**, R = Me; **2**, R = H) formed by insertion of the fragment (η⁵-C₅R₅)Re(CO)₂ into the C−Cl bond of C₆-HCl₅. Complex *trans*-**1** converts to *cis*-(η⁵-C₅Me₅)Re(CO)₂(2,3,4,5-C₆HCl₄)Cl (*cis*-**1**) in MeCN. The stereochemistry of both isomers has been assigned from examination of ν(CO) IR intensities and is supported by an X-ray structure determination of both complexes. A pure sample of either *trans*-**1** or *cis*-**1** dissolved in organic solvents produces an equilibrium mixture. In nonpolar solvents *trans*-**1** is favored, whereas *cis*-**1** is more stable in polar solvents. A mixture of *cis*-**1** and *trans*-**1** in CH₂Cl₂ solution reacts on silica gel to produce the new tetramethylfulvene complex (η⁶-C₅Me₄CH₂)Re(CO)₂(2,3,4,5-C₆HCl₄), **3**.

Introduction

For many years, it has been shown that cyclopentadienylrheniumtricarbonyl complexes, (η⁵-C₅R₅)Re(CO)₃ (R = H, Cp and R = Me, Cp*) serve as useful precursors to produce dicarbonyl complexes of the type (η⁵-C₅R₅)-Re(CO)₂L,[1] when they are UV-irradiated in the presence of THF,[2,3] phosphines,[2,4] phosphites,[2,4] or alkenes.[5] (η⁵-C₅R₅)Re(CO)₃ also reacts photochemically in the presence of H₂[6] and R₃SiH[7] to give the corresponding oxidative addition products (η⁵-C₅R₅)Re(CO)₂H(R′) (R′ = H and R₃Si). However, when they are irradiated in hydrocarbon solvents, e.g., hexane and benzene, (η⁵-C₅R₅)₂Re₂(CO)₅[8,9] and [Cp*Re(CO)₂]₂(μ-η²-η²-C₆H₆)[10] are formed, respectively. More recently, we have demonstrated that these complexes are appropiate photo-

precursors for studying the coordination and C−F bond activation of hexafluorobenzene. For instance, upon irradiation of CpRe(CO)₃ in neat C₆F₆, the complex CpRe(CO)₂(η²-C₆F₆) is formed,[11] whereas Cp*Re(CO)₃ produces the fulvene complex (η⁶-C₅Me₄CH₂)Re(CO)₂-(C₆F₅) under similar conditions.[12,13] Unfortunately, the scarce photochemical reactions of transition metal complexes with chloroarenes described in the literature contrast with numerous examples of stoichiometric and catalytic transformations of these substrates performed under non-photochemical conditions, mediated by metal compounds.[14] As far as we are aware, Co₂(CO)₈ has been reported to catalyze carbonylation of a number of chloroarenes under irradiation (λ = 350 nm),[15] and very recently, Sutton and Leiva reported the photoreaction of Cp*Re(CO)(L)N₂ (L = phosphites and PMe₂Ph) with chlorobenzene to yield the corresponding Cp*Re(CO)-(L)(Ph)Cl complex.[16] By considering our interest in the chemistry and photochemistry of the organometallic rhenium complexes and the significant interest in the reductive dechlorination of aryl chlorides, mainly for the neutralization of toxic polychloroaromatics (e.g., poly-

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‡ Universidad de Chile.
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Scheme 1

Figure 1. X-ray structure of *cis*-Cp*Re(CO)$_2$(2,3,4,5-C$_6$-HCl$_4$)Cl (*cis*-**1**) drawn with 50% probability displacement ellipsoids.
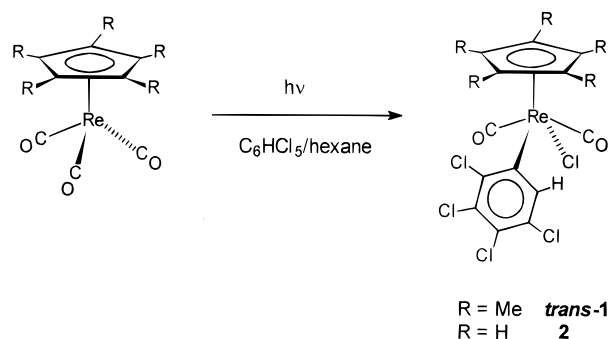
chlorobiphenyls, PCBs) in the environment,[17] we were prompted to study the photoreactions of the cyclopentadienyl rhenium complexes, described above, with polychlorinated arenes. Our initial studies also considered hexachlorobenzene; however, the low solubity of this compound in hexane precluded us from observing any intermolecular reaction with the rhenium complexes. Instead, decomposition of the organic and organometallic species was observed under several experimental conditions examined. Then, we turned to study the photoreactions with the more soluble pentachlorobenzene.

