Synthesis, reactivity and molecular structure of phosphino tetramethyl cyclopentadienyl complex (η^5: η^1-$C_5Me_4CH_2PPh_2$)Re$(CO)_2$†

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The fulvene complex (η^6-$C_5Me_4CH_2$)Re(C_6F_5)$(CO)_2$ reacts at the exocyclic methylene carbon with potassium diphenylphosphide to yield the anionic species [(η^5-$C_5Me_4CH_2PPh_2$)Re(C_6F_5)$(CO)_2$]$^-$ (**1**). Protonation of **1** with HCl at 0 °C produces the hydride complex *trans*-(η^5-$C_5Me_4CH_2PPh_2$)-Re(C_6F_5)(H)$(CO)_2$ (**2**). Thermolysis of a hexanes solution of **2**, under nitrogen atmosphere, produces the chelated complex (η^5:η^1-$C_5Me_4CH_2PPh_2$)Re$(CO)_2$ (**3**) in good yield. The thermolysis under a CO atmosphere affords a mixture of the complexes (η^5:η^1-$C_5Me_4CH_2PPh_2$)Re$(CO)_2$ (**3**) and (η^5-$C_5Me_4CH_2PPh_2$)Re$(CO)_3$ (**4a**). The reaction of **3** with two electron donor ligands yields (η^5-$C_5Me_4CH_2PPh_2$)Re$(CO)_2$(L) (**4a**, L = CO; **4b**, L = PMe_3; **4c**, L = ^{t}BuNC). Complex **3** also reacts with I_2, HBF_4 and MeOTf to yield the cationic compounds *trans*-[(η^5:η^1-$C_5Me_4CH_2PPh_2$)Re(R)$(CO)_2$]$^+$ (**5a**, R = I; **5b**, R = H; **5c**, R = Me). Upon treatment with chloroform, the hydride complex **5b** converts to the corresponding chloro derivative **5d**. The *trans* stereochemistry for complexes **5** have been assigned on basis of ν(CO) IR intensities and ^{13}C-NMR chemical shifts. The reaction of the cationic complexes (**5a**, **5c**) with KI and $Me_3NO\cdot 2H_2O$ yields the neutral species *cis*-(η^5:η^1-$C_5Me_4CH_2PPh_2$)-Re(I)(R)(CO) (**6a**, R = I, **6b**, R = Me). The molecular structure of **3** and **6a** have been determined by X-ray crystallography.

Introduction

In recent years, hetero-bidentate ligands containing a cyclopentadienyl linked to a heteroatom functionality[1] or an alkene[2] group have received considerable attention mainly because they are envisaged as convenient entries to mono and bimetallic complexes (homo or hetero). These ligands belong to the group of *hemilabile ligands*,[3] where the side-chain functionality can either act as donor or as a spectator ligand. The bifunctional character of the hemilabile ligands provides interesting perspectives in terms of stabilization of reactive species, small molecule activation and homogeneous catalysis.[4]

Nevertheless, few half sandwich compounds of this type are known for group 7 metals.[5] For instance, Wang has reported the synthesis and reactivity of the complex (η^5:η^1-$C_5H_4(CH_2)_2$-NHMe)Re$(CO)_2$[6] and Gladysz has prepared diphenylphosphino cyclopentadienyl complexes (η^5-$C_5H_4PPh_2$)Re$(CO)_3$.[7] Other heterodifunctional ligand that contain a phosphine and amino groups connected directly or by a short chain to the cyclopentadienyl ring bound to Re$(CO)_3$ fragment, have been developed by Bolm. This Josiphos type of ligand coordinated to palladium was used as catalyst in asymmetric allylic alkylation reactions.[8] A related chelating derivative (η^5-$C_5H_4PPh_2$)Re-(NO)(R)(PPh_3) (R = PPh_2,CH_2PPh_2) was described by Gladysz and used to prepare heterobimetallic rhenium/rhodium complexes.[9]

As far as we are aware heterodifunctional phosphinotetramethylcyclopentadienyl-rhenium complexes remain unreported in literature. Nevertheless some procedures have been published for the preparation of the heterodifunctional phosphinotetramethylcyclopentadienyl ligands.[10] One of these approaches involve the modification of some of the classical methods used for the preparation of pentamethylcyclopentadienyl ligand.[11] Another method used either tetramethylspiro[2.4]hepta-2,6-diene ($C_5Me_4(CH_2)_2$)[12] or 1,2,3,4-tetramethylfulvene ($C_5Me_4CH_2$).[10,13] in reaction with KPR_2 (R = Ph, Me), producing the potassium salt, which can be easily used to prepare complexes of the type (η^5-$C_5Me_4(CH_2)_nPPh_2$)ML_x (n = 1,2).[10]

