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Cyclopentadienyl transfer reaction: thermal reaction between $Re_2(CO)_{10}$ and a series of cyclopentadienyl transition metal complexes

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Abstract

A thermal ligand transfer reaction between a series of organometallic cyclopentadienyl complexes and $Re_2(CO)_{10}$ as a source of $Re(CO)_3$ is described. The expected $CpRe(CO)_3$ complex, a very robust molecule, is obtained in yields ranging from poor, when the cyclopentadienyl precursor is thermally too stable or subject to a facile decomposition giving rise too easily to the volatile cyclopentadiene molecule, to excellent, such as with Cp_2TiCl_2 or Cp_2Ni. We interpret the observed behavior by the fact that the hapticity of the ligand in the Ti and Ni substrates changes easily allowing for an extra temporary coordination of $[Re_2(CO)_9]$, for example, generated in situ and leading to $CpRe(CO)_3$. Heating titanium compound **1** with $Re_2(CO)_{10}$ led to $CpRe(CO)_3$ and the substituted cyclopentadienyltricarbonylrhenium compound **2** with yields of 36 and 37%, respectively. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ligand transfer reaction; Cyclopentadienyl transfer; Thermal reaction; Rhenium carbonyl; Cyclopentadienyltricarbonylrhenium

1. Introduction

Transfer of an organic ligand from one transition metal unit to another is an interesting reaction when the complex cannot be prepared by conventional methods. Several examples have been discussed in literature [1]. The organic ligands can be, for example, π-allyl, π-cyclobutadiene or π-cyclopentadienyl coordinates. Several types of complexes have been used for such an exchange. For example, Cp_2Ni reacted with $Fe(CO)_5$ to give a mixture of $[CpFe(CO)_2]_2$, $CpNi(CO)_2Fe(CO)Cp$, and $[CpNi(CO)]_2$ [2]. A reaction between Cp_2Ni and $Ni(CO)_4$ produced $[CpNi(CO)]_2$ [3]. $Re_2(CO)_{10}$ is the precursor for most rheniumcarbonyl complexes. The Re–Re bond can be cleaved photochemically leading to the formation of the radical $[Re(CO)_5]$ [4], or under thermal reaction, $Re_2(CO)_{10}$ loses a CO ligand to produce the intermediate $[Re_2(CO)_9]$ [5]. For the purposes of this paper, we chose to focus our work on the formation of cyclopentadienyltricarbonylrhenium from the thermal reaction of $Re_2(CO)_{10}$ with cyclopentadienyl complexes. Besides the fundamental understanding of this ligand transfer process, this reaction may have some interest in the synthesis of bio inspired rhenium complexes. For example, we prepared several cyclopentadienyltricarbonylrhenium complexes of 17α-ethynyloestradiol which might act as radiopharmaceuticals if the complex could be prepared with radioactive rhenium isotopes [6]. Because of time constraints and very low amounts of radioactive rhenium available for the synthesis, our multistep synthetic pathway was not compatible with the access to radioactive hormones. We also demonstrated that $Re_2(CO)_{10}$ can be prepared in 1 h under mild conditions, 1 atm of CO gas at 70°C, from perrhenate [7]. Therefore, a ligand transfer reaction between preformed cyclopentadienyl complexes and $Re_2(CO)_{10}$ would be a solution to organometallic radiopharmaceuticals providing that this reaction proves to be a fast and efficient way to prepare cy-

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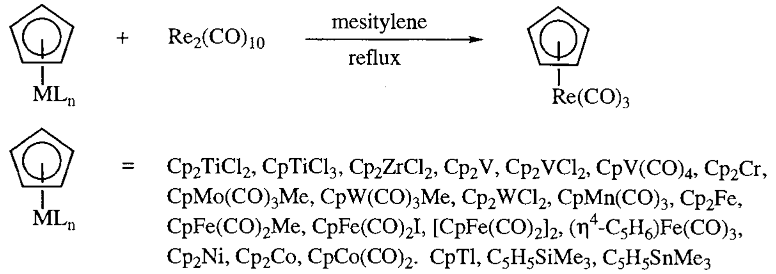


Cp_2TiCl_2, $CpTiCl_3$, Cp_2ZrCl_2, Cp_2V, Cp_2VCl_2, $CpV(CO)_4$, Cp_2Cr, $CpMo(CO)_3Me$, $CpW(CO)_3Me$, Cp_2WCl_2, $CpMn(CO)_3$, Cp_2Fe, $CpFe(CO)_2Me$, $CpFe(CO)_2I$, $[CpFe(CO)_2]_2$, $(\eta^4\text{-}C_5H_6)Fe(CO)_3$, Cp_2Ni, Cp_2Co, $CpCo(CO)_2$. CpTl, $C_5H_5SiMe_3$, $C_5H_5SnMe_3$

Scheme 1.

clopentadienyltricarbonylrhenium complexes from $Re_2(CO)_{10}$.