Results and Discussion

Photolysis of Cp*Re(CO)$_3$ or CpRe(CO)$_3$ ($\lambda = 350$ nm) in a saturated hexane solution of C$_6$HCl$_5$ at room temperature, for 18 and 2 h, respectively, produced one major dicarbonyl product (Scheme 1). Much longer irradiation times produced significant amounts of the corresponding dichloro complexes (η^5-C$_5$R$_5$)Re(CO)$_2$Cl$_2$. In both cases, the products were isolated as air-stable red-orange crystals by sublimation of the excess of pentachlorobenzene and unreacted tricarbonyl complex and subsequent recrystallization from CH$_2$Cl$_2$/hexane and were identified as *trans*-(η^5-C$_5$R$_5$)Re(CO)$_2$(2,3,4,5-C$_6$HCl$_4$)Cl, R = Me (*trans*-**1**) and R = H (**2**). No evidence was found for the formation of the corresponding *cis* isomers or products resulting from coordination or C−H bond activation of C$_6$HCl$_5$. This result correlates well with the higher C−H bond strength when compared to that of the C−Cl bond (E$_{C-H(C6H6)}$ = 461 kJ mol^{-1}, E$_{C-Cl(C6H5Cl)}$ = 398 kJ mol^{-1}).[18] In this regard, very recently, we have demonstrated that the dominant photochemical reaction of C$_6$HF$_5$ and 1,2,4,5-C$_6$H$_2$F$_4$ with (η^5-C$_5$R$_5$)Re(CO)$_3$ is C−H bond activation of the fluoroarene, in agreement with the strength of the C−F vs C−H bonds.[19]

The presence of the C$_6$HCl$_4$ ligand in these complexes was inferred from a single resonance observed in the aromatic region in the ^{1}H NMR spectra. The *trans* orientation of the carbonyl groups was assigned on the basis of the relative intensities of the ν(CO), observed in the IR spectra; the higher wavenumber symmetric stretching mode (ν_s) is weaker than the lower wavenumber stretching mode (ν_{as}). Similar patterns of
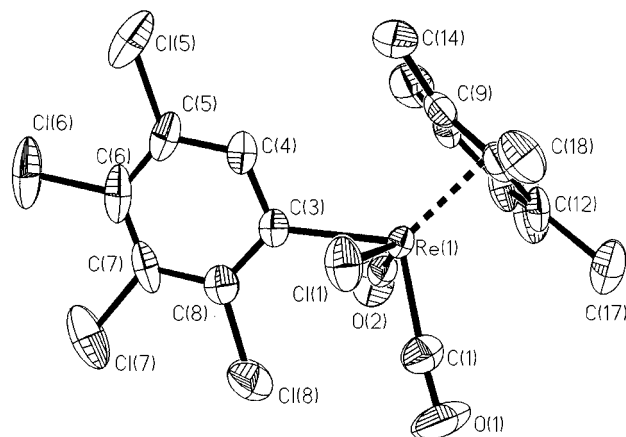
intensity have been observed in other dicarbonyl rhenium complexes possesing a four-legged piano-stool type of structure.[20] The appearance of a single resonance for CO in the ^{13}C NMR spectra is further evidence for the *trans* orientation of the carbonyl ligands in this type of molecule.

X-ray crystallographic analysis of *trans*-**1** (Figure 2) confirms the *trans* geometry deduced from the infrared ν(CO) relative intensities. In addition, it shows that the C−Cl bond in the *ortho* position with respect to the hydrogen atom in pentachlorobenzene has been cleaved. According to our knowledge, the exclusive substitution of the chlorine situated in the *ortho* position of C$_6$HCl$_5$ is unprecedented in the literature, but it seems to follow the same pattern observed in the dehalogenation of 1,2,4-trichlorobenzene catalyzed by Rh(PPh$_3$)$_3$Cl, which occurs preferentially at the less hindered 4-position.[21] This observation can be related to the capacity of the photogenerated rhenium fragment (η^5-C$_5$R$_5$)Re(CO)$_2$, for coordinating the *ortho* chlorine atom of the C$_6$HCl$_5$, prior to the oxidative addition. Gladysz has documented the coordination of chlorobenzene to rhenium in the complex [Cp*Re(PPh$_3$)(NO)(ClC$_6$H$_5$)][BF$_4$], but the C−Cl activation product could not be conclusively identified.[22]