We have previously demonstrated that tetramethylfulvene complexes (η^6-$C_5Me_4CH_2$)Re(R)$(CO)_2$ (R = C_6F_5, I) can be used as good precursors in the syntheses of a series of functionalized tetramethylcyclopentadienyl rhenium complexes. For instance, the fulvene complexes react with allylmagnesium chloride or 2-thienyllithium to yield the anionic species [(η^5-$C_5Me_4CH_2L$)Re(R)$(CO)_2$]$^-$ (L = CH$_2$CH=CH$_2$; 2-C_4H_3S). Protonation with HCl afforded the *trans* hydride complexes, which under thermolysis conditions (hexanes solution under an N_2 atmosphere at 40 °C) yielded the compounds (η^5:η^x-$C_5Me_4CH_2L$)Re$(CO)_2$ (x = 2 and 1 respectively).[14]

In continuation of our studies on new functionally substituted tetramethylcyclopentadienyl rhenium compounds, we now report the synthesis and characterization of the chelated complex

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$(\eta^5:\eta^1\text{-}C_5Me_4CH_2PPh_2)Re(CO)_2$. Also described are reactions of this compound, with two electron donor ligands leading to a series of a three legged piano stool type of complexes of a formula $(\eta^5\text{-}C_5Me_4CH_2PPh_2)Re(L)(CO)_2$.(L = CO, PMe_3, ^{t}BuNC) and the reactions with iodine, HBF_4 and MeOTf to yield the new chelated cationic complexes *trans*-$[(\eta^5:\eta^1\text{-}C_5Me_4CH_2PPh_2)Re(R)(CO)_2]^+$ (R = I, H, Me).

Results and discussion

Reactions of the fulvene complex $(\eta^6\text{-}C_5Me_4CH_2)(C_6F_5)Re(CO)_2$

Addition of a small excess of potassium diphenylphosphide to a solution of the fulvene precursor produced the anionic complex $[(\eta^5\text{-}C_5Me_4CH_2PPh_2)Re(C_6F_5)(CO)_2]^-$ (**1**) (Scheme 1). The anion **1** was not isolated and it was identified only by IR spectroscopy in solution. The two prominent absorption bands (ν(CO)), observed at 1862 and 1774 cm^{-1} in THF, are comparable to those reported for analogous anionic rhenium complexes.[14,15] Complex **1** was reacted *in situ* with HCl at 0 °C to give the hydride complex *trans*-$(\eta^5\text{-}C_5Me_4CH_2PPh_2)Re(C_6F_5)(H)(CO)_2$ (**2**) (Scheme 1). This compound showed characteristic CO absorption bands at 2022 and 1945 cm^{-1} in THF solution, similar to those observed in other hydride fluoroaryl complexes possessing the two CO ligands in a diagonal or *trans* orientation.[16] The ^{1}H-NMR spectrum of **2** in d_6-benzene showed a broad low frequency resonance (δ: −8.82) for the hydride proton, probably broadened by long range couplings to fluorine nuclei, as observed for the related complexes *trans*-$(\eta^5\text{-}C_5Me_5)Re(Aryl_F)(H)(CO)_2$ ($Aryl_F$ = C_6F_5, 2,3,5,6-C_6HF_4).[16] The presence of the (diphenylphosphine-methyl)-tetramethylcyclopentadienyl ligand ($C_5Me_4CH_2PPh_2$) in complex **2**, was unequivocally established by ^{1}H, ^{13}C and ^{31}P-NMR spectroscopy. In addition, the presence of the pentafluorophenyl group was confirmed by ^{19}F NMR spectroscopy.[15,16] The *trans* stereochemistry was confirmed by the presence of a single resonance for the CO groups in the ^{13}C-NMR spectrum. The extreme air sensitivity of the hydride complex **2** both as a solid and in solution, prevented us from obtaining the mass spectrum and elemental analysis.

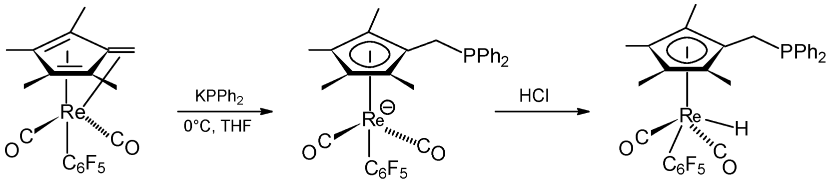
Thermal reactions of *trans*-$(\eta^5\text{-}C_5Me_4CH_2PPh_2)Re(C_6F_5)(H)(CO)_2$ (2)

The hydride complex **2**, underwent reductive elimination of pentafluorobenzene very easily. However, the nature of the organometallic products depended on whether CO or N_2 was used for the reaction (Scheme 2): under nitrogen only the chelated complex $(\eta^5:\eta^1\text{-}C_5Me_4CH_2PPh_2)Re(CO)_2$ (**3**) was obtained in 70% yield, whereas thermal reaction under a CO atmosphere afforded a mixture of **3** and the tricarbonyl $(\eta^5\text{-}C_5Me_4CH_2PPh_2)Re(CO)_3$ **4a**, in a 2 : 1 ratio. Prolonged heating of the mixture resulted exclusively in the formation of the complex **4a**. In both cases, the presence of C_6F_5H was confirmed by GC-MS.

