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Journal of Organometallic Chemistry 662 (2002) 130–136

Journal of Organometallic Chemistry

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# Reactions of the tetramethylfulvene ligand coordinated to rhenium with hydrohalic acids and halogens: synthesis of dicarbonyl complexes with a 'four-legged piano-stool' structure containing mixed-halide ligands

Fernando Godoy, A. Hugo Klahn *, Beatriz Oelckers

*Instituto de Quimica, Universidad Catolica de Valparaiso, Casilla 4059, Valparaiso, Chile*

Received 6 June 2002; received in revised form 3 September 2002; accepted 3 September 2002

## Abstract

The new tetramethylfulvene complexes of rhenium $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2X$, ($X = Cl, Br, I$) have been synthesized from $(\eta^5\text{-}C_5Me_5)Re(CO)_2X_2$ by a two step procedure and fully characterized by elemental analysis, IR and NMR spectroscopies. Reaction of $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2X$ ($X = Br, I$) with $HX'$ regenerated the $(\eta^5\text{-}C_5Me_5)$ ligand with the formation of the mixed-halide complexes *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2XX'$ ($X = I, X' = Br$; $X = I, X' = Cl$; $X = Br, X' = Cl$), whereas, the reaction with halogens ($X'_2$) gave analogous complexes containing a halide substituted tetramethylcyclopentadienyl ligand, *cis*-$(\eta^5\text{-}C_5Me_4CH_2X')Re(CO)_2XX'$ ($X = Br, X' = I$; $X = I, X' = Br$). In both types of complexes the *cis* stereochemistry have been assigned on the basis of $\nu(CO)$ IR intensities and $\delta(CO)$ $^{13}C$-NMR.**4**

*Keywords:* Rhenium; Tetramethylfulvene; Mixed-halide; Ligands

## 1. Introduction

In recent years fulvene complexes with transition metals have attracted considerable interest from structural [1] and theoretical [2] points of view and also for their reactions dealing with the preparation of cyclopentadienyl ligands bearing a pendant arm, which may or may not contain a functional group. Considering the latter aspect, Behrens and co-workers [3] reported the reaction of the complex $(\eta^6\text{-}Fv)Cr(CO)_3$ (Fv = 6,6-dimethyl- or 1,2,3,4-tetraphenylfulvene) with tertiary phosphines to produce the Zwitterionic addition products $(\eta^5\text{-}C_5R_4CR'_2PR''_3)Cr(CO)_3$ ($R = H$ or Ph; $R' = H$ or Me; $R'' = Me$, Et or Ph). Reactions of the exocyclic methylene carbon have also been observed by Maitlis and co-workers [4], in the dimeric fulvene complex $[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2]_2$ with CO to produce $(\eta^5\text{-}C_5Me_4CH_2Cl)Ru(CO)_2Cl$ and by Miller and Sanner [5] in the complex $(\eta^6\text{-}C_5Me_4CH_2)Zr(\eta^5\text{-}C_5Me_5)(Ph)$ with iodine to yield the ring substituted phenyl iodide complex $(\eta^5\text{-}C_5Me_4CH_2I)Zr(\eta^5\text{-}C_5Me_5)(Ph)I$. On the other hand Koelle et al. [6] reported the preparation of several diastereomeric ruthenocene complexes by using the tetramethylfulvene complexes $[(\eta^6\text{-}C_5Me_4CH_2)\text{-}Ru(\eta^5\text{-}Cp^{pc})]^+$ ($Cp^{pc}$ = prochiral cyclopentadienyl ligands). More recently, Beckhaus et al. [7] found that the exocyclic carbon of the fulvene complex $(\eta^6\text{-}C_5H_4CHBu\text{-}t))Ti(\eta^5\text{-}C_5Me_5)Cl$ behave as a nucleophile. For instance, reactions with HX (X = Cl, OH, OR) gave mixed substituted titanocene complexes $(\eta^5\text{-}C_5H_4CH_2\text{-}Bu\text{-}t)Ti(\eta^5\text{-}C_5Me_5)(Cl)X$.

In previous publications, we have demonstrated that the rhenium fulvene complex $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2\text{-}(C_6F_5)$ can be used as a convenient starting material for the preparation of a series of pentamethylcyclopentadienyl complexes [8,9]. For instance, $(\eta^6\text{-}C_5Me_4\text{-}CH_2)Re(CO)_2(C_6F_5)$ reacts with HX (X = Cl, Br or I) to yield $(\eta^5\text{-}C_5Me_5)Re(CO)_2(C_6F_5)X$, while the reaction with $HBF_4$, in acetonitrile, produces the cationic deri-

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* Corresponding author. Tel.: +56-32-273174; fax: +56-32-212746
*E-mail address:* hklahn@ucv.cl (A. Hugo Klahn).

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PII: S0022-328X(02)01899-5

vative $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(C_6F_5)(NCMe)]^+$. Ring substituted cyclopentadienyl complexes $(\eta^5\text{-}C_5Me_4CH_2X)$-$Re(CO)_2(C_6F_5)X$ (X = Cl, Br and I), $[(\eta^5\text{-}C_5Me_4CH_2\text{-}OMe)Re(CO)_2(C_6F_5)]^-$ and $(\eta^5\text{-}C_5Me_4CH_2PMe_3)Re(CO)_2(C_6F_5)$ can be obtained by reaction of $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(C_6F_5)$ with halogens ($X_2$), $MeO^-$ and $PMe_3$, respectively.