Before studying the reaction with sophisticated complexes, it is necessary to investigate the thermal reaction of $Re_2(CO)_{10}$ with a range of cyclopentadienyl complexes to identify the best molecules that might serve as sources of cyclopentadienyl ligands. Since it is not possible to test all of the known cyclopentadienyl complexes, we selected representative models from Groups 4, 5, 6, 7, 8, 9 and 10. The compounds chosen were Cp_2TiCl_2, $CpTiCl_3$, Cp_2ZrCl_2, Cp_2V, Cp_2VCl_2, $CpV(CO)_4$, Cp_2Cr, $CpMo(CO)_3Me$, $CpW(CO)_3Me$, Cp_2WCl_2, $CpMn(CO)_3$, Cp_2Fe, $CpFe(CO)_2Me$, $CpFe(CO)_2I$, $[CpFe(CO)_2]_2$, $(\eta^4\text{-}C_5H_6)Fe(CO)_3$, Cp_2Ni, Cp_2Co, $CpCo(CO)_2$, CpTl, $C_5H_5SiMe_3$, and $C_5H_5SnMe_3$. We extended the exchange reaction to a titanium alkene complex related to tamoxifen in order to evaluate its potential with substituted cyclopentadienyls. We report here our results on this thermal reaction.

2. Results and discussion

2.1. Results

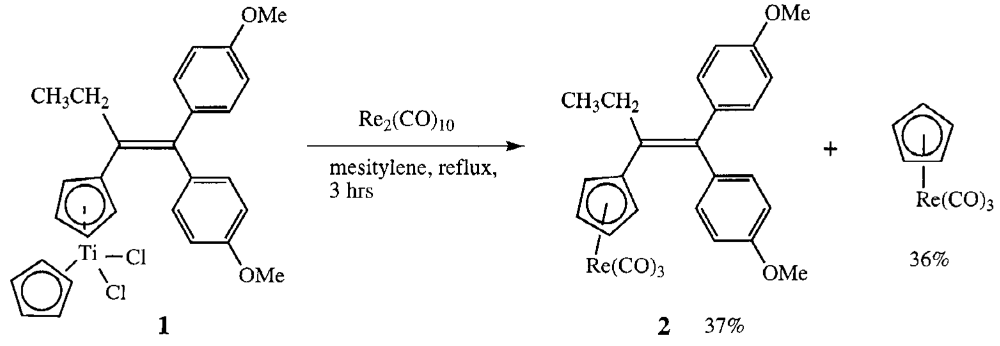
The thermal reactions were performed by heating $Re_2(CO)_{10}$ with cyclopentadienyl complexes in mesitylene at reflux for several hours (Scheme 1). Mesitylene was chosen as a solvent because of its high boiling point (b.p. 162–163°C). In order to consume all of the $Re_2(CO)_{10}$ reagent, the amount of cyclopentadienyl metal complex was calculated to contain two equivalents of Cp for one Re. Any $CpRe(CO)_3$ that was formed was isolated by TLC. The results are presented in Table 1.

The cyclopentadienyl compounds can roughly be divided into two groups. The first group that gives fair to good yields of $CpRe(CO)_3$ involves Cp_2TiCl_2, $CpTiCl_3$, Cp_2ZrCl_2, Cp_2VCl_2, Cp_2V, Cp_2Cr, Cp_2Co, $CpCo(CO)_2$, Cp_2Ni, CpTl. The second group is the group of compounds which does not produce $CpRe(CO)_3$. This group contains: $CpV(CO)_4$, $CpMo(CO)_3Me$, $CpW(CO)_3Me$, $CpMn(CO)_3$, $CpFe(CO)_2Me$, $CpFe(CO)_2I$, $[CpFe(CO)_2]_2$ and $(\eta^4\text{-}C_5H_6)Fe(CO)_3$.

Cp_2TiCl_2, being a complex of Group 4 transition metal, reacted slowly with $Re_2(CO)_{10}$, after 2 h of heating, the solution was still red with a formation of a red mastic on the flask walls. The IR of the solution showed the presence of $CpRe(CO)_3$ but also Cp_2TiCl_2 and $Re_2(CO)_{10}$. Chromatography of the solution permitted the isolation of $CpRe(CO)_3$ with a 45% yield. It is interesting to note that the infrared spectrum of the red mastic showed, besides absorption frequencies of Cp_2TiCl_2, two other frequencies at 2046 and 1985 cm^{-1} which may have belonged to $ClRe(CO)_5$. If the heat was maintained for 4 h, all of the $Re_2(CO)_{10}$ was consumed and $CpRe(CO)_3$ was isolated in a very good yield, 84%. $CpTiCl_3$ did not give a yield as good as Cp_2TiCl_2. After 2 h of heating, much $Re_2(CO)_{10}$ was still present and only a 40% yield of $CpRe(CO)_3$ was obtained. Heating for 4 h did not increase the yield. Cp_2ZrCl_2 was less reactive than Cp_2TiCl_2, after 4 h of heating, $Re_2(CO)_{10}$ was still largely present in the solution, and only a 23% yield of $CpRe(CO)_3$ was obtained.