Complex **3** was isolated as air stable, pale yellow crystals, soluble in most of organic solvents; its solutions are stable for weeks if kept under nitrogen. Infrared data of **3** showed two strong CO absorptions at almost the same frequency to those observed for the complex $(\eta^5\text{-}C_5Me_5)Re(PPh_3)(CO)_2$.[17] The presence of two distinct methyl resonances observed in the ^{1}H NMR spectrum of complex **3** and one doublet for methylene group (J_{PH} = 35 Hz) agree well with the symmetric nature of the complex that results from coordination of the $C_5Me_4CH_2PPh_2$ ligand to rhenium in an $\eta^5:\eta^1$ fashion. In addition, to the expected resonances for the carbon nuclei of the chelated ligand, the ^{13}C NMR spectrum of **3** also showed a high frequency doublet (δ: 207.2; J_{PC} = 7.7 Hz) for the two equivalent CO groups. The $^{31}P\{^1H\}$ NMR spectrum, exhibited a single resonance at δ: −105.9 for the coordinated phosphorus of the phosphine side arm. Further confirmation of the structure of complex **3** was obtained from a X-ray diffraction study (*vide infra*).

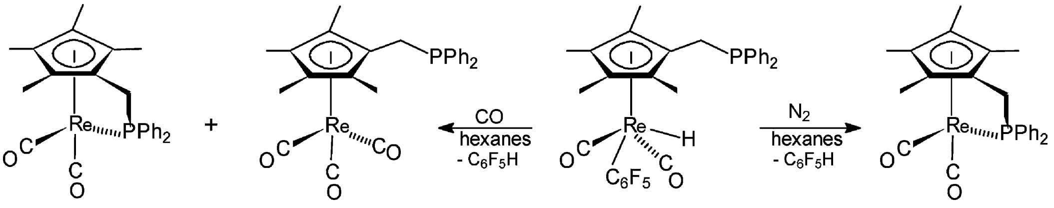
Reaction of the complex $(\eta^5:\eta^1\text{-}C_5Me_4CH_2PPh_2)Re(CO)_2$ (3) with two electron donor ligands

In an effort to explore the reactivity of the phosphine functionalized tetramethylcyclopentadienyl ligand coordinated to rhenium,



1 **2**

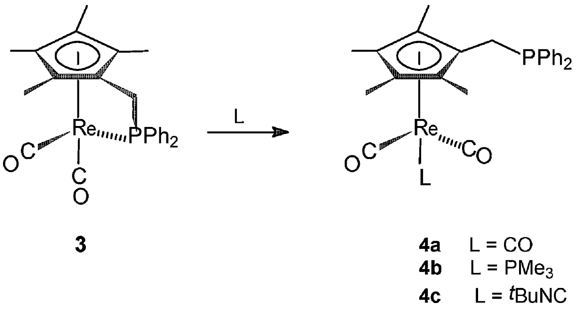
Scheme 1 Godoy *et al*. "Synthesis, Reactivity and Molecular Structure of Phosphino…."



3 **4a** **2** **3**

Scheme 2 Godoy *et al*. "Synthesis, Reactivity and Molecular Structure of Phosphino…."

complex **3** was reacted with CO, PMe_3 and ^{t}BuNC. In all cases, displacement of the coordinated phosphine of the side arm was observed, producing the three-legged piano-stool complexes, (η^5-$C_5Me_4CH_2PPh_2$)Re(L)$(CO)_2$ (**4a**, L = CO; **4b**, L = PMe_3; **4c**, L = ^{t}BuNC) in almost quantitative yields (Scheme 3). The IR spectra of the complexes **4a** and **4b** showed CO absorptions bands at the same wave number as those observed for the complexes Cp*Re$(CO)_3$[18] and Cp*Re(PMe_3)$(CO)_2$[19] respectively. Evidence for the non-coordinated diphenylphosphine side arm of the cyclopentadienyl ligand could be easily inferred from the $^{31}P\{^1H\}$ NMR spectrum of the complexes **4a–c**, since a single resonance was observed at about δ –14 in all cases. A similar low frequency shift of the intermolecular coordinated and non-coordinated phosphine group has been also previously observed in the complexes (η^5-$C_5H_4SiMe_2P$(p-tolyl)$_2$)$_2$ZrMe_2 and (η^5:η^1-$C_5H_4SiMe_2P$(p-tolyl)$_2$)$_2$ZrMe.[20] In addition, the $^{31}P\{^1H\}$ NMR spectrum of **4b** also showed a resonance for the PMe_3 ligand at δ –28.4 which agrees well with that reported for Cp*Re(PMe_3)$(CO)_2$ (δ –27.0).[19]