As part of our continuing interest in the (pentamethylcyclopentadienyl)rhenium half-sandwich complexes, in this paper we report the synthesis of the new fulvene complexes $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2X$ (X = Cl, Br and I) and their reactions with hydrohalic acids (HX′) to produce the complexes $(\eta^5\text{-}C_5Me_5)Re(CO)_2\text{-}XX'$ and with halogens ($X'_2$, X = Cl, Br and I) to form $(\eta^5\text{-}C_5Me_4CH_2X')Re(CO)_2XX'$. To our knowledge, this is the first synthetic method reported for the preparation of the complete series of mixed-halide ligands coordinated to rhenium complexes possessing a four legged piano stool type of structure. A related complex $(\eta^5\text{-}C_5H_4CH_3)Re(CO)_2BrI$ in its *cis* and *trans* forms, have been briefy described by Cheng and Coville [10].

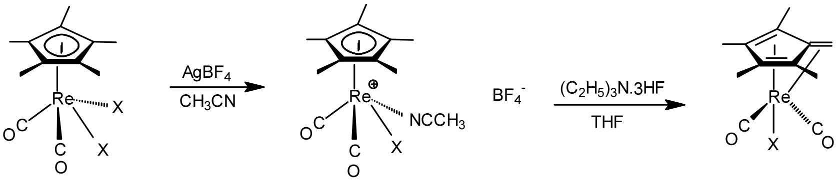
## 2. Results and discussion

### 2.1. Tetramethylfulvene complexes ($\eta^6$-$C_5Me_4CH_2$)Re(CO)$_2$X, X = Cl, Br, I

The previously reported tetramethylfulvene rhenium complex, $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(C_6F_5)$, was accessible directly from the photolysis of the $Cp^*Re(CO)_3$ in neat $C_6F_6$, via intermolecular C–F and intramolecular C–H bonds activation [8,9]. On the contrary, the synthesis of the title compounds involves a non-photochemical, two step procedure, similar to that recently reported from our laboratory for the preparation of $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(2,4,5\text{-}C_6Cl_3H_5)$ [11]. First, the cationic derivatives $[cis\text{-}Cp^*Re(CO)_2(NCMe)X]^+$ (X = I, **1a**; X = Br, **1b**; X = Cl, **1c**) are formed then react with the fluorinating agent $Et_3N\cdot3HF$ to produce the tetramethylfulvene rhenium halide complexes $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2X$, X = I, **2a**; X = Br, **2b**; X = Cl, **2c**, as shown in Scheme 1.

The cationic complexes **1a**–**c** were prepared, in almost quantitative yield, by halide abstraction from the corresponding dihalide complexes $cis\text{-}Cp^*Re(CO)_2X_2$ [12,13] by using $AgBF_4$ in acetonitrile. IR monitoring of these reactions did not show evidence for the formation of any halide-bridged species which could be formed in the reaction mixture. Presumably the excess of silver salt and the coordinating solvent (MeCN) used in these reactions prevent us in observing any intermediates, such those reported by Graham for the reaction of $CpFe(CO)_2I$ with $AgBF_4$ [14]. Complexes **1a**–**c** were isolated as single isomer, dark red microcrystalline solid spectroscopically pure samples. Unfortunately, they did not give satisfactory elemental analysis, even after several crystallization from MeCN–ether, presumably owing their extreme moisture sensitivity. They are insoluble in non-polar organic solvents, but dissolve in MeCN. The cationic nature of these complexes at rhenium was easily recognized by the frequency shift of the two infrared $\nu$(CO) absorption bands to higher wavenumber, when compared with their neutral precursors ($\Delta\nu \cong 26$ cm$^{-1}$). The *cis* stereochemistry was assigned by considering their two characteristic IR absorption intensities in the $\nu$(CO) region, where the higher wavenumber band is the more intense [12,15]. The appearance of two resonances for the carbonyl groups in the $^{13}$C-NMR spectra confirm the above assignment, and are in good agreement with those observed in the analogous cations $[cis\text{-}Cp^*Re(CO)_2(NCMe)(Ar^X)]^+$, $Ar^X = C_6F_5$ [9] and $2,4,5\text{-}C_6Cl_3H_2$ [11].

The reaction of the cations with $Et_3N\cdot3HF$, which has been recommended as an effective fluorinating agent [16], resulted in the formation of the new tetramethylfulvene complexes **2a**–**c**. The reaction presumably occurs via the neutral fluoro intermediate $Cp^*Re(CO)_2\text{-}(X)F$ which simultaneously undergoes a C–H bond activation of one of the ring methyl groups and the release of HF. A similar result was observed in an attempt to form the fluoro complex by direct metathesis reaction of $Cp^*Re(CO)_2I_2$ with the fluorinating agent $Me_3SnF$ [17] in THF. Even though, the fulvene complex **2a** was isolated in 37% yield, the dichloro and dibromo complexes $Cp^*Re(CO)_2X_2$ did not react with $Me_3SnF$,



**1a**; X = I
**1b**; X = Br
**1c**; X = Cl

2a; X = I
2b; X = Br
2c; X = Cl

Scheme 1. Synthesis of tetramethylfulvene rhenium halide complexes.

neither at room temperature nor by refluxing in THF. Then, the formation of complexes **2a**–**c** appears to follow the same reaction pattern to that previously reported for the analogous complexes ($\eta^6$-$C_5Me_4$-$CH_2$)Re$(CO)_2$(2,3,5-$C_6Cl_3H_2$) [11]. Complexes **2a**–**c** were isolated as red microcrystals in moderate (**2a**) or low yield (**2b**–**c**) after recrystallisation from hexanes at −10 °C. They are quite stable as solids under nitrogen, but solutions in organic solvents, slowly decompose to form the corresponding dihalide complex, as indicated by IR and $^1$H-NMR. The most stable was the iodo derivative **2a** while the least stable was the chloro derivative **2c**.

