Synthesis and reactivity of η^5-tetramethylcyclopentadienyl-propenyl rhenium complexes: Molecular structure of [(η^5:η^2-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_2$]

Fernando Godoy [a,*], Alejandra Gómez [a], Gloria Cárdenas-Jirón [b], A. Hugo Klahn [c], Fernando J. Lahoz [d]

[a] Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Santiago, Chile
[b] Departamento de Ciencias del Ambiente, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Santiago, Chile
[c] Instituto de Química, Pontificia Universidad Católica de Valparaíso, Casilla 4059, Valparaíso, Chile
[d] Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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ABSTRACT

The fulvene complexes [(η^6-C$_5$Me$_4$CH$_2$)Re(CO)$_2$(R)] (**1a**, R=I; **1b**, R=C$_6$F$_5$) react at the exocyclic methylene carbon with a vinylmagnesium bromide solution to produce the anionic species [(η^5-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_2$(R)]$^-$. Protonation with HCl at 0 °C produces the hydride complexes [*trans*-(η^5-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_2$(R)(H)] (**2a**, R=I; **2b**, R=C$_6$F$_5$). Thermolysis of an hexane solution of the iodo-hydride (**2a**) under a CO atmosphere yields the complex [(η^5-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_3$] (**3**) and [Re(CO)$_5$I] as by-product. Thermolysis of **2b** produced three new products, mainly the chelated complex [(η^5:η^2-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_2$] (**4**) and complex **3**, with a non-coordinated olefin group, in moderated yield, and traces of [Re(CO)$_5$(C$_6$F$_5$)]. Thermolysis of an hexane solution of **2** in presence of an excess of PMe$_3$, afforded the phosphine derivative [(η^5-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_2$(PMe$_3$)] (**5**). All the complexes were characterized by IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopies and mass spectrometry. The molecular structure of **4** has also been determined. The molecule exhibits a formal three-legged piano-stool structure, with two CO groups, and the third position corresponding to the η^2-coordination of the propenyl side arm of the η^5-C$_5$Me$_4$ ring.

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1. Introduction

Organometallic complexes containing the cyclopentadienyl and tetramethylcyclopentadienyl functionalized ligands (C$_5$H$_4$R and C$_5$Me$_4$R) have become of great importance because of their capacity for binding to hard and soft metal centers in a hemilabile manner, giving unique chemical and physical properties to the complex. The fragment tethered to the C$_5$H$_4$ or C$_5$Me$_4$ ligands may included phosphines [1], amines [2], ethers [3], and sulfide [4] groups, which have been widely studied. By choosing appropriate systems and conditions the *intra*molecular stabilization of electron-deficient centers can be observed in a reversible or irreversible way. For this reason, these types of compounds have found significant applications in catalysis (olefin polymerization [1–4], hydrogenation of ketones [5], alcohol oxidation [6], etc.) and in the construction of molecular materials, however, from the large amount of these ligand reported in literature, those containing alkene pendant side chains are far less abundant [7]. For instance, Erker et al. have reported the formation of sandwich and half-sandwich titanium and zirconium complexes with allyl substituted cyclopentadienyl groups, which have resulted active

in the homogenous catalytic polymerization of ethylene and propene [8], while Mountford and co-workers [9] synthesized tetramethylcyclopentadienyl titanium and zirconium derivatives with a butenyl pendant side chain. On the other hand, few half-sandwich compounds of this type are known for group 7 metals, for instance, Gable and Brown [10] reported the synthesis of the [(η^5-C$_5$Me$_4$CH$_2$CH$_2$CH=CH$_2$)Re(CO)$_3$] complex which was used as precursor to produce the Re(VII) epoxide complex [(η^5-C$_5$Me$_4$-CH$_2$CH$_2$CHCH$_2$O)Re(O)$_3$]. Almost simultaneously, our group reported the same tetramethylcyclopentadienyl-(3-butenyl) complex using an alternative route which involves the use of the fulvene complex [(η^6-C$_5$Me$_4$CH$_2$)Re(CO)$_2$(I)] as starting material. We also have reported that, the fulvene complexes [(η^6-C$_5$Me$_4$-CH$_2$)Re(CO)$_2$(R)] (R=I, C$_6$F$_5$) react with allylmagnesium chloride, 2-thienyllithium and potassium diphenylphosphide to yield the anionic species [(η^5-C$_5$Me$_4$CH$_2$L)Re(R)(CO)$_2$]$^-$ (L=CH$_2$CH=CH$_2$; 2-C$_4$H$_3$S; PPh$_2$). Protonation with HCl afforded the *trans* hydride complexes, which under thermolysis conditions (hexane solution under an N$_2$ atmosphere at 40 °C) yielded the compounds [(η^5:η^x-C$_5$Me$_4$CH$_2$L)Re(CO)$_2$] (x = 2 and 1, respectively) [11,12].