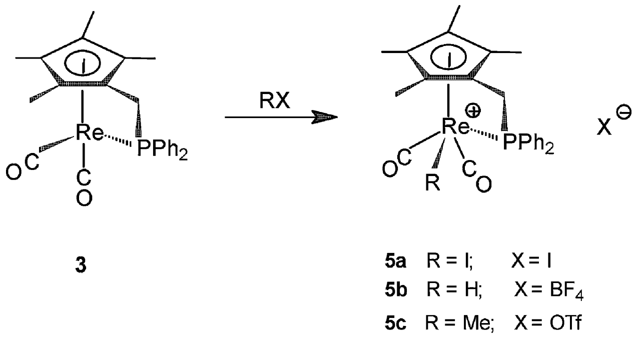
Scheme 3 Godoy *et al*. "Synthesis, Reactivity and Molecular Structure of Phosphino...."

The presence of the ^{t}BuCN ligand coordinated to rhenium in complex **4c** was confirmed by IR (ν(C≡N) at 2132 cm^{-1} (s)), ^1H and ^{13}C-NMR spectroscopy (see Experimental section). The spectroscopic parameters are in good agreement with those reported for the complex CpRe(CN^{t}Bu)$(CO)_2$.[21]

The lability of the phosphine ligand in compound **3** is not surprising, it has been previously observed in other Cp–phosphine metal complexes.[22] This can be associated to the ring strain, which can be evidenced by the structural studies of **3**; the angle between the methylene carbon, the phosphorus atom and the rhenium atom is smaller than 109.5°, *i.e.* a tetrahedral angle. As C(10) appears to be displaced from the plane defined by C(1) to C(5), upon ring-opening C(10) remains in the plane defined by C(1) to C(5) yielding complexes **4a–c**.

When exposed to air, solutions of compounds **4a–c** suffered partial oxidation of the phosphine group to yield the complexes (η^5-$C_5Me_4CH_2P(O)Ph_2$)Re(L)$(CO)_2$ (L = CO, PMe_3, ^{t}BuNC). Oxidation is indicated by an high frequency shift of the $^{31}P\{^1H\}$ NMR resonance ($\Delta\delta$ ~ 42) as well as by mass spectra of the final products. We did not make further efforts to isolate and characterize these oxidation products. This kind of oxidation reaction was also observed in the molecule ($C_5Me_4HPPh_2$); in both cases, the $^{31}P\{^1H\}$ NMR spectrum showed a single resonance shifted high frequency ($\Delta\delta$ ~ 42) with respect to the unoxidised phosphorus atoms. Green *et al.* reported the oxidation of the phosphine ligand in the complex [(η^5-$C_5Me_4CH_2PMe_2$)]$_2$Fe, which was confirmed by X-Ray diffraction.[10]

Oxidative addition reactions to (η^5:η^1-$C_5Me_4CH_2PPh_2$)Re$(CO)_2$ (3). While the reaction of **3** with two electron donor ligands produced Re(I) complexes possessing a three-legged piano-stool type of structure, reaction of this complex with I_2, HBF_4 and MeOTf yielded Re(III) cationic complexes *trans*-[(η^5:η^1-$C_5Me_4CH_2PPh_2$)-Re(R)$(CO)_2$]$^+$ (**5a**, R = I; **5b**, R = H; **5c**, R = Me) (Scheme 4). As cationic species, these complexes are insoluble in non polar solvents but dissolve in $CHCl_3$, CH_2Cl_2 and THF, in which they are stable with respect to thermal isomerization. The presence of the (diphenylphosphinomethyl)-tetramethylcyclopentadienyl ligand coordinated to the rhenium in an η^5:η^1-fashion was unequivocally established by ^1H and ^{13}C NMR spectroscopy.



Scheme 4 Godoy *et al*. "Synthesis, Reactivity and Molecular Structure of chelated complex...."

Like many other hydrido rhenium complex,[23] **5b** transforms to the chloro derivative *trans*-[(η^5:η^1-$C_5Me_4CH_2PPh_2$)Re(Cl)$(CO)_2$]$^+$ (**5d**) when dissolved in chlorinated solvents. After 16 h in $CDCl_3$ the hydride complex transforms completely into **5d**. An example of this type of chlorination has been reported by Jones *et al.*;[24] addition of CCl_4 to (η^5:η^1-$C_5H_4SiMe_2CH_2PPh_2$)Rh(H)(C_6F_5) led to the complex (η^5:η^1-$C_5H_4SiMe_2CH_2PPh_2$)Rh(Cl)(C_6F_5).