The spectral properties of these complexes are consistent with a single pure compound. Thus, their $^1$H- and $^{13}$C-NMR spectra exhibit only the resonances expected for two different ring methyl groups and a low field signal for the methylene group. For the latter, the C–H coupling constants observed in the $^{13}$C–$^1$H coupled spectra ($J_{C\text{–}H}$ ~ 162 Hz) agree well with the tetramethylfulvene ligand bound to rhenium in a $\eta^6$-triolefinic fashion [8,9,11] [18]. The 200 MHz, $^1$H-NMR spectra did not indicate the presence of isomers which could be formed by rotation of the ($\eta^6$-$C_5Me_4CH_2$) group with respect to the iodo ligand, such as those observed in the previouly reported tetramethylfulvene complexes containing a halogenated aryl ligand [8,9,11,18]. The IR spectra of these compounds exhibit two $\nu$(CO) absorption bands, with the lower wavenumber one much more intense. Based on the relative intensity pattern, as well as the correspondence between the IR frequencies of these complexes to those of other dicarbonyl derivatives possessing a four-legged piano-stool type of structure [12,15], we assign the two CO ligand in a *diagonal* or *trans* orientation in the complexes **2a**–**c**.

### 2.2. Mixed-halide complexes cis-Cp*Re$(CO)_2$XX′ and cis-($\eta^5$-$C_5Me_4CH_2X$)Re$(CO)_2$XX′

Considering the remarkable reactivity observed for the analogous fulvene complex ($\eta^6$-$C_5Me_4CH_2$)Re$(CO)_2(C_6F_5)$ toward hydrohalic acids HX and halogens $X_2$, (X = Cl, Br or I) [9], we decided to use these complexes for the preparation of the first examples of the mixed-halide rhenium complexes containing pentamethylcyclopentadienyl and halomethyltetramethylcyclopentadienyl ligands. It is surprising, in view of the current activity on carbonyl–halide chemistry in several laboratories, that prior to this work only one simple rhenium dicarbonyl mixed-halide complex was known [10] and reports of other transition metal carbonyl complexes bearing two distinct halide ligands have received little or no attention when compared with their homohalide analogues. For example, iron carbonyl halides *cis*-$Fe(CO)_4X_2$ (X = Cl, Br, I) are very well documented [19], but the mixed halides *cis*-$Fe(CO)_4IX$, X = Cl and Br, known since 1940 [20], have been characterised only very recently [21] by spectroscopic techniques in solution and vapour phase. Other organometallic mixed-halide derivatives reported are *fac*-$[Os(CO)F_3Br_2]^{2-}$, *mer*-$[Os(CO)F_3Cl_2]^-$ [22], $Mo(CO)_3$-$L_2$(I)Cl, (L = NCMe, $PPh_3$, $AsPh_3$, $SbPh_3$) [23] $W(CO)_3$(NCMe)L(I)Br (L = NCMe and PhCCPh) [24], $[Cp_2M(Cl)F]^+$ (M = Nb [25], Zr [26]) and $Ti(CO)_2$-$ClBr(dmpe)_2$ [27].

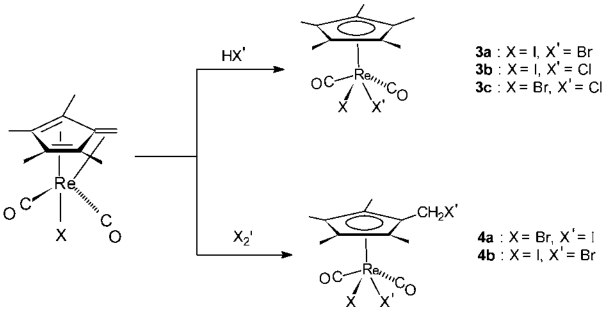
Two traditional synthetic methods have been used for the preparation of mixed-halide transition metal complexes. The more common method uses simple ligand exchange reactions with halogenating agents or cross halogenation of two different halide complexes. Although both type of reactions provide a convenient method for synthesizing mixed-halide compounds, in most of the cases pure species cannot be isolated, since mixtures are inevitably produced. However, these difficulties have been overcome by using detection techniques which allow the in situ characterization of individual species within the mixtures [21,22,26].

A different synthetic approach has been reported by Baker for the preparation and isolation of pure samples of molybdenum and tungten iodo–chloro and iodo–bromo derivatives, through oxidative addition reaction of interhalogen molecules IX (X = Cl, Br) to $M(CO)_3(NCMe)_3$ [23,24].