Table 1
$Cp_nML_m + Re_2(CO)_{10} \xrightarrow[\text{reflux}]{\text{mesitylene}} CpRe(CO)_3$

Cp_nML_m	Heating time (h)	Yield of $CpRe(CO)_3$ (%)
Cp_2TiCl_2	4	82
	2	45
$CpTiCl_3$	2	40
Cp_2ZrCl_2	4	23
Cp_2V	2	30
Cp_2VCl_2	2	60
$CpV(CO)_4$	2	6
Cp_2Cr	2	24
$CpMo(CO)_3Me$	3	0
$CpW(CO)_3Me$	7	0
Cp_2WCl_2	2	0
$CpMn(CO)_3$	4	0
Cp_2Fe	8	0
$CpFe(CO)_2Me$	2	0
$CpFe(CO)_2I$	2	0
$[CpFe(CO)_2]_2$	2	0
$(\eta^5\text{-}C_5H_6)Fe(CO)_3$	2	0
Cp_2Co	2	25
$CpCo(CO)_2$	2	27
	7	45
Cp_2Ni	2	75
CpTl	1	95
$C_5H_5SnMe_3$	2	26



Scheme 2.

Vanadium complexes also reacted with $Re_2(CO)_{10}$. Heating Cp_2V with $Re_2(CO)_{10}$ for 4 h gave only a 23% yield of $CpRe(CO)_3$. The $Re_2(CO)_{10}$ had almost disappeared. Cp_2VCl_2 gave a better yield of $CpRe(CO)_3$, 60% after 2 h of heating. By contrast, $CpV(CO)_4$ produced only a 6% yield of $CpRe(CO)_3$. $CpV(CO)_4$ disappeared progressively from the solution, and after 2 h of heating, it had disappeared completely but $Re_2(CO)_{10}$ was still present. This was due to a simple thermal decomposition of $CpV(CO)_4$.

Cp_2Cr gave a moderate yield, 24%, of $CpRe(CO)_3$. No $CpRe(CO)_3$ was detected in the reaction medium with $CpMo(CO)_3Me$, and $CpW(CO)_3Me$ but a red product was formed in both cases. $CpMo(CO)_3Me$ completely disappeared after 2 h of heating. In the case of Cp_2WCl_2, this compound was not soluble in mesitylene even at high temperature. After 4 h of heating, the solution was almost colorless and there was a black solid on the flask walls. No $CpRe(CO)_3$ was detected.

$CpMn(CO)_3$, as expected, did not react with $Re_2(CO)_{10}$. After 4 h of heating, no $CpRe(CO)_3$ was detected, and $CpMn(CO)_3$ was still present in the solution.

Iron complexes such as Cp_2Fe, $CpFe(CO)_2Me$, $CpFe(CO)_2I$, $[CpFe(CO)_2]_2$, $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ were tested. None of the iron compounds yielded any $CpRe(CO)_3$. Ferrocene was unchanged even after heating for 8 h. $CpFe(CO)_2I$ disappeared after 2 h of heating, leading to the formation of a yellow solution and a black solid. Chromatography of the yellow solution gave 73% yield of ferrocene. Neither Re–Fe clusters nor $[CpFe(CO)_2]_2$ were observed. We noticed that a heating of $CpFe(CO)_2I$ alone for 2 h also produced ferrocene indicating that $Re_2(CO)_{10}$ was not involved in the reaction. $[CpFe(CO)_2]_2$ is a robust compound, no $CpRe(CO)_3$ was formed from this compound. Heating $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ gave only $[CpFe(CO)_2]_2$, in a yield of 47%. This is not surprising because $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ is thermally sensitive and is transformed easily into $[CpFe(CO)_2]_2$ via $CpFe(CO)_2H$ [8].

Cp_2Co and $CpCo(CO)_2$ react with $Re_2(CO)_{10}$ to produce $CpRe(CO)_3$ in moderate yields, 25 and 27%, respectively. After 2 h of heating, $Re_2(CO)_{10}$ had completely disappeared. In contrast with other metallocenes Cp_2Fe, Cp_2V, Cp_2Cr, and Cp_2Co, nickelocene Cp_2Ni gave a good yield of $CpRe(CO)_3$, 75%.

Reactions with other cyclopentadienyl metals: CpTl reacted very quickly with $Re_2(CO)_{10}$. Within 1 h of heating, a 95% yield of $CpRe(CO)_3$ was obtained. CpTl, a classic reagent, is usually used to react with $Re(CO)_5X$ to produce $CpRe(CO)_3$ but the yield was lower, 60% [9]. $C_5H_5SiMe_3$ produced $(\eta^5\text{-}C_5H_4SiMe_3)Re(CO)_3$, and not $CpRe(CO)_3$ while $C_5H_5SnMe_3$ gave a mixture of $CpRe(CO)_3$ and $(\eta^5\text{-}C_5H_4\ SnMe_3)Re(CO)_3$.