We also demonstrate that under UV irradiation of [(η^5-C$_5$Me$_4$CH$_2$CH$_2$CH=CH$_2$)Re(CO)$_3$] the chelated complex [(η^5:η^2-C$_5$Me$_4$CH$_2$CH$_2$CH=CH$_2$)Re(CO)$_2$] is formed in moderate yield, species that surprisingly do not react with CO even at 1100 psi.

* Corresponding author. Tel.: +56 02 7181034.
E-mail address: fernando.godoy@usach.cl (F. Godoy).

With the aim of getting a more deep insight into the formation of this type of rhenium compounds, in this work, we describe the thermal reactions of the hydride complexes [*trans*-(η^5-$C_5Me_4CH_2CH=CH_2$)Re(CO)$_2$(R)(H)] (R=I, C_6F_5) with CO and PMe$_3$. The organometallic products were isolated and characterized by spectroscopic techniques. In addition, the reductive elimination of HI and C_6F_5H from [*trans*-(η^5-$C_5Me_4CH_2CH=CH_2$)Re(CO)$_2$(R)(H)] to produce complexes with a non-coordinated and coordinated propenyl side arm is also described.

2. Results and discussion

2.1. Synthesis of the hydride complexes

The fulvene complexes [(η^6-$C_5Me_4CH_2$)Re(CO)$_2$(R)] (**1a**, R=I; **1b**, R=C_6F_5) were prepared by methods described in the literature [13,14]. Addition of vinylmagnesium bromide to THF solutions of **1a–b** yield the anionic complexes [(η^5-$C_5Me_4CH_2CH=CH_2$)-Re(CO)$_2$(R)]$^-$ (Scheme 1). These anionic species were not isolated due to their extreme air sensitivity, and they were characterized only by IR spectroscopy. Two absorption ν(CO) bands were observed at 1875 and 1728 cm^{-1}, comparable to those reported for analogous rhenium anions [11,15]. Further reaction of [(η^5-$C_5Me_4CH_2CH=CH_2$)Re(CO)$_2$(R)]$^-$ with HCl at 0 °C gave the hydride complexes [*trans*-(η^5-$C_5Me_4CH_2CH=CH_2$)Re(CO)$_2$(R)(H)] (**2a–b**) (Scheme 1). After work up the hydride complexes were isolated as pale brown solids which were soluble in most organic solvents. The extreme air sensitivity of the solids precluded satisfactory elemental analyses. These compounds showed CO absorption bands at 2022 (v) and 1960 (vs) cm^{-1} in hexane solution, with the signal at lower wavenumber much more intense. On the basis of the relative intensity pattern, as well as the similarities between the IR frequencies of these complexes and those of other dicarbonyl derivatives with a four-legged piano-stool type of structure [16], we assigned the two CO ligands in a *diagonal* or *trans* orientation in the complexes **2a–b**.

The ^{1}H NMR spectrum of **2a–b** in benzene-d_6 showed at low frequency one singlet (δ: -8.95 and 9.12, respectively) for the hydride proton; this chemical shift is almost identical to those reported for the closely related complexes [*trans*-(η^5-C_5Me_5)Re(Aryl$_F$)(CO)$_2$(H)] (Aryl$_F$ = C_6F_5, 2,3,5,6-C_6HF_4) [15] and [*trans*-(η^5-$C_5Me_4CH_2$P-Ph$_2$)Re(C_6F_5)(CO)$_2$(H)] [12]. The presence of the (propenyl)-tetramethylcyclopentadienyl ligand ($C_5Me_4CH_2CH=CH_2$) in complex **2a–b**, were established by ^{1}H NMR spectroscopy. Partial transformation of the hydrides complexes **2a–b** in solutions of d_6-C_6D_6, were observed by ^{1}H NMR and IR spectroscopy, the products were characterized as [(η^5-$C_5Me_4CH_2CH=CH_2$)Re(CO)$_3$] (**3**) and [(η^5:η^2-$C_5Me_4CH_2CH=CH_2$)Re(CO)$_2$] (**4**) (*vide infra*).

Both IR and NMR parameters are similar to those found in the analogous iodo and fluoroaryl rhenium complexes [*trans*-(η^5-$C_5Me_4CH_2L$)Re(CO)$_2$(R)(H)] (L=CH$_2$CH=CH$_2$, PPh$_2$; R=I, C_6F_5) [11,12].

2.2. Thermal reactions of hydride complexes

Hydride complexes [*trans*-(η^5-$C_5Me_4CH_2CH=CH_2$)Re(CO)$_2$(R)(H)] (**2a–b**) in hexane solution under a CO atmosphere, at 45 °C undergo reductive elimination reactions of HI and C_6F_5H, respectively. However, the observed organometallic product depends on the nature of the R group coordinated to the rhenium atom (Scheme 2).