A non-traditional method for the preparation of the two isomers of ($\eta^5$-$C_5H_4CH_3$)Re$(CO)_2$BrI, described by Cheng and Coville uses a solid state photochemical reaction of an equimolar mixture of ($\eta^5$-$C_5H_4CH_3$)Re-$(CO)_2Br_2$ and ($\eta^5$-$C_5H_4CH_3$)Re$(CO)_2I_2$ or ($\eta^5$-$C_5H_4CH_3$)Re$(CO)_2Br_2$ and NaI supported on the surface of silica gel [10].

The new mixed-halide rhenium complexes are readily accessible by the reaction of the corresponding fulvene complex (**2a** or **2b**) with HX (**3a**–**c**) and $X_2$ (**4a**–**b**), as shown in Scheme 2.

The red microcrystalline solid compounds **3a**–**c**, were isolated as single products, analytically and spectrocopically pure samples. However, complexes **4a** and **4b** were always contaminated with small amount ( ~ 2%) of



Scheme 2. Reactions of tetramethylfulvene complexes with hydrohalic acids and halogens.

the corresponding homodihalide complexes *cis*-($\eta^5$-$C_5Me_4CH_2X$)Re$(CO)_2X_2$, (X = Br, I), which are probably formed by halogen exchange of the halide bound to rhenium with $X_2$. Attempts to separate these compounds from **4a** and **4b** were unsuccessful, even after several recrystallizations. The $^1$H- and $^{13}$C-NMR spectra of complexes **3a**–**c** and **4a**–**b**, exhibit only the resonances expected for a single isomer. Similarly, the IR spectra in each case consist of only two $\nu$(CO) absorptions in the carbonyl region. Like in the cationic complexes mentioned before, the *cis* orientation of the two CO ligands was assigned by considering the relative intensity of the two $\nu$(CO) bands and confirmed by the presence of two distinct resonances for the CO's in the $^{13}$C-NMR spectra (see Section 3). Additionally, both the IR and $^{13}$C-NMR spectra of the complexes **3a**–**c** showed some interesting features. Owing the close similarity of these complexes to their dihalide analogues, the two $\nu$(CO) absorptions lie approximately midway between comparable bands of the corresponding *cis*-Cp*Re$(CO)_2X_2$ [12]. This trend has been observed previously by Young for the complexes *cis*-Fe$(CO)_4$IX, X = Br, Cl) and their dihalide *cis*-Fe$(CO)_4X_2$ [21]. On the other hand, the two $\delta$(CO) observed in the $^{13}$C-NMR spectra correlate quite well with similar resonances reported for their homodihalide analogues. For instance, **3a** exhibits $\delta$(CO) at 199.3 and 202.0 whereas in *cis*-Cp*Re$(CO)_2X_2$, X = I and Br, the $\delta$(CO) occur at 199.5 and 201.5, respectively [12]. Thus we tentatively assign the high field resonance to the CO *cis* to the iodo ligand and the low field to the CO *cis* to bromo. This assignment is also in good agreement with similar data reported for the complexes CpMo$(CO)_3$X and *cis*-CpMo$(CO)_2(PPh_3)$X, (X = Cl, Br, I), for which was found that the $\delta$(CO) of both CO groups, *cis* or *trans* to X, depend on the electron donor properties of the halide ligand, the best electron donor halide has the most shielded carbonyl resonance [28].

The presence of four inequivalent resonances for the methyl groups in the $^1$H- and $^{13}$C-NMR spectra and two distinct hydrogen atoms for the methylene group observed in the $^1$H-NMR spectra for the (halogenomethyl)tetramethylcyclopentadienyl ligands in complexes **4a**–**b**, is further evidence of the *cis* stereochemistry assigned to these complexes. Additionally, the $^1$H-NMR spectra of these compounds showed small resonances in the methyl and methylene region which were assigned to the corresponding homohalide complexes *cis*-($\eta^5$-$C_5Me_4CH_2X$)Re$(CO)_2X_2$. To prove this assumption, the bromo and iodo complexes *cis*-($\eta^5$-$C_5Me_4CH_2X$)Re$(CO)_2X_2$ were prepared by an alternative method and characterized by IR, $^1$H-NMR and MS (see Section 3).

Each of the above *cis* isomers is stable in the solid state and in solution with respect to thermal isomerization. No isomerization was observed even in boiling toluene or *o*-xylene, though the complexes do not survive for long at these temperatures. Surprisingly, the mixed-halide complexes **3a**–**c** and **4a**–**b** showed little propensity to disproportionate to give the corresponding homodihalide derivative.