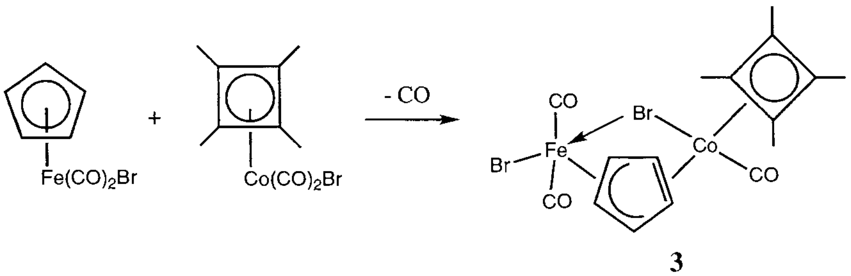
Titanium complex **1** was synthesized. **1** contains both cyclopentadienyl and substituted cyclopentadienyl ligands. Heating **1** with $Re_2(CO)_{10}$ in mesitylene for 3 h produced rhenium complex **2** and $CpRe(CO)_3$ in 37 and 36% yields, respectively (Scheme 2).

2.2. Discussion

The thermal reaction of $Re_2(CO)_{10}$ with cyclopentadienyl complexes may follow several mechanisms. Two different mechanisms have been advanced for the activation of $Re_2(CO)_{10}$. The reaction may start by the loss of a CO ligand to form $[Re_2(CO)_9]$ or by the cleavage of the Re–Re bond to produce the $[Re(CO)_5]$ radical (Scheme 3) [4,5]. The substitution reaction of $Re_2(CO)_{10}$ was carefully studied by Stolzenberg and Muetterties [5a]. They heated $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$ together, at 150°C in a sealed tube, either under argon or under pressure of CO gas. They observed that, under

$$\begin{aligned} Re_2(CO)_{10} &\rightleftharpoons 2\ [Re(CO)_5] \\ Re_2(CO)_{10} &\rightleftharpoons [Re_2(CO)_9] + CO \qquad (1) \\ [Re(CO)_5] &\rightleftharpoons [Re(CO)_4] + CO \end{aligned}$$

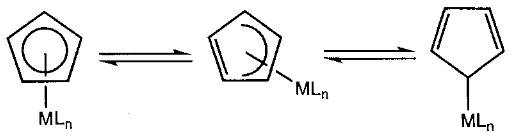
Scheme 3.



3

Scheme 4.

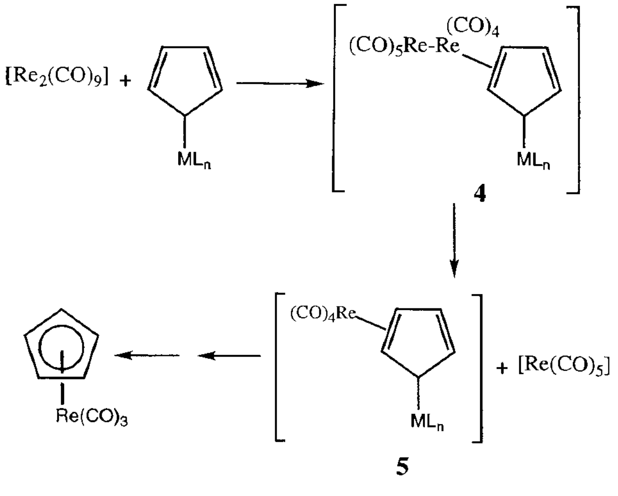
argon, the crossover took place while, under CO gas, this crossover did not occur. They concluded that the thermal ligand substitution of $Re_2(CO)_{10}$ proceeded by reversible CO dissociation and not by a scission of the Re–Re bond as suggested by Poë et al. [10]. The same mechanism has been found with $Mn_2(CO)_{10}$ [11]. On the other hand, it has been demonstrated that the cleavage of Re–Re bond is the main process in photolysis [4]. Therefore it is reasonable to admit that, in our case, $Re_2(CO)_{10}$ begins its activation by losing a CO ligand before the scission of Re–Re bond. Considering cyclopentadienyl complexes, at high temperatures, these compounds may lose their ligands and completely decompose to produce [Cp] radical and ultimately CpH [12]. Another possibility is the change in the hapticity of the Cp ligand from η^5 to η^3 or η^1 (Eq. 2).



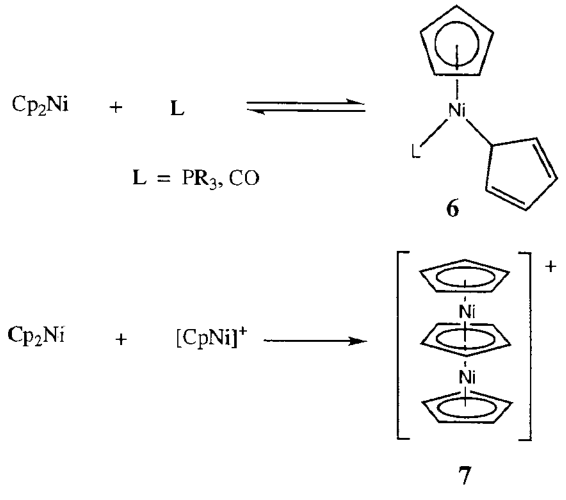
(2)