The iodo-hydride complex **2a** in presence of CO produced the tricarbonyl complex [(η^5-$C_5Me_4CH_2CH=CH_2$)Re(CO)$_3$] (**3**) which was isolated as an analytically pure white solid in low yield (26%) and [Re(CO)$_5$I] as by-product. The latter was characterized by IR spectroscopy and MS. The IR data was identical to those reported for this compound by Schmidt et al. [17]. Complex **3**, showed two CO absorption bands at 2014 and 1924 cm^{-1}, almost identical to those reported for the related pentamethyl and tetramethylcyclopentadienyl functionalized tricarbonyl complexes [11]. The ^{1}H NMR spectrum of **3** shows two singlets at about 2 ppm, attributed to methyl groups of the cyclopentadienyl ligand, and a signal at δ 3.17 assigned to the methylenic protons. The olefinic protons were observed as three signals in the region 4.9–5.8 ppm. The chemical shifts are in good agreement with those reported for the complexes [(η^5-$C_5H_4CH_2CH=CH_2$)TiCl$_3$], [(η^5:η^5-$C_5H_4SiMe_2C_5H_4CH_2CH=CH_2$)ZrCl$_2$] [8], [TiCl$_2${$\eta^5$-$C_5Me_4$-(SiMe$_2CH=CH_2$)}$_2$] [18], and [($\eta^5$-$C_5Me_4CH_2CH_2CH=CH_2$)Re(CO)$_3$] [10]. The ^{13}C NMR showed, in addition to the carbons of the C_5Me_4 fragment, two singlets at δ: 116.0 and 137.0 attributed to alkenyl group, and a singlet for the CO groups at δ 198.2. Identical values were found for [(η^5-$C_5Me_4CH_2CH_2CH=CH_2$)Re(CO)$_3$] [11]. The mass spectrum of **3** exhibits a typical fragmentation pattern for rhenium complexes: 432 [M$^+$], 404 [M$^+$−CO], 391 [M$^+$−CH$_2$CH=CH$_2$] and 374 [M$^+$−2CO−2H].

The HI formed in the thermolysis was extracted with water (25 mL) and the pH was determined potentiometrically giving a value of 1.68, indicating the presence of a strong acid; addition of AgNO$_3$ caused the quantitative precipitation of AgI.

In the thermolysis of **2b** under a CO atmosphere three carbonyl complexes were observed by IR spectroscopy. The reaction mixture was chromatographed on neutral alumina and the first fraction eluted with hexane confirmed the presence of hexafluorobenzene (by GC–MS). The second fraction, [Re(CO)$_5$(C_6F_5)], was isolated in low yield and characterized by IR spectroscopy and MS [19]. The third fraction (eluted with hexane) afforded the neutral species **3** in a 26% yield, while the chelated complex [(η^5:η^2-$C_5Me_4CH_2CH=CH_2$)Re(CO)$_2$] (**4**) was obtained with successive elution with hexane and isolated as a white microcrystalline solid in good yield (43%). The latter was soluble in most common organic solvents, air stable, and did not decompose after several months stored under nitrogen. The IR spectra of **4** show two CO absorption bands at 1962 and 1891 cm^{-1} described in experimental which are similar to those reported for the ethylene complex [(η^5-C_5Me_5)Re(CO)$_2$(η^2-C_2H_4)] (ν(CO) 1964 and 1894 cm^{-1}, in hexane) [20] and for the butenyl derivative [(η^5:η^2-$C_5Me_4CH_2CH_2$-CH=CH$_2$)Re(CO)$_2$] [11]. The frequency

1a, R=I
1b, R=C_6F_5

2a, R=I
2b, R=C_6F_5
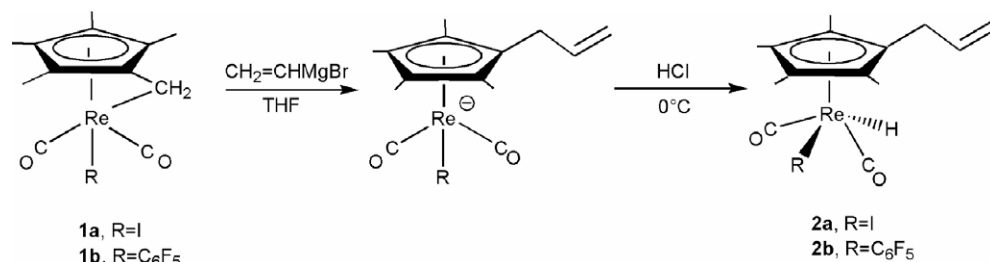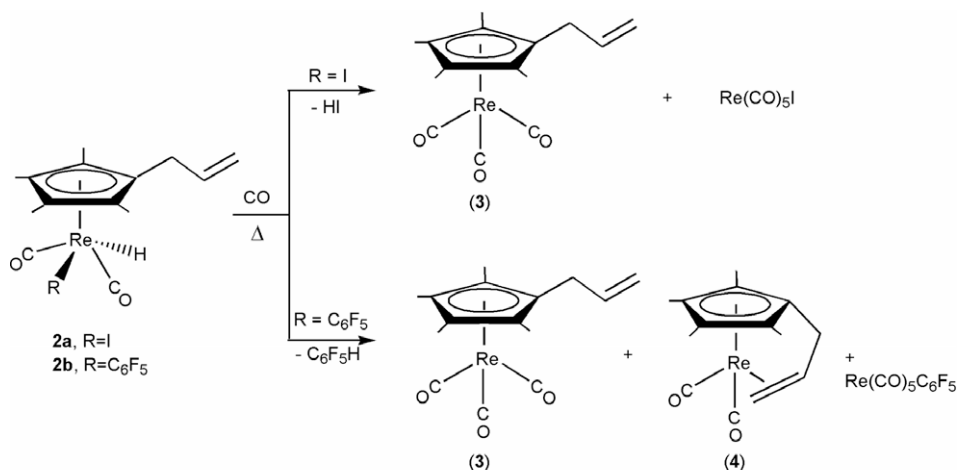
Scheme 1.