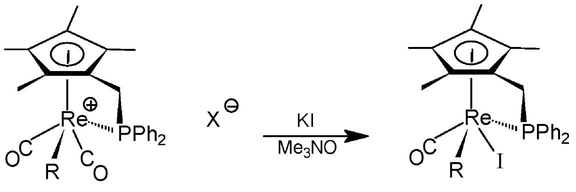
The IR spectra of compounds **5a–d** showed only two ν(CO) absorptions. Furthermore, the relative intensity of these absorptions are typical for a *trans* arrangement of the two CO groups *i.e.* the higher wavenumber absorption being much less intense of the pair. As expected, the two ν(CO) absorptions band are shifted to much higher frequency when compared to those observed for **3** as a result of reduction of the electron density at the Re(III) in complexes **5a–d**.

The $^{31}P\{^1H\}$ NMR spectra of **5a–d** also confirmed the coordination of the diphenylphosphine group to rhenium, since a single resonance is observed at about δ –150. The low frequency shift of about 50 ppm when compared with the Re(I) starting material, agrees well with those observed for the complexes (η^5:η^1-$C_5Me_4SiMe_2CH_2PPh_2$)Rh(C_2H_4) and (η^5:η^1-$C_5Me_4SiMe_2CH_2PPh_2$)RhI_2.[25]

The presence of a doublet at δ ~ 195 (J_{PC} ≅ 16 Hz) for the CO groups observed in the $^{13}C\{^1H\}$ NMR spectra of **5a–d** is further evidence for a *trans* stereochemistry exhibited for these compounds.

The ^1H-NMR spectrum of the hydride complex (**5b**) showed a doublet at δ –6.56 (J_{HP} = 20.8 Hz) which confirmed the coordination of the diphenylphosphine ligand to the rhenium fragment. This chemical shift is very close to those reported for $[(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2\ CH_2CH{=}CH_2)Re(H)(CO)_2]^+$ (*δ*: –6.64)[14] and other rhenium hydride complexes.[23] It is important to note that the values of the coupling constant J_{PH} can also be used to support the *trans* stereochemistry previously proposed. For example, Faller and Anderson reported the synthesis and characterization of a series of hydride complexes, $(\eta^5\text{-}C_5H_5)Mo(PR_3)(H)(CO)_2$ (R = Me, n-Bu, Ph), the ^{1}H-NMR spectra of the *trans* complexes exhibit one resonance at ~ –6.2 ppm ($J_{HP} \cong 22$ Hz), while the *cis* isomers showed a coupling significantly larger ($J_{HP} \cong 60$ Hz).[26] A similar coupling constant was found in the complex *trans*-$[(Cp)Re(PPh_3)(H)(CO)_2]^+$, where the J_{HP} is 2.5–3 times smaller than in the corresponding *cis* isomer.[27]

With the aim of having a more complete understanding of the effect of the oxidation state of rhenium on the coordination of the lateral phosphine ligand, we carried out the reaction of the cationic complexes *trans*-$[(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2PPh_2)Re(R)(CO)_2]^+$ (**5a**, R = I and **5c**, R = Me) with KI in the presence of the decarbonylation agent $Me_3NO{\cdot}2H_2O$ in CH_2Cl_2 at room temperature. In both cases, the neutral chelated complexes *cis*-$(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2PPh_2)Re(I)(R)(CO)$ (**6a**, R = I and **6b**, R = Me) were obtained, as shown in Scheme 5. The products were isolated as a single isomers, as red–brown and orange microcrystals respectively, and characterized by IR and NMR spectroscopies. In addition the molecular structure of *cis*-$(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2PPh_2)ReI_2(CO)$ (**6a**) was determined by X-ray crystallography. Similar decarbonylation reactions, have been observed previously in our laboratory in the cationic complexes $[Cp^*ReI(CO)_2(L)]^+\ I_3^-$ (L = CO, $P(OMe)_3$, $P(OPh)_3$, PMe_3, PMe_2Ph) which yield the neutral complexes $Cp^*ReI_2(L)(CO)$.[28] Complex **6a** showed a single *ν*(CO) absorption band at 1906 cm^{-1} and a single resonance (δ 217; J_{PC} = 17 Hz) for the CO group in the ^{13}C NMR spectrum, both parameters are almost identical to those recorded for the monocarbonyl diiodo complex *cis*-$Cp^*ReI_2(PMe_2Ph)(CO)$.[28]



5a R = I; X = I
5c R = Me; X = OTf

6a R = I
6c R = Me

Scheme 5 Godoy *et al*. "Synthesis, Reactivity and Molecular Structure of Phosphino....