Several situations must be considered. First, the cyclopentadienyl complex does not resist high temperatures and decomposes to produce free cyclopentadiene. In this case, the situation becomes similar to the classic heating of $Re_2(CO)_{10}$ with dicyclopentadiene and substituted cyclopentadienes [13]. Usually an excess of the cyclopentadiene ligand is used in this reaction. In our situation, the amount of cyclopentadiene formed was always low. As cyclopentadiene is a volatile compound, b.p. = 40°C, cyclopentadiene can be lost at high temperatures. Therefore, the yield of $CpRe(CO)_3$ should have been very low. This probably occurred with Cp_2V, $CpV(CO)_4$, Cp_2Cr, Cp_2Co, $CpCo(CO)_2$, and $CpMo(CO)_3Me$. Prolonged heating, even under an argon atmosphere, progressively decomposed the complex to produce cyclopentadiene which was captured by $[Re_2(CO)_9]$. When the decomposition rate was faster than the dissociation of $Re_2(CO)_{10}$, the free cyclopentadiene could not be captured by $[Re_2(CO)_9]$. That was the case for $CpMo(CO)_3Me$ which decomposed at 124°C [14], no $CpRe(CO)_3$ was isolated from the reaction. $CpV(CO)_4$ showed a rapid decomposition too. Following the reaction by IR, $CpV(CO)_4$ was found to disappear rapidly from the solution while $Re_2(CO)_{10}$ remained in the mixture. Only a 6% yield of $CpRe(CO)_3$ was isolated.

Another situation was when the cyclopentadienyl complexes were thermally stable. These compounds were Cp_2TiCl_2, $CpTiCl_3$, Cp_2ZrCl_2, Cp_2VCl_2, Cp_2Fe, $[CpFe(CO)_2]_2$, and Cp_2Ni. The yields of $CpRe(CO)_3$ obtained were different from one compound to another. Cp_2TiCl_2, $CpTiCl_3$, Cp_2ZrCl_2, Cp_2VCl_2, and Cp_2Ni gave fair to good yields while Cp_2ZrCl_2, Cp_2Fe, and $[CpFe(CO)_2]_2$ did not produce $CpRe(CO)_3$. To explain the result with Cp_2TiCl_2, we postulate a change in the hapticity of the cyclopentadienyl ligand from η^5 to η^3 or η^1 as the key process. This is not uncommon behavior for CpTi complexes. Tsutsui and Hudman demonstrated that Cp_2TiCl_2 undergoes $(\eta^1\text{-}C_5H_5)_2TiCl_2$ upon dissolution in DMSO even at −70°C [15]. Brubaker et al. also suggested this π–σ rearrangement of Cp_2TiCl_2 for the reaction between Cp_2TiCl_2 and $(\eta^5\text{-}C_4D_5)_2TiCl_2$ [16]. In addition, a π–σ cyclopentadienyl scrambling has been found on Cp_4Ti [17]. It has also been suggested that $CpFe(CO)_3Br$ reacts with $(R_4C_4)Co(CO)_2Br$ to form $(R_4C_4)CoCp$ via the intermediate **3** (Scheme 4) [1]. We propose that this situation occurred during our reaction as drawn in Scheme 5.



Scheme 5.



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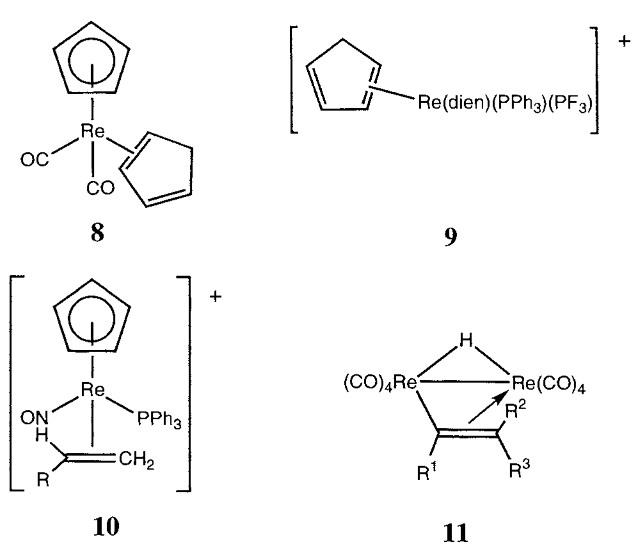

Scheme 7.