Complexes *trans*-**1** and **2** are stable in the solid state at room temperature with respect to isomerization. However, treatment of complex *trans*-**1** in acetonitrile, at room temperature, results in partial isomerization to *cis*-Cp*Re(CO)$_2$(2,3,4,5-C$_6$HCl$_4$)Cl, *cis*-**1**, which could be isolated in 90% yield, after recrystallization from CH$_2$Cl$_2$/hexane at 4 °C. The ^{1}H NMR spectrum of a freshly prepared sample of *cis*-**1** in CDCl$_3$ at room temperature showed the presence of a single compound. However, the ^{13}C NMR spectrum, in the same solvent (in which is less soluble than its *trans* isomer) after about 4 h scaning, showed also resonances for *trans*-**1**. The appearance of two resonances in the CO region in the ^{13}C NMR spectrum of *cis*-**1** indicates the *cis* orientation of the carbonyl ligands in this type of molecule.

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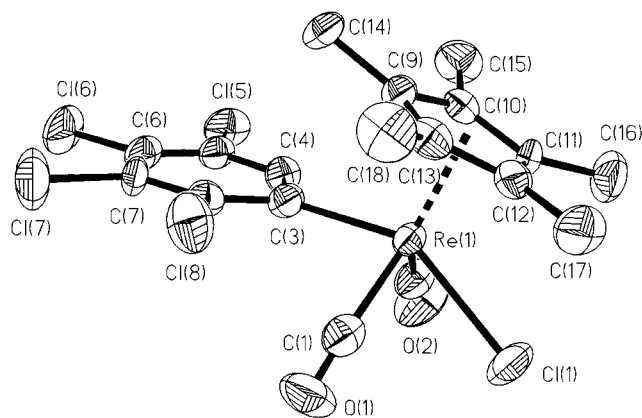
Figure 2. X-ray structure of *trans*-Cp*Re(CO)$_2$(2,3,4,5-C$_6$-HCl$_4$)Cl (*trans*-**1**) drawn with 50% probability displacement ellipsoids.
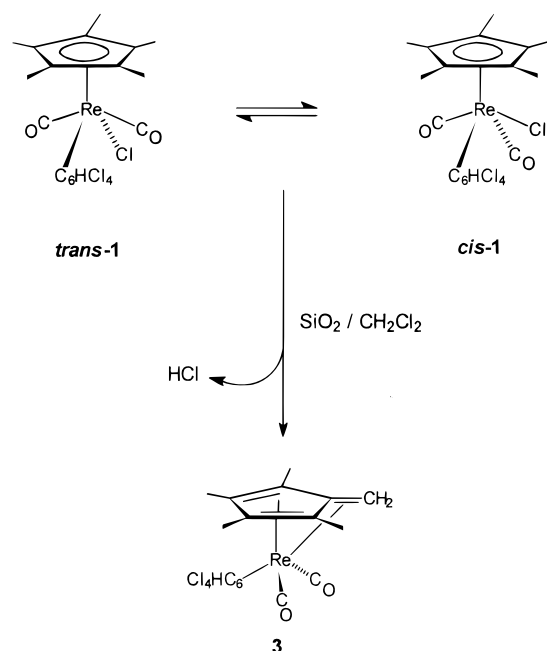
Scheme 2

Table 1. Equilibrium Constants (K_{eq}) at 25 °C for the *trans*-Cp*Re(CO)$_2$(2,3,4,5-C$_6$HCl$_4$)Cl ⇌ *cis*-Cp*Re(CO)$_2$(2,3,4,5-C$_6$HCl$_4$)Cl Isomerization Process[a]

solvent	K_{eq}[b]
C$_6$D$_6$	0.33
CDCl$_3$	0.69
(CD$_3$)$_2$CO	2.2
CD$_3$CN	3.0

[a] Calculated from integration of peaks in the ¹H NMR spectra.
[b] Estimated error limits ±5%.

Furthermore, the X-ray structure of *cis*-**1** (see below and Figure 1) confirms the above assumption.