X-Ray structure of 3 and 6a. The molecular structures of $(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2PPh_2)Re(CO)_2$ (**3**) and $(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2PPh_2)Re(I)_2(CO)$ (**6a**) are shown in Fig. 1 and 2, respectively. Table 1 collects the most relevant bond distances

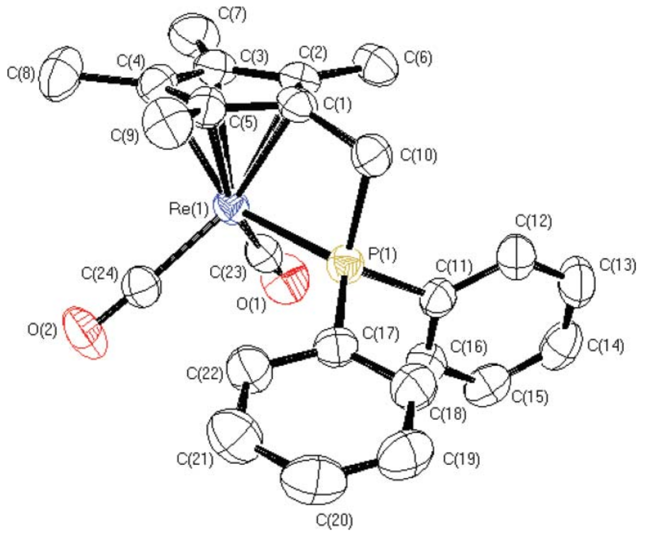


Fig. 1 Molecular structure of $(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2PPh_2)Re(CO)_2$ (**3**) drawn with 50% probability displacement ellipsoids. Hydrogen atoms omitted.

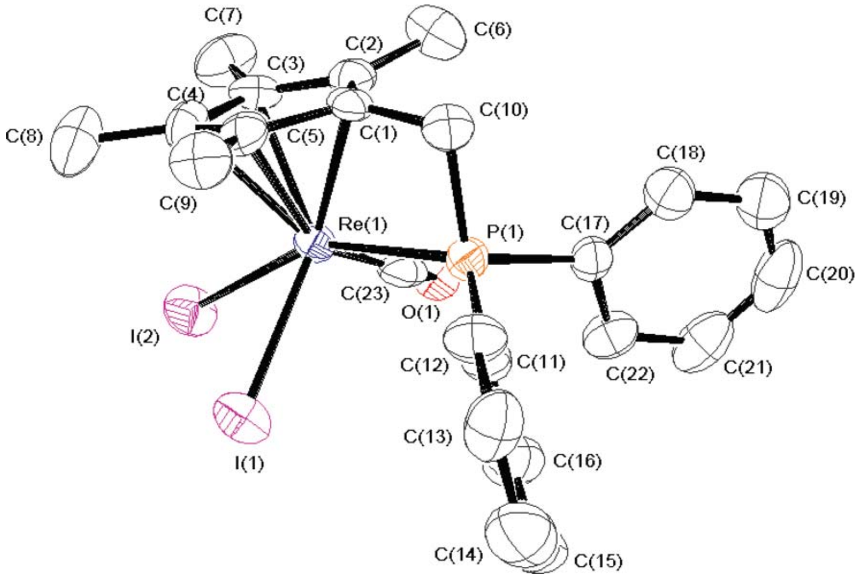


Fig. 2 Molecular structure of $(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2PPh_2)Re(I)_2(CO)$ (**6a**) drawn with 50% probability displacement ellipsoids. Hydrogen atoms omitted.

Table 1 Selected bond lengths (Å) and angles (°) for complexes **3** and **6a**

	3	6a
Re(1)–P(1)	2.320 (8)	2.436(3)
Re(1)–C(1)	2.259 (3)	2.257(9)
Re(1)–C(23)	1.896 (3)	1.865(10)
Re(1)–C(24)	1.905 (3)	—
Re(1)–I(1)	—	2.7868(9)
Re(2)–I(2)	—	2.7855(8)
Re(1)–G[a]	1.929 (3)	1.940 (3)
C(23)–O(1)	1.156 (4)	1.080(9)
C(24)–O(2)	1.151 (4)	—
C(1)–C(10)	1.525 (4)	1.524(14)
C(10)–P(1)	1.856 (3)	1.832(10)
C(23)–Re(1)–C(24)	89.08 (14)	—
Re(1)–P(1)–C(10)	91.16 (10)	91.9(3)
C(1)–C(10)–P(1)	97.78 (19)	95.6(6)
Re(1)–C(5)–C(9)	127.8 (2)	128.5(7)
I(1)–Re(1)–I(2)	—	81.69(3)

[a] G = Centroid ($C_5Me_4CH_2PPh_2$)

and angles. Complex **3** exhibits a three-legged piano-stool type of structure, where the two basal positions are occupied by carbonyls groups and the third is used for the phosphorus atom of the cyclopentadienyl diphenylphosphine moiety, whereas complex **6a** exhibits a four-legged piano-stool structure with a CO, two iodines and the phosphorus occupying the basal positions.