$[Re_2(CO)_9]$ adds to the first double bond released from the cyclopentadienyl ligand (intermediate **4**). Perhaps, then, the next step is the cleavage of the Re–Re bond followed by complexation of the second double bond. The breaking of the Cp–M bond eventually produces $CpRe(CO)_3$. A cyclopentadienyl transfer with Cp_2TiCl_2 is a known process. Heating Cp_2TiCl_2 with $TiCl_4$ at reflux of xylene gave $CpTiCl_3$ in a very good yield [18]. The yields of $CpRe(CO)_3$ from $CpTiCl_3$ and Cp_2ZrCl_2 were moderate while Cp_2VCl_2 gave a fairly good yield, 60%. We are not aware of any evidence for a hapticity change of the Cp ligand in $CpTiCl_3$ and Cp_2ZrCl_2, but the behavior of Cp_2VCl_2 was found to be similar to that of Cp_2TiCl_2 [16b]. Thus irradiating Cp_2VCl_2 with $(MeCp)_2VCl_2$ produced $(MeCp)CpVCl_2$. We suggest that the same process, as shown in Scheme 5, occurred with Cp_2VCl_2 although at a slower rate. In order to verify the thermal stability of Cp_2TiCl_2 and $CpTiCl_3$, these compounds were separately heated in mesitylene at reflux for 4 h. Neither compound showed any decomposition, and they were quantitatively recovered. Therefore, it is clear that $Re_2(CO)_{10}$ reacts with Cp_2TiCl_2 and $CpTiCl_3$ and not with their decomposition species. Cp_2Ni gave $CpRe(CO)_3$ with a good yield. Cp_2Ni is a versatile compound, it reacted with $Fe(CO)_5$ to give a mixture of $[CpFe(CO)_2]_2$, $CpNi(CO)_2Fe(CO)Cp$, and $[CpNi(CO)]_2$ [2], and the reaction with $Ni(CO)_4$ produced $[CpNi(CO)]_2$ and $Cp_3Ni_3(CO)_2$ [3]. Some substituted cyclopentadienes were conveniently obtained from the reaction of Cp_2Ni with RX in the presence of PR'_3 [19]. This reaction has been explained in terms of a π–σ rearrangement of cyclopentadienyl ligand to produce the intermediate **6** (Scheme 6) [19a]. Furthermore, it was shown that Cp_2Ni reacts with $[CpNi]^+$, generated from Cp_2Ni, to give a triple-decker sandwich $[Cp_3Ni_2]^+$ cation **7** [20]. Other compounds such as $[Cp^*Ru(\mu\text{-}Cp)RuCp^*]^+$ and $[Cp^*Fe(\mu\text{-}Cp)RuCp^*]^+$ were also isolated from the attack of $[CpRu(L)_3]^+$ on Cp_2Ru and Cp_2Fe [21]. We are not aware of these types of compounds with rhenium. In addition, many rhenium complexes containing a Re-$[\eta^2$-ene] bond have been synthesized [22]. For example: $CpRe(CO)_2(\eta^2\text{-}C_5H_6)$ (**8**) [22a], $[fac\text{-}Re(dien)(PPh_3)(PF_3)(\eta^2\text{-}C_5H_6)][OTf]$ (**9**) [22b], $[CpRe(NO)(PPh_3)(\eta^2\text{-}(RHC{=}CH_2))]BF_4]$ (**10**) [22c], $(\mu\text{-}H)(\mu\text{-}R^1C{=}CR^2R^3)Re_2(CO)_8$ (**11**) [22d] (Scheme 7). $CpMn(CO)_2(\eta^2\text{-}C_5H_6)$ and $[CpMn(CO)_2]_2(\eta^2,\eta^2\text{-}C_5H_6)$ have also been isolated [23]. Moreover, a photochemical reaction of $Re_2(CO)_{10}$ with cyclopentadiene has produced different complexes, one of them has shown a Re–$(\eta^2\text{-}C_5H_6)$ bond [24]. These examples demonstrate that a Re–$[\eta^2$-ene] bond is often generated and can be relatively stable. We suggest that the intermediate **4** is the most plausible for the thermal reaction with $Re_2(CO)_{10}$. Cp_2Fe, $[CpFe(CO)_2]_2$, and Cp_2WCl_2 are robust 18 electron compounds, they are inert in the reaction with $Re_2(CO)_{10}$. Even heated for 8 h, ferrocene did not give $CpRe(CO)_3$. Nevertheless, Cp_2Fe has been found to react with $RuCl_3$ at 250°C to afford Cp_2Ru in a 42% yield [25], and both Cp_2Fe and $[CpFe(CO)_2]_2$ reacted with $TiCl_4$ to produce $CpTiCl_3$ in only 5% yield [26]. The ease of the reaction with $C_5H_5SiMe_3$ and $C_5H_5SnMe_3$ is another example of the reactivity of σ-cyclopentadienyl compounds [27].

Some mixed metal–metal complexes have been reported in literature. For examples, $[CpCr(CO)_3][Re(CO)_5]$ [28], $[CpMo(CO)_3][Re(CO)_5]$ and $[CpW(CO)_3][Re(CO)_5]$ [29], $C[p\text{-}MeC_6H_4][Co(CO)_3]_2[Re(CO)_4]$ [30], $(CO)_4ReOs_2(H)(CO)_8$ [31], $(CO)_5ReCo(CO)_4$ [32]. One may expect that mixed metal–metal complexes can be formed from the thermal reaction of $Re_2(CO)_{10}$. We could not isolate any mixed metal–metal complexes, but the disappearance of $Re_2(CO)_{10}$ without formation of $CpRe(CO)_3$ in certain cases could be the consequence of the intermediate formation of such complexes.