Although the isomers of Cp*Re(CO)$_2$(2,3,4,5-C$_6$HCl$_4$)-Cl are stable in the solid state with respect to interconversion, freshly prepared solutions of either *trans*-**1** or *cis*-**1** in several organic solvents produce equilibrium mixtures (Scheme 2, Table 1), as evidenced by integration of the Cp* resonances in the ¹H NMR spectra, which showed the same *trans*-**1**:*cis*-**1** ratio. The K_{eq} values shown in Table 1 indicate that complex *trans*-**1** is favored in nonpolar organic solvents, whereas com-

Table 2. Crystal Structure Data for Complexes *cis*-1 and *trans*-1

	cis-1	*trans*-1
empirical formula	C$_{18}$H$_{16}$Cl$_5$O$_2$Re	C$_{18}$H$_{16}$Cl$_5$O$_2$Re
cryst size, mm³	0.40 × 0.18 × 0.10	0.50 × 0.40 × 0.15
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
unit cell dimens		
a, Å	8.581(2)	7.4400(10)
b, Å	13.252(3)	8.572(2)
c, Å	18.272(4)	17.645(3)
α, deg	90	97.63(2)
β, deg	94.65(2)	95.37(2)
γ, deg	90	111.850(10)
V, Å³	2071.0(8)	1022.6(3)
Z	4	2
D_{calcd}, g cm⁻³	2.013	2.039
μ(Mo Kα), mm⁻¹	6.523	6.605
F(000)	1200	600
θ range for data collection, deg	2.24–22.56	2.36–22.55
h	0 to 9	−4 to 8
k	−14 to 14	−9 to 8
l	−19 to 19	−19 to 18
no. of reflns collected	9032	3042
no. of unique reflns	2720	2672
no. of obs reflns ($I > 2\sigma(I)$)	2377	2607
final R indices ($I > 2\sigma(I)$)	R1 = 0.0229, wR2 = 0.0561	R1 = 0.0340, wR2 = 0.0899
R indices (all data)	R1 = 0.0287, wR2 = 0.0605	R1 = 0.0347, wR2 = 0.0906
goodness-on-fit on F^2	1.108	1.077
largest diff peak and hole, e Å⁻³	0.675, −0.942	1.156, −1.119

plex *cis*-**1** is the most stable species in polar solvents. Thus, *trans*-**1** to *cis*-**1** conversion depends on the polarity of the solvent. This result contrasts with the unidirectional isomerization (*cis* to *trans*) observed for the dibromo complexes ((η^5-C$_5$H$_4$R)Re(CO)$_2$Br$_2$ (R = Me, Et, t-Bu, SiMe$_3$) in benzene and chloroform[23] and for the dihydride complex (η^5-C$_5$H$_5$)Re(CO)$_2$H$_2$ in THF,[24] at room temperature.

Despite the considerable number of dicarbonylcyclopentadienyl rhenium complexes, possessing a four-legged piano-stool type of structure, described in the literature in the past decade, crystallographic information is still scarce, especially for those containing a *cis* or *lateral* orientation of the carbonyl groups. With the aim of providing typical metrical data for this class of compounds, containing identical ligands, X-ray structure analyses of *cis*-**1** and *trans*-**1** were conducted. Table 2 provides a listing of the crystal structure and refinement data, Table 3 shows selected bond distances and angles, and Figures 1 and 2 show the molecular structure of *cis*-**1** and *trans*-**1**. As can be noted in the latter, the rhenium atom can be considered seven-coordinated, assuming the Cp* ring functions as a three-coordinated monoanion. The Re–Cp* (centroid) (1.995 Å for *cis*-**1** and 1.971 Å for *trans*-**1**) and Re–C(Ar^{Cl}) distances in *cis*-**1** and *trans*-**1** are quite similar and evidently insensitive to the differing *cis* or *trans* arrangement of the carbonyl ligands in the two structures. The lack of reported Re–Cl bond distances for similar rhenium complexes precludes us from a comparison with the ones found in *cis*-**1** and *trans*-**1**. However, and as expected, both distances are shorter when compared with the Re–