The Re–CO bond distances (1.896(3) and 1.905(3) Å) of **3** are in a good agreement with those reported for [(η^5-$C_5Me_4CH_2PMe_3$)Re(CO)$_2$(PMe$_3$)]$^+$ I$^-$ (1.877 and 1.912 Å).[29] The C(10)–P(1) and C(1)–C(10) distances (1.856(3) and 1.525(4) Å) are comparable to those of the complexes [(η^5:η^1-$C_5H_4CMe_2P$(*p*-tolyl$_2$))$_2$Zr(X)]$^+$ (X = Me, Cl).[20]

In relation of the Re-P length (2.320(8) Å) of 3 is shorter than the Re(III) complex **6a** (2.436(3) Å), and is very close to other phosphine complexes of rhenium(I).[14,28]

The Re–I(1) and Re–I(2) distances in **6a** are 2.7855(8) and 2.7868(9) Å, respectively, indicating that they are unaffected by the ligand *trans* to them. The I(1)–Re–I(2) angle is 81.69(3)°, which clearly establishes the *cis* orientation of these ligands. This value is in good agreement with those reported for the complex *cis*-(η^5-C_5Me_5)Re(I)$_2$(CO)$_2$.[29]

Conclusion

The fulvene complex (η^6-$C_5Me_4CH_2$)Re(C_6F_5)(CO)$_2$ acts as a good precursor for the synthesis of several functionalized tetramethylcyclopentadienyl rhenium complexes. Reaction with KPPh$_2$ followed by HCl yields *trans*-(η^5-$C_5Me_4CH_2PPh_2$)Re(C_6F_5)(H)(CO)$_2$. Reductive elimination of C_6F_5H yields the chelated species (η^5:η^1-$C_5Me_4CH_2PPh_2$)Re(CO)$_2$ containing an intramolecularly coordinated diphenylphosphine fragment. The PPh$_2$ group is easily displaced by two electron donor ligands such as CO, PMe$_3$ and ^{t}BuNC. The phosphorus atom of the side chain of the functionalized tetramethylcyclopentadienyl system, is partially oxidized when the unchelated species are exposed to air. Reaction with I$_2$, HBF$_4$ and MeOTf yielded Re(III) cationic species with a *trans* stereochemistry, in which the PPh$_2$ sidearm remained coordinated. A CO group could be abstracted from the cationic species with Me$_3$NO in the presence of KI.

Experimental

General

All reactions 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. Potassium diphenylphosphide and hydrogen chlorine in ether were obtained from Aldrich. Infrared spectra were recorded in solution (CaF$_2$ cell) on a Perkin-Elmer FT-1605 spectrophotometer. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker AC 400 instrument. All ^{1}H NMR chemical shifts are referenced using the chemical shifts of residual solvent resonance. ^{13}C NMR chemical shifts were referenced to solvent peaks. ^{19}F NMR spectra were referenced to internal C_6F_6 at δ −162.9 and ^{31}P{^{1}H} NMR chemical shifts were referenced to external H_3PO_4 (85%) at δ 0.0.

Mass spectra (VG Autospec) were obtained at the Chemistry Department of the University of York, England. Elemental analyses were obtained at the Centro de Instrumentación, Pontificia Universidad Católica de Chile, Santiago, Chile.

Syntheses

The fulvene complex (η^6-$C_5Me_4CH_2$)Re(CO)$_2$(C_6F_5) was prepared from (η^5-C_5Me_5)Re(CO)$_3$ according to the procedure described in literature.[15b]

***Trans*-(η^5-$C_5Me_4CH_2PPh_2$)Re(C_6F_5)(H)(CO)$_2$ (2).** To a solution of (η^6-$C_5Me_4CH_2$)Re(C_6F_5)(CO)$_2$ (100 mg, 0.184 mmol) in THF (15 mL) stirred at 0 °C was added 0.40 mL (0.200 mmol) of KPPh$_2$ (0.5 M in THF). The reaction mixture turned pale yellow immediately and the IR spectrum only showed CO absorptions at 1862 and 1774 cm^{-1}. Then the 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 species and new CO absorptions at 2015, 1942 cm^{-1}. The solvent was removed under vacuum. Hexanes (3 × 10 mL) was added to the residue, and the mixture filtered. The solvent was pumped off to afford **2** as a pale yellow solid. IR [hexane, ν(CO), cm^{-1}]: 2024 (s), 1959 (vs). ^{1}H NMR (C_6D_6) δ: −8.82 (Re-H), 1.40 (s, 6H, C_5Me_4), 1.42 (s, 6H, C_5Me_4), 4.95 (d, J_{PH} 9.9 Hz, 2H, CH_2), 7.65 (m, 10 H, PPh_2). ^{13}C{^{1}H} NMR (C_6D_6) δ : 10.7 (s, C_5Me_4), 10.8 (s, C_5Me_4), 26.6 (d, J_{PC} 18 Hz, CH_2), 97.5 (s, C_5Me$_4$), 98.6 (s, C_5Me$_4$), 99.6 (s, C_5Me$_4$); 128.5 (d, J_{PC} 11 Hz, C$_{meta}$ Ph), 130.1 (d, J_{PC} 2 Hz, C$_{para}$, Ph), 132.2 (d, J_{PC} 13 Hz, C$_{ortho}$, Ph), 134.6 (d, J_{PC} 47 Hz, C$_{ipso}$, Ph), 195.4 (s, CO). ^{31}P{^{1}H} NMR δ: -16.2. ^{19}F (C_6D_6) δ: -102.9 (d, J_{FF} 22.9 Hz, 2F$_{ortho}$), -157.6 (t, J_{FF} = 22.9 F$_{para}$), -162.4 (t, J_{FF} = 22.9 F$_{meta}$).