Previously, we have shown that tetramethylfulvene ligand bound to rhenium offers considerable opportunities to form ring functionalized cyclopentadienyl complexes or the regeneration of the Cp* ligand [8,9]. More recently, we have observed similar reactions of the complexes ($\eta^6$-$C_5Me_4CH_2$)Re$(CO)_2$X, (X = $C_6F_5$ and I), with organolithium reagents (RLi) to form complexes containing the ($\eta^5$-$C_5Me_4CH_2R$) ligands (R = methyl, allyl, 2-thiophene and 2-pyridine) [29]. The above reactions clearly demonstrate the electrophilic character of the methylene carbon of the tetramethylfulvene ligand. In the light of these results and similarly to the reactions observed for ($\eta^6$-$C_5Me_4CH_2$)Re$(CO)_2(C_6F_5)$ with hydrohalic acids [9], it seems unlikely that the acids HX (X = Cl, Br or I) attack directly at the methylene group of the complex ($\eta^6$-$C_5Me_4CH_2$)Re$(CO)_2$X to regenerate the Cp* ligand and form the dihalide or mixed-halide complexes. An alternative pathway that seems more likely to ocurr in these reactions, could involve initial attack of $H^+$ at rhenium followed by migration to the $CH_2$ group and coordination of $X^-$ to the metal. Intramolecular migration of the metal-bound hydrogen to a coordinated fulvene ligand has been shown in the reaction of $(C_5Me_3(CH_2)_2)Ta(H)_2(PMe_3)_2$ with CO affording Cp*Ta$(CO)_2(PMe_3)_2$ [30].

Consequently with the electrophilic character of the $CH_2$ group, the reaction of the fulvene complexes **2a**–**c** with halogens ($X_2'$) could involve direct attack of the halogen molecule at the metal center, leading to the cationic intermediates [($\eta^6$-$C_5Me_4CH_2$)Re$(CO)_2$(X)X$']^+$ which then could react at the methylene group with $X'^-$. Support for the formation of cationic intermediates in the reaction of complexes **2a**–**c** with HX and $X_2$ is given by the reaction of CpRe$(CO)_2PPh_3$ with trichloroacetic acid to produce [CpRe$(CO)_2(PPh_3)H]^+$ [31] and the reaction of Cp*Re$(CO)_3$ with halogens which yield the cationic complexes [Cp*Re$(CO)_3X]^+$ [12,13]. The mechanism of the reaction and the reason for the production of only the *cis* isomer of these mixed-halide complexes, remain as unanswered questions for further study.

## 3. Experimental

All manipulations were carried out under nitrogen using standard Schlenk techniques. All solvents were purified and dried by conventional methods, and distilled under nitrogen prior to use. The dihalide complexes Cp*Re$(CO)_2X_2$ (X = Cl, Br, I) were synthesized according to a procedure reported for our laboratory [13]. Infrared spectra were recorded in solution (NaCl cell) on a Perkin–Elmer FT-1605 spectrophotometer. $^1$H- and $^{13}$C-NMR spectra were measured on a Bruker AC 200 instrument. All $^1$H-NMR chemical shifts were referenced using the chemical shifts of residual solvent resonances ($CDCl_3$, $\delta$ 7.27). $^{13}$C-NMR chemical shifts were referenced to solvent peaks ($CDCl_3$, $\delta$ 77.0). Mass spectra and elemental analyses were obtained at the Chemistry Department of University of York, England, and at the Centro de Instrumentación of Pontificia Universidad Católica de Chile, Santiago, Chile.

### 3.1. Preparation of [*cis*-Cp*Re(CO)$_2$(MeCN)I]BF$_4$ (**1a**)

To a solution of *cis*-Cp*Re(CO)$_2$I$_2$ (100 mg, 0.158 mmol) in MeCN (15 ml) was added solid $AgBF_4$ (61 mg, 0.316 mmol) under stirring at room temperature (r.t.). The mixture was then stirred for 2 h at 40 °C in the dark. After this time, it changed from red to dark red with a white solid in suspension. At this step, the IR spectrum in MeCN showed only two $\nu$(CO) absorptions at 2051 and 1985 cm$^{-1}$. The solvent was pumped off and the residue was dissolved in 10 ml of $CH_2Cl_2$ and treated with a 10% NaCl aqueous solution in a separation funnel, in order to eliminate the excess of $Ag^+$. The organic layer was dried over anhydrous $Na_2SO_4$ and filtered through Celite. The red oily solid obtained after evaporation of $CH_2Cl_2$ was crystallized from MeCN–$Et_2O$ at −10 °C to give dark red crystals of **1a** in 95% yield. IR [$CH_3CN$, $\nu$(CO), cm$^{-1}$]: 2051 vs, 1985 s. $^1$H-NMR ($CD_3CN$): $\delta$ 2.20 (s, 15H, $CH_3$), 2.83 (s, 3H, $CH_3CN$); $^{13}$C{$^1$H}-NMR ($CD_3CN$): $\delta$ 4.78 (s, $CH_3CN$), 9.84 (s, $C_5Me_5$), 109.14 (s, $C_5Me_5$), 137.73 (s, MeCN), 191.22 (s, CO), 200.27 (s, CO). Mass spectrum-FAB (based on $^{187}$Re): *m/z* 504 [M$^+$], 476 [M$^+$ −CO], 448 [M$^+$ −2CO].

### 3.2. Preparation of [*cis*-Cp*Re(CO)$_2$(MeCN)Br]BF$_4$ (**1b**)

This complex was prepared in a similar manner to that of **1a** but using the complex *cis*-Cp*Re(CO)$_2$Br$_2$. Yield: 94%. IR [$CH_3CN$, $\nu$(CO), cm$^{-1}$]: 2058 vs, 1988 s. $^1$H-NMR ($CD_3CN$): $\delta$ 2.12 (s, 15H, $CH_3$), 2.82 (s, 3H, $CH_3CN$). $^{13}$C{$^1$H}-NMR ($CD_3CN$): $\delta$ 4.56 (s, $CH_3CN$), 9.51 (s, $C_5Me_5$), 110.22 (s, $C_5Me_5$), 136.62 (s, $CH_3CN$), 193.37 and 200.08 (s, CO).