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for *trans*-1 and *cis*-1

	trans-1	*cis*-1
Re(1)C(1)	1.965(9)	1.921(6)
Re(1)C(2)	1.931(9)	1.941(6)
Re(1)C(3)	2.197(8)	2.197(5)
Re(1)C(11)	2.258(7)	2.273(5)
Re(1)C(10)	2.296(7)	2.302(5)
Re(1)C(12)	2.302(7)	2.367(5)
Re(1)C(9)	2.352(7)	2.350(5)
Re(1)C(13)	2.363(7)	2.383(5)
Re(1)Cl(1)	2.488(2)	2.4377(14)
O(1)C(1)	1.132(10)	1.141(7
O(2)C(2)	1.147(10)	1.114(6)
C(9)C(13)	1.435(11)	1.445(7)
C(9)C(10)	1.442(11)	1.419(8)
C(10)C(11)	1.417(11)	1.443(8)
C(11)C(12)	1.430(11)	1.417(8)
C(12)C(13)	1.406(11)	1.406(8
C(2)Re(1)C(1)	99.8(3)	82.3(2)
C(2)Re(1)C(3)	80.5(3)	74.80(19)
C(1)Re(1)C(3)	83.8(3)	107.8(2)
C(2)Re(1)Cl(1)	75.1(2)	141.53(16)
C(1)Re(1)Cl(1)	73.8(2)	81.44(19)
C(3)Re(1)Cl(1)	143.1(2)	77.43(13)
O(1)C(1)Re(1)	176.0(7)	175.3(6)
O(2)C(2)Re(1)	176.5(8)	179.5(5)

Br and Re−I bond length observed in the same class of complexes (*trans*-CpRe(CO)$_2$(C$_6$HF$_4$)Br, 2.6113(2) Å;[25] *trans*-(η^5-C$_5$Me$_4$CH$_2$Br)Re(CO)$_2$(C$_6$F$_5$)Br, 2.6254(13) Å;[13] and *trans*-Cp*Re(CO)$_2$(C$_6$H$_5$)I, 2.803(1) Å[26]). The most interesting features of these structures are the inter-bond angles relating the carbonyls and the (Ar^{Cl})−Re−Cl moiety, which allow a comparison of the two distinct enviroments of the same ligands, on the basis of the square pyramid geometry. As expected, the OC−Re−CO angle in *trans*-1 (99.8°) is larger than in *cis*-1 (82.3°). The value of 99.8° for *trans*-1 is quite similar to that observed in several other dicarbonyl rhenium complexes possessing the same stereochemistry: (*trans*-CpRe(CO)$_2$-(C$_6$HF$_4$)Br, 99.7°;[25] *trans*-CpRe(CO)$_2$(SnPh$_3$)$_2$, 100.5°;[27] *trans*-(η^5-C$_5$Me$_4$CH$_2$Br)Re(CO)$_2$(C$_6$F$_5$)Br, 100.5°[13]). On the other hand, the carbonyl interbond angle of 82.3° found for *cis*-1 can be compared to that determined for *cis*-Cp*Re(CO)$_2$I$_2$ (78.5°), to our knowledge, the only other complex of this type studied by X-ray crystallography.[20]

In an attempt to separate a mixture of the two isomers of **1** by column chromatography on silica gel, we observed a yellow band when the column was first washed with hexane. We found that longer contact time of the mixture of complex **1** with silica gel increased the proportion of the yellow band, and 32% conversion was obtained after 6 days (Scheme 2). The orange-yellow solid isolated after solvent evaporation was identified as the tetramethylfulvene complex (η^6-C$_5$Me$_4$CH$_2$)Re-(CO)$_2$(2,3,4,5-C$_6$HCl$_4$), **3**. This unexpected product presumably resulted by HCl elimination from either *trans*-1 or *cis*-1, which is absorbed on the silica gel. Support for HCl elimination is provided by HF formation in the reaction of the photogenerated fragment Cp*Re(CO)$_2$ with C$_6$F$_6$ to produce the complex (η^6-C$_5$Me$_4$CH$_2$)Re-

(CO)$_2$(C$_6$F$_5$).[12,13] We have also demonstrated that the fulvene complex (η^6-C$_5$Me$_4$CH$_2$)Re(CO)$_2$(C$_6$F$_5$) reacts with HCl to regenerate the Cp* ligand and form Cp*Re-(CO)$_2$(C$_6$F$_5$)Cl,[13] and accordingly we believe that the silica gel plays the essential role of removing the HCl formed in the reaction.