Scheme 2.

shift of the ν(CO) bands of **4** compared to **3** suggests a stronger d–p back-bonding between rhenium and the alkene ligand. Coordination of the olefin group to the rhenium fragment was confirmed by ^{1}H NMR spectroscopy from the presence of three new sets of resonances shifted to high field, which are similar to that reported for the spectroscopy data reported for butenyl derivative [(η^5:η^2-C$_5$Me$_4$CH$_2$CH$_2$CH=CH$_2$)Re(CO)$_2$] [11]. The ^{13}C NMR spectrum of **4** showed two singlets at δ 31.3 and 58.3 attributed to CH$_2$ and CH, respectively, of the coordinated —CH=CH$_2$ fragment. This assignment was confirmed by ^{1}H–^{13}C HSQC NMR and by comparison with analogous complexes [11]. The high field shift of these resonances compared to those found for the uncoordinated olefin in **3** (δ 116.0 and 137.0) can be explained in terms of the Dewar–Chatt–Duncanson model, which implies a change in the hybridization of the alkene carbon from sp^2, in the uncoordinated fragment, to a sp^3-like carbon in complex **4** [21]. Further evidence obtained from the ^{13}C NMR spectrum are the two distinct resonances for the CO groups observed at about δ: 207, due to the unsymmetrical nature of the side chain coordinated to the metal center. This result is in a good agreement with that reported for the complex [(η^5-η^2-C$_5$Me$_4$CH$_2$CH$_2$CH=CH$_2$)Re(CO)$_2$] [11], and in addition the mass spectrum and elemental analysis are in good agreement for the proposed structure.

With the aim of exploring the hemilabile character of the propenyl group coordinated to the rhenium center in complex **4**, we treated it with CO (500 psi). After 3 h the IR and ^{1}H NMR spectra showed the presence of the tricarbonyl derivative **3** (Scheme 3). This result highly contrasts with that found for the complex [(η^5:η^2-C$_5$Me$_4$CH$_2$CH$_2$CH=CH$_2$)Re(CO)$_2$] which even at high CO pressure (2000 psi) remained intact.

Interestingly, the process is reversible under UV irradiation (hexane solution, λ = 300 nm, room temperature). Although the spectroscopic data (IR and ^{13}C NMR) for complex **4** are almost iden-

tical to those reported for the analogous species [(η^5:η^2-C$_5$Me$_4$CH$_2$CH$_2$CH=CH$_2$)Re(CO)$_2$], fact that led us to think that both chelated compounds have similar electron density, the effect of the different side carbon chain apparently plays a fundamental role in the dissociation process of the alkene group for complex **4**.

Thermolysis of the hydrido complexes **2a–b**, in presence of an excess of PMe$_3$, afforded the unchelated complex [(η^5-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_2$(PMe$_3$)] (**5**) in good yield when starting from iodo-hydride complex **2a**, but a 5:2 mixture of complexes **4** and **5**, were obtained on the thermolysis of [trans-(η^5-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_2$(C$_6$F$_5$)(H)] (**2b**). The trimethylphosphine complex **5**, was isolated as a light yellow oil after work up. The IR and ^{31}P NMR data of **5** are in a good agreement with those reported for analogous rhenium complexes [(η^5-C$_5$Me$_4$CH$_2$L)Re(CO)$_2$(PMe$_3$)] (L= CH$_2$CH=CH$_2$, 2-C$_4$H$_3$S, PPh$_2$) [11,13]. The ^{1}H and ^{13}C NMR data are consistent with the proposed structure and clearly showed the uncoordination of the 2-propenyl side chain.