### 3.3. Preparation of [*cis*-Cp*Re(CO)$_2$(MeCN)Cl]BF$_4$ (**1c**)

By stirring the dichloro complex *cis*-Cp*Re(CO)$_2$Cl$_2$ with $AgBF_4$ in MeCN for 6 h and following the same procedure to that described above, complex **1c** was obtained in 91% yield. IR [$CH_3CN$, $\nu$(CO), cm$^{-1}$]: 2060 vs, 1990 s. $^1$H-NMR ($CD_3CN$): $\delta$ 2.08 (s, 15H, $CH_3$), 2.78 (s, 3H, $CH_3CN$). $^{13}$C{$^1$H}-NMR ($CD_3CN$): $\delta$ 4.50 (s, $CH_3CN$), 9.35 (s, $C_5Me_5$), 110.73 (s, $C_5Me_5$), 136.08 (s, $CH_3CN$), 195.15 and 200.25 (s, CO).

### 3.4. Preparation of ($\eta^6$-C$_5$Me$_4$CH$_2$)Re(CO)$_2$I (**2a**)

To a red solution of complex **1a** (100 mg, 0.158 mmol) in THF (10 ml) at r.t. was added 0.65 ml of a solution of $Et_3N \cdot 3HF$ (0.08 mmol, prepared by dissolving 0.2 ml in 10 ml of THF). After 10 min the IR spectrum (in THF) showed the complete disappearance of **1a** and new and strong bands at 2000 and 1928 cm$^{-1}$. The solvent was removed under vacuum, and the resulting red oil was extracted with hexanes (three portions of 10 ml). The red hexanes solution was filtered through Celite and the solvent evaporated to dryness. The red–brown solid was recrystallized from THF–hexanes at −10 °C. A light red microcrystalline solid was isolated (61 mg, 77% yield), which decomposed above 164 °C. Anal. Calc. for $C_{12}H_{14}IO_2Re$: C, 28.63; H, 2.80. Found: C, 29.04; H, 2.68%. IR [hexanes, $\nu$(CO), cm$^{-1}$]: 2011 s, 1943 vs. $^1$H-NMR ($CDCl_3$): $\delta$ 1.92 (s, 6H, $CH_3$), 2.19 (s, 6H, $CH_3$), 3.96 (s, 2H, $CH_2$), $^{13}$C{$^1$H}-NMR ($CDCl_3$): $\delta$ 9.82 (s, $CH_3$), 10.80 (s, $CH_3$), 40.18 (s, $CH_2$), 90.20 (s, $C_5Me_4$), 107.69 (s, $C_5Me_4$) 108.58 (s, $C_5Me_4$) 195.16 (s, CO). Mass spectrum-EI (based on $^{187}$Re): *m/z* 504 [M$^+$], 476 [M$^+$ −CO], 448 [M$^+$ −2CO].

### 3.5. Preparation of ($\eta^6$-C$_5$Me$_4$CH$_2$)Re(CO)$_2$Br (**2b**)

By using the complex **1b** and following the same procedure to that previously described for **2a**, the bromo-fulvene complex **2b** was isolated as red–brown crystals in 32% yield. This complex decomposed over 152 °C. Anal. Calc. for $C_{12}H_{14}BrO_2Re$: C, 31.58; H, 3.09. Found: C, 31.87; H, 2.98%. IR [hexanes, $\nu$(CO), cm$^{-1}$]: 2015 s, 1943 vs. $^1$H-NMR ($CDCl_3$): $\delta$ 1.94 (s, 6H, $CH_3$), 2.00 (s, 6H, $CH_3$), 3.73 (s, 2H, $CH_2$). $^{13}$C{$^1$H}-NMR ($CDCl_3$): $\delta$ 9.17 (s, $CH_3$), 9.83 (s, $CH_3$), 40.42 (s, $CH_2$), 89.26 (s, $C_5Me_4$), 109.26 (s, $C_5Me_4$), 109.47 (s, $C_5Me_4$), 196.85 (s, CO). Mass spectrum-EI (based on $^{187}$Re and $^{79}$Br): *m/z* 456 [M$^+$], 428 [M$^+$ −CO], 400 [M$^+$ −2CO].

### 3.6. Preparation of ($\eta^6$-C$_5$Me$_4$CH$_2$)Re(CO)$_2$Cl (**2c**)

This complex was prepared from **1c** and following the same procedure as that used for **2a**, as red crystals in 25% yield. Decomposed over 145 °C. Anal. Calc. for $C_{12}H_{14}ClO_2Re$: C, 34.92; H, 3.42. Found: C, 34.82; H, 3.27%. IR [hexanes, $\nu$(CO), cm$^{-1}$]: 2016 s, 1942 vs. $^1$H-NMR ($CDCl_3$): $\delta$ 1.92 (s, 6H, $CH_3$), 1.97 (s, 6H, $CH_3$), 3.60 (s, 2H, $CH_2$). $^{13}$C{$^1$H}-NMR ($CDCl_3$): $\delta$ 8.49 (s, $CH_3$), 9.84 (s, $CH_3$), 40.85 (s, $CH_2$), 88.97 (s, $C_5Me_4$), 109.62 (s, $C_5Me_4$), 110.64 (s, $C_5Me_4$), 197.98 (s, CO). Mass spectrum-EI (based on $^{187}$Re and $^{35}$Cl): *m*/*z* 412 [$M^+$], 384 [$M^+$ −CO], 356 [$M^+$ −2CO].