Our results shows that Cp_2TiCl_2 is a good candidate for ligand transfer reaction. $CpCp'TiCl_2$ or Cp'_2TiCl_2 could also be used. An example is shown in Scheme 2, heating **1** with $Re_2(CO)_{10}$ for 3 h gave both **2** and $CpRe(CO)_3$. Clearly, titanium compounds can act as versatile sources of the cyclopentadienyl ligand via a metal exchange reaction. The moderate yields in isolated compounds may be the consequence of the low solubility of **1** in mesitylene. Indeed, **2** may also be prepared from a classic reaction, namely the reaction of $BrRe(CO)_5$ on lithium intermediate, but the thermal reaction is a straightforward one from $Re_2(CO)_{10}$ without involving lithium salt.

3. Experimental

The synthesis of all the compounds was performed under an argon atmosphere, using the Schlenk line technique and Schlenk flasks. Anhydrous THF and anhydrous diethyl ether were obtained by distillation from sodium–benzophenone. Mesitylene (Aldrich) was used without any further purification. TLC chromatography was performed on silica gel 60 GF254. Infrared spectra were obtained on a IR-FT BOMEM Michelson-100 spectrometer. ^1H- and ^{13}C-NMR spectra were recorded on 200 MHz and 250 MHz Bruker spectrometers. Mass spectrometry was performed with a Nermag R 10-10C spectrometer. Melting points were measured with a Kofler device. Elemental analyses were performed by the regional microanalysis department of Université Pierre et Marie Curie.

3.1. General procedure for the synthesis of CpRe(CO)$_3$

The reaction was carried out under argon in a 5 ml flask equipped with a reflux condenser. $Re_2(CO)_{10}$ and the cyclopentadienyl compound were put in the flask containing a magnetic stirrer. In a typical procedure, 98 mg of $Re_2(CO)_{10}$ (0.15 mmol) were used, the quantity of cyclopentadienyl compound was calculated in order to have two Cp ligands per Re. The flask was purged with argon, and 0.5 ml of mesitylene was added. The flask was then heated with an oil bath preheated to 190°C. The reaction was monitored by TLC and IR. Unless otherwise mentioned, the reaction was stopped after 2 h of heating. Products formed were separated by classic chromatography on silica gel plates with pentane as an eluent. $CpRe(CO)_3$ was identified by NMR and IR. ^1H-NMR (ppm, $CDCl_3$): 5.38 (s, 5H). IR (cm^{-1}, CH_2Cl_2) ν_{CO}: 1925s, 2023s.

- Reaction with Cp_2TiCl_2. 75 mg of Cp_2TiCl_2 (0.3 mmol) were used. After 4 h of heating, a green–black solid was formed and the solution was still red. 83 mg of $CpRe(CO)_3$ were isolated by TLC with an 82% yield. In a second experiment, Cp_2TiCl_2 was heated for 2 h. A red solid was observed on the walls of the flask. Diethyl ether was added, the solution was chromatographed. 45 mg of $CpRe(CO)_3$ were isolated with a 45% yield. The red solid on the flask walls was identified as a mixture of unreacted Cp_2TiCl_2 and $Re(CO)_5Cl$ by IR and ^1H-NMR (IR, CH_2Cl_2, ν_{CO}: 2046 and 1985 cm^{-1}; ^1H-NMR, $CDCl_3$, 6.60 (s, 10H).
- Reactions with $CpTiCl_3$, Cp_2ZrCl_2, Cp_2Cr, Cp_2VCl_2, Cp_2V, $CpV(CO)_4$, Cp_2Ni. After the heating time, the IR spectrum of the solution showed that all the $Re_2(CO)_{10}$ was not consumed. $CpRe(CO)_3$ was isolated by TLC. The yields of $CpRe(CO)_3$ are indicated in Table 1.
- Reactions with $CpMo(CO)_3Me$, $CpW(CO)_3Me$, Cp_2WCl_2, $CpMn(CO)_3$, Cp_2Fe, $CpFe(CO)_2Me$, $Cp_2(CO)_4Fe_2$. No significant yield of $CpRe(CO)_3$ was obtained with these compounds.
- Reactions with $CpFe(CO)_2I$ and $(\eta^4\text{-}C_5H_6)Fe(CO)_3$. Both compounds had disappeared during heating, but $Re_2(CO)_{10}$ was still in the solution in large amounts. The reaction with $CpFe(CO)_2I$ gave ferrocene (73% yield) instead of $CpRe(CO)_3$, while $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ was transformed into $Cp_2(CO)_4Fe_2$ (47% yield).
- Reactions with Cp_2Co and $CpCo(CO)_2$. Both compounds gave a dark red solution with the formation of a red mastic after heating. The infrared spectrum showed absorption for $CpRe(CO)_3$ but no trace of $Re_2(CO)_{10}$. Dichloromethane was added. After filtration and evaporation, diethyl ether was added to extract $CpRe(CO)_3$ which was purified by chromatography. A red solid, insoluble in diethyl ether, was isolated. IR spectrum of the red solid showed some ν_{CO} absorptions (for the reaction with Cp_2Co: ν_{CO} 2074w, 2005m, 1972s, 1960s cm^{-1} (CH_2Cl_2); for the reaction with $CpCo(CO)_2$: ν_{CO} 1967, 1889 cm^{-1}(KBr).
- Reaction with CpTl. 331 mg of CpTl (1.2 mmol) and 198 mg of $Re_2(CO)_{10}$ (0.3 mmol) were heated in 1 ml of mesitylene. After 1 h of heating, the $Re_2(CO)_{10}$ had completely disappeared. 195 mg of $CpRe(CO)_3$ were isolated by TLC, with a 93% yield.
- Reaction with $CpSiMe_3$. 324 mg of $CpSiMe_3$ (3 mmol) and 326 mg of $Re_2(CO)_{10}$ (0.5 mmol) were heated in 0.4 ml of mesitylene. After 3 h of heating, $Re_2(CO)_{10}$ had completely disappeared. 184 mg of $[\eta^5\text{-}C_5H_4SiMe_3]Re(CO)_3$ were isolated by TLC, with 93% yield. ^1H-NMR (ppm, $CDCl_3$): 5.41 (m, 4H), 0.24 (s, 9H). IR(cm^{-1}, CH_2Cl_2) ν_{CO}: 2020s, 1922s cm^{-1}.
- Reaction with $CpSnMe_3$. 284 mg of $CpSnMe_3$ (1.2 mmol) and 198 mg of $Re_2(CO)_{10}$ (0.3 mmol) were heated in 1 ml of mesitylene. After 2 h of heating, the solution became orange. Three compounds were isolated by chromatography. The first compound