The fulvene complex **3** was isolated as an air-stable microcrystalline orange-yellow solid, soluble in most organic solvents, and exhibited a mass spectrum which showed M$^+$, [M − CO]$^+$, and [M − 2CO]$^+$ peaks. The presence of the tetramethylfulvene ligand in **3** was easily identified since its showed ^{1}H and ^{13}C NMR parameters similar to those recently reported by our laboratory.[12,13,19] Two extreme canonical forms, η^6-conjugated triene (tetramethylfulvene) **3a** or η^5-tetram-ethylcyclopentadienyl σ-alkyl ("tucked-in") **3b**, can be considered for the bonding of the (η^6-C$_5$Me$_4$CH$_2$) ligand. The chemical shift of the methylene group in the ^{1}H NMR spectrum (δ 4.08) and the C−H coupling constant (δ 48.5, J_{CH} 163 Hz) observed in the ^{13}C-gated spectrum imply that the ligand is bound to Re in a η^6-triolefinic fashion, **3a**. Values of J_{CH} > 150 Hz for the methylene carbon have been taken to indicate an sp^2-hybridized carbon in several η^6-C$_5$R$_4$CH$_2$ complexes.[28] The ^{1}H NMR spectrum of **3** also shows a set of weak resonances in the δ 1.57−4.77 region. They are assigned to a minor isomer with the (η^6-C$_5$Me$_4$CH$_2$) ligand rotated relative to the C$_6$HCl$_4$ group, i.e., a "*cis*" orientation between the CH$_2$ and the chloroaryl ligand. Under this situation all the methyl groups and the CH$_2$ protons are inequivalent. The proportion of the minor isomer in CDCl$_3$ is 12% at 295 K. Similar patterns of resonances have been observed in the tetramethylfulvene analogues (η^6-C$_5$Me$_4$CH$_2$)Re(CO)$_2$(aryl), aryl = C$_6$F$_5$, C$_6$F$_4$CF$_3$, and C$_6$HF$_4$.[12,13,19]

Experimental Section

General Procedures. All manipulations were carried out under nitrogen using standard Schlenk techniques. Photolysis reactions were carried out at 350 nm with a Rayonet RPR 100 photoreactor in Pyrex tubes. All solvents were purified and dried by conventional methods and distilled under nitrogen prior to use. Cp*Re(CO)$_3$ and CpRe(CO)$_3$ were prepared according to the procedures reported by Gladysz.[29] Pentachlo-robenzene (98%) from Aldrich was used as received. Infrared spectra were recorded in solution (NaCl cell) on a Perkin-Elmer FT-1605 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 200 and AMX 500 instruments. All ^{1}H NMR chemical shifts were referenced using the chemical shifts of residual solvent resonances (CDCl$_3$, δ 7.27; (CD$_3$)$_2$-CO, δ 2.05). ^{13}C NMR chemical shifts were referenced to solvent peaks (CDCl$_3$, δ 77.0; (CD$_3$)$_2$CO, δ 29.5, 205.7). Coupling assignments are indicated, where known. Mass spectra and elemental analyses were obtained at the Mi-croanalysis Department of Simon Fraser University, Canada, and the Centro de Instrumentación of Pontificia Universidad Católica de Chile, Santiago, Chile.

***trans*-Cp*Re(CO)$_2$(2,3,4,5-C$_6$HCl$_4$)Cl (*trans*-1).** Cp*Re-(CO)$_3$ (200 mg, 0.49 mmol) was dissolved in 35 mL of a saturated solution of pentachlorobenzene in hexanes. The resulting solution was bubbled with nitrogen for 10 min and then irradiated for 18 h. The mixture turned yellow, a dark

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precipitate was formed, and orange crystals were formed on the walls of the tube. The crystals were separated from the reaction mixture and then washed with cold hexanes. The solution was filtered and then evaporated to dryness under vacuum. The orange solid was sublimed at 6×10^{-2} Torr and 60 °C to eliminate unreacted Cp*Re(CO)$_3$ and the excess of pentachlorobenzene. The residue and the orange crystals were dissolved in the minimum amount of CH$_2$Cl$_2$, and a layer of hexanes was slowly poured into the flask. After 48 h, orange-reddish crystals were formed. Yield: 133 mg (43%). The compound decomposed over 150 °C, without melting. IR (hexanes, ν(CO), cm^{-1}): 2054 (m), 1973 (vs). ^{1}H NMR (CDCl$_3$) δ: 1.76 (s, 15H, Cp*), 7.80 (s, 1H, C$_6$HCl$_4$). ^{13}C{^{1}H} NMR (CDCl$_3$) δ: 9.7 (CH$_3$), 104.9 (C$_5$Me$_5$), 145.9 (C$_6$HCl$_4$), 192.7 (CO); other aromatic carbon resonances appear between 130.1 and 145.9, but they were not assigned due to the presence of the corresponding resonances for the *cis* isomer. Mass spectrum (EI, based on ^{187}Re, ^{35}Cl) *m*/*z*: 626 (M$^+$), 598 (M$^+$ − CO), 570 (M$^+$ − 2CO). Anal. Calcd for C$_{18}$H$_{16}$Cl$_5$O$_2$Re: C, 34.44; H, 2.57. Found: C, 34.55; H, 2.59.