### 3.7. Preparation of cis-Cp*Re(CO)$_2$(I)Br (**3a**)

The fulvene complex ($\eta^6$-$C_5Me_4CH_2$)Re$(CO)_2$I (**2a**) (80 mg, 0.159 mmol) dissolved in THF (15 ml) was stirred at room temperature with 0.86 ml (0.150 mmol) of HBr solution (prepared by dissolving 0.2 ml of aqueous HBr (47%, $d = 1.50$ g ml$^{-1}$) in 9.8 ml of THF). After 10 min under these conditions, the starting fulvene complex almost disappeared (by IR). Solvent was removed under vacuum and the resulting red–brown residue washed three times with 5 ml of hexanes, to remove the small amount of unreacted fulvene complex. The solid was dissolved in 5 ml of $CH_2Cl_2$ and filtered through a short column of Florisil. The red solution was concentrated to about 2 ml and carefully layered with hexanes. The dark red microcrystalline solid obtained (76 mg, 81% yield) decomposed over 201 °C. Elemental analysis for **3a**. Anal. Calc. for $C_{12}H_{15}BrIO_2Re$: C, 24.67; H, 2.59. Found: C, 24.44; H, 2.46%. IR [$CH_2Cl_2$, $\nu$(CO), cm$^{-1}$]: 2027 vs, 1956 s. $^1$H-NMR ($CDCl_3$): $\delta$ 2.13 (s, $CH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 10.85 (s, $CH_3$), 105.89 ($C_5Me_5$), 199.30 (s, CO) and 201.97 (s, CO). Mass spectrum-EI (based on $^{187}$Re and $^{79}$Br): *m*/*z* 584 [$M^+$], 556 [$M^+$ − CO], 528 [$M^+$ −2CO].

### 3.8. Preparation of cis-Cp*Re(CO)$_2$(I)Cl (**3b**)

This complex was prepared following the same procedure as that used for **3a** but using HCl in ether solution. Compound **3b** was obtained as reddish crystals after crystallization from $CH_2Cl_2$–hexanes (50 mg, 59%). M.p. 189 °C with decomposition. Anal. Calc for $C_{12}H_{15}ClIO_2Re$: C, 26.71; H, 2.80. Found: C, 26.54; H, 2.61%. IR [$CH_2Cl_2$, $\nu$(CO), cm$^{-1}$]: 2030 vs, 1958 s. $^1$H-NMR ($CDCl_3$): $\delta$ 2.09 (s, $CH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 10.69 (s, $CH_3$), 106.58 (s, $C_5Me_5$), 199.70, 204.10 (s, CO). Mass spectrum (based on $^{187}$Re and $^{35}$Cl): *m*/*z* 540 [$M^+$], 512 [$M^+$ −CO], 484 [$M^+$ −2CO].

### 3.9. Preparation of cis-Cp*Re(CO)$_2$(Br)Cl (**3c**)

This complex was prepared by a procedure similar to that described for complex **3b**, but using the fulvene complex **2b** in reaction with HCl (ether solution). This complex was isolated as a red microcrystalline solid after crystallization (42 mg, 48%). M.p. 183 °C (decomposition). Anal. Calc. for $C_{12}H_{15}BrClO_2Re$: C, 29.25; H, 3.07. Found: C, 29.11; H, 2.86%. IR [$CH_2Cl_2$, $\nu$(CO), cm$^{-1}$]: 2035 vs, 1959 s. $^1$H-NMR ($CDCl_3$): $\delta$ 2.01 (s, $CH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 10.37 (s, $CH_3$), 107.55 (s, $C_5Me_5$), 201.92, 203.72 (s, CO). Mass spectrum-EI (based on $^{187}$Re, $^{79}$Br and $^{35}$Cl): *m*/*z* 492 [$M^+$], 464 [$M^+$ −CO], 436 [$M^+$ −2CO].