2.3. Crystal structure of complex 4

The molecular structure of complex **4** is shown in Fig. 1 and the most relevant bond distances and angles are collected in Table 1. This mononuclear metal complex exhibits a typical three-legged
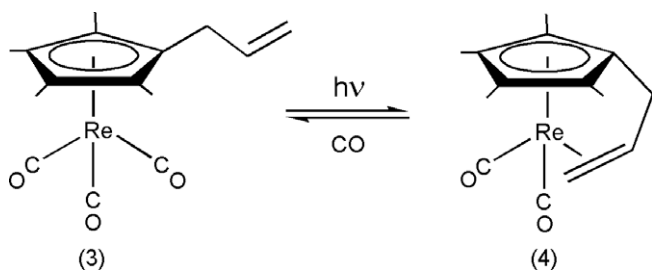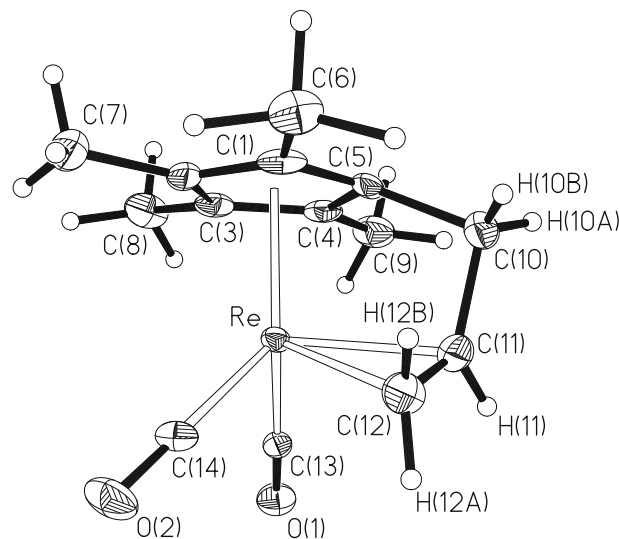

Scheme 3.

Fig. 1. Molecular drawing of complex **4** with atomic numbering scheme.

Table 1
Selected bond lengths (Å), and angles (°) for $[(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH=CH_2)Re(CO)_2]$ (**4**).

Re–C(1)	2.295(4)	Re–G[a]	1.9327(18)
Re–C(2)	2.316(4)	Re–M[b]	2.137(3)
Re–C(3)	2.312(4)	Re–C(11)	2.244(4)
Re–C(4)	2.259(4)	Re–C(12)	2.252(4)
Re–C(5)	2.233(4)	Re–C(13)	1.905(4)
C(5)–C(10)	1.543(6)	Re–C(14)	1.913(4)
C(10)–C(11)	1.543(6)	C(13)–O(1)	1.166(5)
C(11)–C(12)	1.395(7)	C(14)–O(2)	1.161(5)
G[a]–Re–M[b]	105.95(12)	C(1)–C(5)–C(4)	109.4(3)
G[a]–Re–C(13)	125.90(13)	C(1)–C(5)–C(10)	124.2(4)
G[a]–Re–C(14)	132.38(13)	C(4)–C(5)–C(10)	120.4(4)
M[b]–Re–C(13)	100.8(2)	C(5)–C(10)–C(11)	101.0(3)
M[b]–Re–C(14)	100.1(2)	C(10)–C(11)–C(12)	119.6(4)
C(13)–Re–C(14)	85.96(16)		

[a] G represents the centroid of the substituted cyclopentadienyl ring.
[b] M represents the midpoint of the C(11)–C(12) olefinic bond.

piano-stool structure. A 2-propenyl-functionalized tetramethyl-cyclopentadienyl ligand, linked in a $\eta^5:\eta^2$ chelated bonding mode, together with two terminal carbonyl ligands, complete the rhenium coordination sphere.

Only a few examples of transition metal compounds with an alkenyl-substituted C_5Me_4 ring intramolecularly coordinated in a $\eta^5:\eta^2$ bonding mode have been structurally characterized: $[(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH=CH_2)Co(Me_3SiCCSiMe_3)]$ [22], $[(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH=CH_2)Ru(\eta^3\text{-}C_3H_5)]$ [7e] and the closely related analogous rhenium complex $[(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH=CH_2)Re(CO)_2]$ [11]. Unique structural features of 4 have been sought by comparison with the related nonchelated $[Cp^*Re(CO)_2(\eta^2\text{-}(CH_3)_2C=CHCOMe)]$, to our knowledge the only complex of the type $[Cp^*Re(CO)_2(\eta^2\text{-olefin})]$ studied by X-ray crystallography [23].

In terms of the Re–CO (1.905 and 1.913(4) Å) and Re–C(ring centroid) (1.9327(18) Å) bond distances, the molecular parameters of **4** compare well with those found in $[Cp^*Re(CO)_2(\eta^2\text{-}(CH_3)_2C=CHCOMe)]$ and in the 3-butenyl rhenium derivative. The Re–C(olefin) bond lengths are also comparable, 2.244 and 2.252(4) Å in **4**, vs. 2.233 and 2.298(6) Å in the butenyl rhenium analog, as well as the OC–Re–CO and C(olefin)–Re–C(olefin) bond angles (85.96(16) and 36.4° vs. 87.4(3) and 36.9°, respectively). All the bond distances and angles of the propenyl side arm seem to be normal for C–C single bonds (C(5)–C(10) 1.543(6) and C(10)–C(11) 1.543(6) Å) and very similar to those observed in the closely related ruthenium complex $[(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH=CH_2)Ru(\eta^3\text{-}C_3H_5)]$, where also a symmetric Ru–olefin interaction has been determined (Ru–C(olefin) 2.167 and 2.161 Å).