cis-Cp*Re(CO)$_2$(2,3,4,5-C$_6$HCl$_4$)Cl (cis-1). Complex *trans*-Cp*Re(CO)$_2$(2,3,4,5-C$_6$HCl$_4$)Cl (100 mg, mmol) was suspended in acetonitrile (25 mL), and the mixture was stirred for 2 h at room temperature. At this time, almost all the starting complex was dissolved. The solution was filtered through glass wool and then evaporated to dryness under vacuum. The orange-reddish residue was recrystallized from hexanes/CH$_2$-Cl$_2$ diffusion at 4 °C. Complex *cis*-1 was isolated as red plates. Yield: 90 mg (90%). *cis*-1 starts to decompose above 130 °C. IR (hexanes, ν(CO), cm^{-1}): 2027 (vs), 1954 (m). ^{1}H NMR (CDCl$_3$) δ: 2.02 (s, 15H, Cp*), 7.00 (s, 1H, C$_6$HCl$_4$). ^{13}C{^{1}H} NMR (CDCl$_3$) δ: 10.4 (CH$_3$), 107.3 (C$_5$Me$_5$), 139.1 (C$_6$HCl$_4$), 202.5 (CO), 204.9 (CO); other aromatic carbon resonances appear between 130.1 and 145.9, but they were not assigned due to the presence of the corresponding resonances for the *trans* isomer. Mass spectrum (EI, based on ^{187}Re, ^{35}Cl) *m*/*z*: 626 (M$^+$), 598 (M$^+$ − CO), 570 (M$^+$ − 2CO). Anal. Calcd for C$_{18}$H$_{16}$Cl$_5$O$_2$Re: C, 34.44; H, 2.57. Found: C, 34.81; H, 2.61.

(η^6-C$_5$Me$_4$CH$_2$)Re(CO)$_2$(2,3,4,5-C$_6$HCl$_4$) (3). A 100 mg (0.159 mmol) portion of a mixture of *cis*-1 and *trans*-1 was dissolved in 50 mL of CH$_2$Cl$_2$. Silica gel (10 g) was added to the flask and the mixture stirred at room temperature for 6 days. Then the mixture was filtered, and the silica gel was washed with THF. The filtrate was evaporated under vacuum, and the orange residue was chromatographed over silica gel. A yellow band was eluted with hexanes, from which (η^6-C$_5$-Me$_4$CH$_2$)Re(CO)$_2$(2,3,4,5-C$_6$HCl$_4$), 3, was isolated (30 mg, 0.05 mmol, 32%). Hexanes/CH$_2$Cl$_2$ (4:1) moved an orange band, from which the unreacted mixture of the starting isomers was isolated (45 mg, mmol, 45%). 3 decomposed over 140 °C without melting. IR (hexanes, ν(CO), cm^{-1}): 2005 (vs), 1923 (vs). Mass spectrum (EI, based on ^{187}Re, ^{35}Cl) *m*/*z*: 590 (M$^+$), 534 (M$^+$ − 2CO). Anal. Calcd for C$_{18}$H$_{15}$Cl$_4$O$_2$Re: C, 36.56; H, 2.56. Found: C, 36.98; H, 2.48.

Major isomer (trans CH$_2$ and C$_6$HCl$_4$): ^{1}H NMR (CDCl$_3$) δ: 1.63 (s, 6H, C$_5$Me$_4$CH$_2$), 2.01 (s, 6H, C$_5$Me$_4$CH$_2$), 4.08 (s, 2H, C$_5$Me$_4$CH$_2$), 7.69 (s, 1H, C$_6$HCl$_4$). ^{13}C{^{1}H} NMR (CDCl$_3$) δ: 9.4 (q, J_{CH} = 129 Hz, ^{13}C{^{1}H} (gated) (C$_5$Me$_4$CH$_2$), 9.8 (q, J_{CH} = 129 Hz, ^{13}C{^{1}H} (gated) (C$_5$Me$_4$CH$_2$), 48.5 (t, J_{CH} = 163 Hz, ^{13}C{^{1}H} (gated) (C$_5$Me$_4$CH$_2$), 97.9 (C$_5$Me$_4$CH$_2$), 107.3 (C$_5$-Me$_4$CH$_2$), 108.5 (C$_5$Me$_4$CH$_2$), 128.2 (C$_6$HCl$_4$), 130.6 (C$_6$HCl$_4$), 144.2 (C$_6$HCl$_4$), 145.6 (CH−C$_6$HCl$_4$), 147.1 (C$_6$HCl$_4$), 199.1 (CO); one aromatic carbon resonance not observed.