was $Re_2(CO)_{10}$, 25 mg. The second compound was a colorless oil, 60 mg, which was identified as $(\eta^5\text{-}C_5H_4SnMe_3)Re(CO)_3$. ^{1}H-NMR (ppm, $CDCl_3$): 5.49 (t, 2H), 5.31 (t, 2H), 0.32 (s, 9H). IR(cm^{-1}, CH_2Cl_2) ν_{CO}: 2019s, 1920s cm^{-1}. The third compound was $CpRe(CO)_3$, 52 mg, with a 26% yield.

- Reaction with **1** [34]. 154 mg of **1** (1.2 mmol) and 261 mg of $Re_2(CO)_{10}$ (0.4 mmol) were heated in 1 ml of mesitylene. After 3 h of heating, the mixture was cooled and diethyl ether was added to extract the products. The solution was concentrated, 92 mg of unreacted $Re_2(CO)_{10}$ precipitated from the solution. A chromatography of the solution by using ether–pentane 1:6 as an eluent, gave 36 mg of $CpRe(CO)_3$, with a 36% yield, and 67 mg of colorless solid which was identify as **2**, with a 37% yield (m.p. 110°C). ^{1}H-NMR (ppm, $CDCl_3$): 7.08, 7.02, 6.85, 6.81 (d, d, d, d, 8H, $2C_6H_4$); 5.12, 5.07 (m, m, 4H, C_5H_4); 3.81, 3.80 (s, s, 6H, 2MeO); 2.28 (q, 2H, CH_2CH_3); 1.07 (t, 3H, CH_2CH_3). IR(cm^{-1}, CH_2Cl_2) ν_{CO}: 2019, 1923 cm^{-1}. Mass spectrum (EI) m/z for Re = 187: 602 $(M)^+$, 518 $(M\text{–}3CO)^+$.

4. Conclusion

We have shown that $Re_2(CO)_{10}$ reacts with a range of cyclopentadienyl complexes acting as a source of the cyclopentadienyl ligand to produce $CpRe(CO)_3$ as the main product. It appears that free cyclopentadiene obtained from the thermal decomposition of some of the complexes was not the major process of the reaction. The modification of the hapticity of Cp ligands, which is possible in some instances, may be the key to the reaction. Two metallocenic precursors, Cp_2TiCl_2 and Cp_2Ni, give particularly good yields of $CpRe(CO)_3$. Thermally robust saturated compounds, such as ferrocene or $CpMn(CO)_3$, did not promote the Cp exchange reaction. Actually, the preparation of unsubstituted $CpRe(CO)_3$ was not the final goal of this study. This approach can indeed become interesting in the preparation of sophisticated molecules because it allows the synthesis of tricarbonylrhenium complex from $Re_2(CO)_{10}$ in a one step reaction. The synthesis of **2** by heating **1** with $Re_2(CO)_{10}$ is the first example of this application. In a related idea, the synthesis of substituted cyclopentadienyltricarbonylrhenium $(C_5H_4\text{-}COR)Re(CO)_3$ from the reaction of ferrocenyl derivatives with perrhenate has been reported [33].

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