Remarkably, atom C(10) is clearly out of the least-squares plane defined by the five carbon atoms of the cyclopentadienyl ring 0.598(5) Å towards the metal center and the bond angle C(5)—C(10)—C(11) (101.0(3)°) is noticeably smaller than the ideal tetrahedral angle. These values provide evidence of the strain originated by the chelate coordination of the cyclopentadienyl-propenyl ligand, and this fact could explain the different reactivity with CO observed for **4**, clearly opposed to that reported for the butenyl analog, where the bond angle in the carbon atoms of the side arm exhibit a mean value of 111.9(4)° [11].

3. Conclusion

The fulvene complexes $[(\eta^6\text{-}C_5Me_4CH_2)Re(R)(CO)_2]$ (R=I, C_6F_5) acts as a good precursors for the synthesis of several functionalized tetramethylcyclopentadienyl rhenium complexes. Reaction with $CH_2=CHMgBr$ followed by HCl yields $[trans\text{-}(\eta^5\text{-}C_5Me_4CH_2CH=CH_2)Re(R)(H)(CO)_2]$. Reductive eliminations of HI or C_6F_5H afforded propenyl tetramethylcyclopentadienyl derivatives. As

summarized in Scheme 3, photodissociation of one CO ligand yields the chelated complex $[(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH=CH_2)Re(CO)_2]$ containing an intramolecularly coordinated propenyl fragment, the latter species reacts with CO to afforded $(\eta^5\text{-}C_5Me_4CH_2CH=CH_2)Re(CO)_3$ in a reversible way.

4. Experimental

4.1. General methods

All reactions were carried out using the standard Schlenck technique under nitrogen. All solvents were purified and dried by conventional methods, and were distilled under nitrogen prior to use. Vinylmagnesium bromide and hydrogen chloride in diethyl ether (Aldrich) were used as received. $[Re_2(CO)_{10}]$ and $[Cp^*Re(CO)_3]$ were synthesized following literature procedures [24]. The fulvene complexes $[(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(I)]$ (**1a**) and $[(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(C_6F_5)]$ (**1b**) were prepared according to known procedures [13,14]. Infrared spectra were recorded in solution (CaF_2 cell) on a Perkin–Elmer FT-1605 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded 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. Mass spectra were recorded on a GCMS-QP5050A Shimadzu instrument.

4.2. Preparation

4.2.1. $[trans\text{-}(\eta^5\text{-}C_5Me_4CH_2CH=CH_2)Re(CO)_2(I)(H)]$ (**2a**)

The fulvene complex $[(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(I)]$ (**1a**) (100 mg, 0.199 mmol) was dissolved in THF (15 mL) at 0 °C under nitrogen, and vinylmagnesium bromide solution 1.0 M/THF 0.3 mL (0.300 mmol) was added. The reaction mixture was stirred for 5 min, and the IR spectrum showed only two CO absorptions at 1875 and 1728 cm^{-1}, attributed to the anionic species $[(\eta^5\text{-}C_5Me_4CH_2CH=CH_2)Re(CO)_2(I)]^-$. Then an HCl solution in diethyl ether (0.3 mL, 0.300 mmol) was added. The IR spectrum of the solution showed the complete disappearance of the anionic complex and new CO absorptions at 2021 (s) and 1958 (vs) cm^{-1}. The solvent was pumped off and hexane (3 × 10 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. Complex **2a** was isolated as a pale brown solid, 92.6 mg (0.174 mmol) yield: 87.3%. IR (hexane, ν(CO) cm^{-1}): 2022 (s), 1960 (s). ^1H NMR (C_6D_6) δ: −9.12 (Re–H), 1.40 (s, 6H, C_5Me_4), 1.42 (s, 6H, C_5Me_4), 3.02 (m, 2H, CH_2—CH), 4.85 (m, 1H, =CH_2), 5.28 (m, 1H, =CH_2), 5.69 (m, 1H, CH=).

4.2.2. $[trans\text{-}(\eta^5\text{-}C_5Me_4CH_2CH=CH_2)Re(CO)_2(C_6F_5)(H)]$ (**2b**)

Complex **2b** was obtained following the same procedure as for **2a**, but using **1b** (100 mg, 0.184 mmol). It was isolated as a pale brown solid, 95.3 mg (0.167 mmol) yield: 90.8%. IR (hexane, ν(CO) cm^{-1}): 2022 (s), 1960 (s). ^1H NMR (C_6D_6) δ: −8.95 (Re–H), 1.38 (s, 6H, C_5Me_4), 1.43 (s, 6H, C_5Me_4), 2.98 (m, 2H, CH_2—CH), 4.77 (m, 1H, =CH_2), 5.22 (m, 1H, =CH_2), 5.58 (m, 1H, CH=).