Minor isomer (cis CH$_2$ and C$_6$HCl$_4$): ^{1}H NMR (CDCl$_3$) δ: 1.57 (s, 3H, C$_5$Me$_4$CH$_2$), 2.03 (s, 3H, C$_5$Me$_4$CH$_2$), 2.26 (s, 3H, C$_5$Me$_4$CH$_2$), 2.30 (s, 3H, C$_5$Me$_4$CH$_2$), 4.06 (d, J_{HH} 1.2 Hz, 1H, C$_5$Me$_4$CH$_2$), 4.77 (d, J_{HH} 1.2 Hz, 1H, C$_5$Me$_4$CH$_2$), 7.63 (s, 1H, C$_6$HCl$_4$).

trans-CpRe(CO)$_2$(2,3,4,5-C$_6$HCl$_4$)Cl (2). CpRe(CO)$_3$ (100 mg, 0.30 mmol) was dissolved in 15 mL of a saturated solution of pentachlorobenzene in hexanes. The resulting solution was bubbled with nitrogen for 10 min and then irradiated for 2 h. The solution turned brown. The solvent was evaporated under vacuum, and the resulting brown solid was chromatographed over silica gel. Elution with hexanes resulted in a mixture of unreacted CpRe(CO)$_3$ and pentachlorobenzene. Elution with hexanes/CH$_2$Cl$_2$ (7:3) moved an orange band, from which *trans*-CpRe(CO)$_2$(2,3,4,5-C$_6$HCl$_4$)Cl, 2 (20 mg, 0.036 mmol), was isolated as a red solid. Yield: 12%. IR (CH$_2$Cl$_2$, ν(CO), cm^{-1}): 2064 (m), 1985 (vs). ^{1}H NMR ((CD$_3$)$_2$CO) δ: 5.80 (s, 5H, C$_5$H$_5$), 8.32 (s, 1H, C$_6$HCl$_4$). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO) δ: 95.6 (s, C$_5$H$_5$), 121.7 (s, C$_{ipso}$−C$_6$HCl$_4$), 130.2 (C$_6$HCl$_4$), 131.5 (C$_6$HCl$_4$), 131.9 (C$_6$HCl$_4$), 146.5 (C$_6$HCl$_4$), 148.3 (CH−C$_6$HCl$_4$), 192.1 (s, CO). Mass spectrum (EI, based on ^{187}Re, ^{35}Cl) *m*/*z*: 556 (M$^+$), 528 (M$^+$ − CO), 500 (M$^+$ − 2CO). Anal. Calcd for C$_{13}$H$_6$Cl$_5$O$_2$-Re: C, 27.98; H, 1.07. Found: C, 28.01; H, 1.11.

Crystal Structure Determination. The intensity data were collected at 298 K on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation in the 2θ/θ scan mode with two standard reflections monitored every 100 reflections. Lattice parameters and their esd's were derived from the setting angles of 25 reflections with 5° ≤ 2θ ≤ 40°. The structures were solved by direct phase determination using the SHELXS-97 program. The positional and anisotropic thermal parameters for all non-hydrogen atoms were refined on F^2 against all reflections by full-matrix least-squares cycles using the SHELXL-97 program. The weighted R-factor R_w and goodness on fit are based on F^2, and conventional R-factors R are based on F. The hydrogen atom positions were calculated geometrically and were allowed to ride on their parent carbon atoms with fixed isotropic U. The atomic scattering factors were taken from the SHELXL-97 program. Selected interatomic distances and bond angles are included in Table 3. All other data are provided as Supporting Information.

Supporting Information Available: Tables of coordinates and displacement coefficients for the non-hydrogen atoms, all bond lengths and interbond angles, anisotropic displacement coefficients, and H atom coordinates and isotropic displacement coefficients for *cis*-1 and *trans*-1. This material is available free of charge via the Internet at http://pubs.acs.org.

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