### 3.10. Preparation of cis-($\eta^5$-$C_5Me_4CH_2I$)Re(CO)$_2$(I)(Br) (**4a**)

To a solution of the fulvene complex **2b** (100 mg, 0.219 mmol) in THF (10 ml) was added 55 mg (0.217 mmol) of solid iodine and the mixture stirred at r.t. After 10 min, the IR spectrum of the mixture showed no evidence for the starting material. Solvent was removed under vacuum and the residual red brown solid dissolved in $CH_2Cl_2$ (5 ml) and filtered through a short column of Florisil. The volume of $CH_2Cl_2$ was reduced to about one third under vacuum, and a layer of $C_6H_{14}$ was carefully added. The mixture was allow to stand for 3 days at r.t. from which nice red crystals were obtained. However, the $^1$H-NMR spectrum of these crystals showed small resonances (about 4%) assigned to complex *cis*-($\eta^5$-$C_5Me_4CH_2I$)Re$(CO)_2I_2$, (vide supra). After several crystallization from $CH_2Cl_2$–hexanes the impurity was reduced to about 2% (by $^1$H-NMR). Although optically excellent crystals can be grown from $CH_2Cl_2$–hexanes, all thus far examined have been twinned and no X-ray structure is available. Complex **4a** was obtained in 80% yield (124 mg), it decomposed over 240 °C. Anal. Calc. for $C_{12}H_{14}BrI_2O_2Re$: C, 20.30; H, 1.99. Found: C, 19.73; H, 1.97%. IR [$CH_2Cl_2$, $\nu$(CO), cm$^{-1}$]: 2028 vs, 1956 s. $^1$H-NMR ($CDCl_3$): $\delta$ 2.13 (s, 3H, $CH_3$), 2.15 (s, 3H, $CH_3$), 2.17 (s, 3H, $CH_3$), 2.18 (s, 3H, $CH_3$), 3.92 (s, 1H, $CH_2$), 3.93 (s, 1H, $CH_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ −5.67 (s, $CH_2I$) 10.73, 10.80 (br), 10.99 (s, $CH_3$), 103.53; 105.20; 105.84; 105.94; 106.43 ($C_5Me_4CH_2$), 197.69 and 200.52 (s, CO). Mass spectrum-EI (based on $^{187}$Re and $^{79}$Br): *m*/*z* 710 [$M^+$], 682 [$M^+$ −CO) and 654 [$M^+$ −2CO].

### 3.11. Preparation of cis-($\eta^5$-$C_5Me_4CH_2Br$)Re(CO)$_2$(I)(Br) (**4b**)

This complex was prepared by the reaction of complex **2a** (100 mg, 0.199 mmol) with 0.9 ml (0.175 mmol) of a THF solution of bromine (prepared by dissolving 0.1 ml of $Br_2$, in 10 ml of THF). After 1 h stirring at r.t. the IR spectrum of the mixture still showed small absorptions for the starting fulvene complex. After 3 h the spectrum remained unchanged, solvent was pumped off and the residual red solid washed three times with hexanes to remove the unreacted **2a**. The residue was then dissolved in $CH_2Cl_2$ and crystallized as was described above for complex **4a**. Complex **4b** was isolated in 55% yield as red crystals, decompose above 225 °C. Anal. Calc. for $C_{12}H_{14}Br_2IO_2Re$: C, 20.30; H, 1.99. Found: C, 20.65; H, 2.03%. IR [$CH_2Cl_2$, $\nu$(CO), cm$^{-1}$]: 2032 vs, 1962 s. $^1$H-NMR ($CDCl_3$): $\delta$ 2.17 (s, 3H, $CH_3$), 2.18 (s, 3H,

$CH_3$), 2.21 (s, 3H, $CH_3$), 2.24 (s, 3H, $CH_3$), 4.05 (s, 1H, $CH_2$), 4.06 (s, 1H, $CH_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 10.69, 10.79, 10.97, 11.16 (s, $CH_3$), 23.77 (s, $CH_2Br$), 104.60, 105.73, 106.14, 107.85, 108.35 ($C_5Me_4CH_2$), 198.53 and 203.47 (s, CO). Mass spectrum (based on $^{187}$Re and $^{79}$Br): $m/z$ 662 [$M^+$], 634 [$M^+ - CO$], 606 [$M^+ - 2CO$].

### *3.12. Preparation of cis-*($\eta^5$-$C_5Me_4CH_2X$)$Re(CO)_2X_2$*,* $X = I$ *and Br*

Following the same procedure to that described for the previous complex, but using iodine in reaction with complex **2a** (or bromine and **2b**), these compounds were obtained in about 90% yield as dark red microcrystalline solids.

*cis*-($\eta^5$-$C_5Me_4CH_2I$)$Re(CO)_2I_2$: IR [$CH_2Cl_2$, $\nu$(CO), $cm^{-1}$]: 2023 vs, 1957 s. $^1H$-NMR ($CDCl_3$): $\delta$ 2.24 (s, 12H, $CH_3$), 3.97 (s, 2H, $CH_2$). Mass spectrum (based on $^{187}$Re): $m/z$ 758 [$M^+$], 730 [$M^+ - CO$] and 631 [$M^+ - I$], 603 [$M^+ - CO - I$].

*cis*-($\eta^5$-$C_5Me_4CH_2Br$)$Re(CO)_2Br_2$: IR [$CH_2Cl_2$, $\nu$(CO), $cm^{-1}$]: 2030 vs, 1959 s. $^1H$-NMR ($CDCl_3$): $\delta$ 2.08 (s, 6H, $CH_3$), 2.17 (s, 6H, $CH_3$), 4.01 (s, 2H, $CH_2$).). Mass spectrum (based on $^{187}$Re and $^{79}$Br): $m/z$ 614 [$M^+$], 586 [$M^+ - CO$] and 558 [$M^+ - 2CO$].

## Acknowledgements

This work was supported by Universidad Catolica de Valparaiso (DI-125.710) and FONDECYT-Chile (grant 1990788). We appreciate the unsuccessful attempts of Professor Raphael Raptis from University of Puerto Rico, to solve the X-ray structure of compound **4a**. We also thank the financial support of Fundación Andes for a NMR instrument (Convenio C-13672). F.G. acknowledges CONYCYT for a Doctoral fellowship and FONDECYT (Proyect 2010033).

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