4.2.3. $[(\eta^5\text{-}C_5Me_4CH_2CH=CH_2)Re(CO)_3]$ (**3**)

The hexane solution of **2a**, (prepared from **1a**, 100 mg, 0.199 mmol), in ca. 10 mL, was bubbled with CO for 3 min and was heated at 40 °C for 3 h. The IR spectra showed the formation of two new products. The solution was then chromatographed through a neutral alumina column. Elution with hexane produced the complex $[Re(CO)_5(I)]$ as a white solid after crystallization from hexane. Yield: 3.2 mg (0.007 mmol), 3.5%. IR (hexane, ν(CO) cm^{-1}): 2045(w), 2004(vs). MS (EI, based on ^{187}Re) m/z: 454 [M$^+$], 426

[M$^+$–CO], 398 [M$^+$–2CO], 370 [M$^+$–3CO]. Elution with hexane produced (η^5-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_3$ (**3**) as a white solid after crystallization from hexane. Yield: 21 mg (0.260 mmol), 26%. IR (hexane, ν(CO) cm^{-1}): 2014 (s), 1924 (s). ^{1}H NMR (CDCl$_3$) δ: 2.15 (s, 6H, C$_5$*Me*$_4$), 2.17 (s, 6H, C$_5$*Me*$_4$), 3.17 (td, J_{HH} = 5,9; 1,6 Hz, 2H, *CH*$_2$–CH), 4.95 (qd, 1H, J_{HH} = 17,2; 1,6 Hz, =C*H*$_2$), 5.02 (qd, 1H, J_{HH} 10,3; 1,6 Hz, =C*H*$_2$), 5.74 (m, 1H, C*H*=). ^{13}C{^{1}H} RMN (CDCl$_3$) δ: 10.8 (s, C$_5$*Me*$_4$), 12.0 (s, C$_5$*Me*$_4$), 30.2 (s, *C*H$_2$), 98.9 (s, C$_5$Me$_4$), 99.2 (s, C$_{ipso}$, C$_5$Me$_4$), 100.0 (s, C$_5$Me$_4$), 116.0 (s, CH=*C*H$_2$), 137.0 (s, *C*H=CH$_2$), 198.2 (s, CO). MS (EI, based on ^{187}Re) m/z: 432 [M$^+$], 404 [M$^+$–CO], 391 [M$^+$–CH$_2$CH=CH$_2$], 374 [M$^+$–2CO–2H]. Anal. Calc. for C$_{15}$H$_{17}$O$_3$Re: C, 41.75; H, 3.97. Found: C, 42.06; H, 4.08%.

4.2.4. [(η^5:η^2-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_2$] (4)

A solution of pentafluorophenyl hydride (**2b**) (prepared from **1b**, 100 mg, 0.184 mmol) in hexane (10 mL), was heated under CO at 45 °C for 6 h. An IR spectrum recorded at this time showed three new complexes. The reaction mixture was concentrated under reduced pressure to ca. 3 mL. and then was chromatographed through an alumina column. The hexane elutions afforded [Re(CO)$_5$(C$_6$F$_5$)]. The second fraction produced [(η^5-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_3$] (**3**), while successive elution with hexane yielded [(η^5:η^2-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_2$] (**4**) as a white solid after crystallization from hexane. [Re(CO)$_5$(C$_6$F$_5$)] was obtained as a white solid after pumped off the solvent, 2.4 mg (0.005 mmol) yield: 2.6%. IR (hexane, ν(CO) cm^{-1}): 2039(w), 2004(vs). MS (EI, based on ^{187}Re) m/z: 494 [M$^+$], 466 [M$^+$–CO], 438 [M$^+$–2CO], 410 [M$^+$–3CO]. Complex **3** was isolated as a white solid 21.0 mg (0.049 mmol) yield 26%. Complex **4** was obtained as pure sample with successive elution with hexane, 32 mg (0.079 mmol), yield: 43%. IR (hexane, ν(CO), cm^{-1}): 1962 (s), 1891 (s). ^{1}H MNR (CDCl$_3$) δ: 1.39 (dd, 1H, J_{HH} = 2.9, 9.8 Hz, C*H*$_2$CH), 1.59 (s, 3H, C$_5$*Me*$_4$), 2.16 (s, 3H, C$_5$*Me*$_4$), 2.18 (m, 1H, *CH*$_2$), 2.34 (s, 6H, C$_5$*Me*$_4$), 2.39 (m, 1H, CH), 2.41 (s, 6H, C$_5$*Me*$_4$), 2.68 (dd, 1H, J_{HH} = 2.9, 7.0 Hz, =C*H*$_2$), 3.20 (ddd, 1H, J_{HH} = 1.0, 7.0, 13.7 Hz, =C*H*$_2$). ^{13}C^{1}H NMR (CDCl$_3$) δ: 9.3 (s, C$_5$*Me*$_4$), 11.5 (broad, C$_5$*Me*$_4$), 12.6 (s, C$_5$*Me*$_4$), 22.0 (s, *C*H$_2$), 31.3 (s, *C*H$_2$), 58.3 (s, *C*H), 93.6 (s, C$_5$Me$_4$), 95.0 (s, C$_5$Me$_4$), 96.01 (s, C$_5$Me$_4$), 99.7 (s, C$_5$Me$_4$), 116.0 (s, C$_{ipso}$–C$_5$Me$_4$), 207.5 (s, CO), 207.7 (s, C*O*). MS (EI, based on ^{187}Re) m/z: 404 M$^+$, 374 M$^+$–CO–2H, 346 M$^+$-2CO-2H. Anal. Calc. for C$_{14}$H$_{17}$O$_2$Re: C, 41.67; H, 4.25. Found: C, 41.98; H, 4.12%.

4.2.5. [(η^5-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_2$(PMe$_3$)] (5)

(a) To an hexane solution of **2a** (prepared from **1a**, 100 mg, 0.199 mmol), in ca. 10 mL, PMe$_3$ was added (0.2 mL, 1.0 M THF solution) and the reaction mixture was stirred for 5 min at room temperature. After this time, the IR spectra showed two absorption bands at 1924 and 1860 cm^{-1}. The solution was concentrated to ca. 3 mL chromatographed through a short alumina column. Elution with hexane moved the complex [(η^5-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_2$-(PMe$_3$)] (**5**), (68 mg, 0.138 mmol, 69%). IR (hexane, ν(CO), cm^{-1}): 1924 (s), 1860 (s). ^{1}H MNR (CDCl$_3$) δ: 1.59 (d, J = 9.0, 9H, P*Me*$_3$), 2.09 (s, 12H, C$_5$*Me*$_4$), 3.27 (td, J_{HH} = 6.0, 1,5 Hz, 2H, C*H*$_2$–CH), 4.96 (qd, 1H, J_{HH} = 17,0; 1,5 Hz, =C*H*$_2$), 5.01 (qd, 1H, J_{HH} 10,1; 1,5 Hz, =C*H*$_2$), 5.79 (m, 1H, C*H*=). ^{13}C{^{1}H} NMR (CDCl$_3$) δ: 11.4 (s, broad, C$_5$*Me*$_4$), 22.7 (d, J = 34.8 Hz, P*Me*$_3$), 30.8 (s, *C*H$_2$), 98.8 (s, C$_5$Me$_4$), 99.4 (s, C$_{ipso}$, C$_5$Me$_4$), 100.4 (s, C$_5$Me$_4$), 116.1 (s, CH=*C*H$_2$), 136.8 (s, *C*H=CH$_2$), 206.2 (d, J = 7.6 Hz, CO). ^{31}P NMR (CDCl$_3$) δ: −28.2. MS (EI, based on ^{187}Re) m/z: 480 [M$^+$], 465 [M$^+$–Me], 452 [M$^+$–CO].

(b) The hexane solution of **2b**, (prepared from **1b**, 100 mg, 0.184 mmol), ca. 10 mL, was added PMe$_3$ (0.2 mL, 1.0 M THF solution) and the reaction mixture was stirred at room

temperature for 15 min. After this time, the solution was concentrated to ca. 3 mL chromatographed through a short alumina column. Elution with hexane moved the complex [(η^5-C$_5$Me$_4$CH$_2$CH=CH$_2$)Re(CO)$_2$(PMe$_3$)] (**5**), (44 mg, 0.092 mmol, yield: 46%). Successive elution with hexane afforded the complex **4**, which was obtained as pure sample 8 mg (0.019 mmol), yield: 10%.

4.3. X-ray structural determination of 4

Suitable yellow crystals for X-ray diffraction experiment were obtained by slow diffusion of hexane into concentrated dichloromethane solution of **4**. Intensity data were collected at low temperature (100(2) K) on a Bruker SMART CCD area detector diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using narrow frames (0.3° in ω). Cell parameters were refined from the observed setting angles and detector positions of strong reflections (4806 refl., 2θ < 56.56°). Data were corrected for Lorentz and polarization effects, and multi-scan absorption corrections were applied with SADABS program [25]. The structures were solved by Patterson method and completed by successive difference Fourier syntheses [25]. Refinement, by full-matrix least-squares on F^2 with SHELXL97 [26], was carried out including isotropic and subsequent anisotropic displacement parameters for all non-hydrogen atoms. Hydrogens for the methyl groups were included at calculated positions and refined with positional and thermal riding parameters; those of the allylic lateral chain were included from observed positions and freely refined as isotropic atoms. The highest electronic residuals (around 1.0 e/Å^3) were observed in close proximity of the Re metal and have no chemical sense. Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program [26].

Crystal data for compound **4**: C$_{14}$H$_{17}$O$_2$Re, M = 403.48; yellow cubic block, 0.163 × 0.141 × 0.095 mm^3; monoclinic, $P2_1/n$; a = 8.5254(9), b = 12.9818(14), c = 11.6783(13) Å, β = 93.649(2)°, Z = 4; V = 1289.9(2) Å^3; D_c = 2.078 g/cm^3; μ = 9.408 mm^{-1}, minimum and maximum transmission factors 0.262 and 0.424; $2\theta_{max}$ = 56.56°; 8404 reflections collected, 3045 unique [R_{int} = 0.0280]; number of data/restrains/parameters 3045/0/178; final GOF 1.046, R_1 = 0.0238 [2799 reflections, I > 2σ(I)], wR_2 = 0.0552 for all data.

Appendix A. Supplementary material

CCDC 748385 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.042.

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