(η^5:η^1-$C_5Me_4CH_2PPh_2$)Re(CO)$_2$ (3). The hexanes solution containing the hydride complex **2** (prepared from fulvene complex, 100 mg, 0.184 mmol), was heated under N$_2$ at 40 °C for 3 h. The solution turned pale yellow and yellow solid was formed. An IR spectrum recorded at this time showed two strong absorption bands at 1926 and 1866 cm^{-1} (hexanes). The reaction mixture was concentrated under vacuum, and the solid was chromatographed through a short Florisil column. Elution with hexanes–CH$_2$Cl$_2$ (1 : 1) moved a light yellow band from which complex **3** was isolated in 70% as yellow solid (72 mg, 0.128 mmol). IR [CH$_2$Cl$_2$, ν(CO), cm^{-1}]: 1920 (vs), 1855 (vs). ^{1}H-NMR (C_6D_6) δ: 2.16 (s, 6H, C_5Me_4), 2.28 (s, 6H, C_5Me_4), 4.06 (d, J_{PH} 8.8 Hz, 2H,CH_2), 7.42 (m, 6H, PPh_2), 7.66 (m, 4H, PPh_2). ^{13}C{^{1}H} NMR (CDCl$_3$)

δ : 11.2 (s, C_5Me_4), 11.9 (s, C_5Me_4), 24.5 (d, J_{PC} 35 Hz, CH_2), 80.2 (d, J_{PC} 3 Hz, C_5Me_4), 91.4 (d, J_{PC} 2 Hz, C_5Me_4), 98.5 (d, J_{PC} 3 Hz, C_5Me_4), 128.5 (d, J_{PC} 11 Hz, C_{meta} Ph), 130.1 (d, J_{PC} 2, C_{para}, Ph), 132.2 (d, J_{PC} 13 Hz, C_{ortho}, Ph), 134.6 (d, J_{PC} 47 Hz, C_{ipso}, Ph), 207.2 (d, J_{PC} 8 Hz, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: -105.9 (s, PPh_2). Mass spectrum (low energy) (IE, based on ^{187}Re) m/z : 562 [M^+], 532 [M^+ – CO –2H], 506 [M^+ – 2CO].

*(a) From complex **2***

(η^5-$C_5Me_4CH_2PPh_2$)Re(CO)$_3$ (4a). The hexanes solution containing the hydride complex **2** (prepared from **1**, 100 mg, 0.184 mmol), was bubbled with CO and then heated at 40 °C for 3 h. An IR spectrum recorded at this time showed two strong absorption bands at 2026 and 1966 cm^{-1}, and also minor absorptions at 2013 and 1923 cm^{-1}. The reaction mixture was concentrated under vacuum to *ca.* 3 mL, and then it was filtered through a short Florisil column (3 cm) under a N_2 atmosphere. Elution with hexanes removed the complex (η^5-$C_5Me_4CH_2PPh_2$)Re(CO)$_3$ (**4a**), which was obtained as a white solid after evaporation of the solvent. Recrystallisation from hexanes yielded **4a** as solid as with (26 mg, 0.044 mmol, 24% yield) elution with hexanes : CH_2Cl_2 (1:4) removed the chelated complex **3** (42 mg, 0.075 mmol, 41% yield). (η^5-$C_5Me_4CH_2PPh_2$)Re(CO)$_3$ (**4a**). IR [hexanes, ν(CO), cm^{-1}]: 2013 (s) 1923 (s); ^1H NMR ($CDCl_3$) δ: 1.81 (s, 6H, C_5Me_4), 2.14 (s, 6H, C_5Me_4), 3.25 (s, 2H, CH_2), 7.57 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 10.7 (s, C_5Me_4), 10.8 (s, C_5Me_4), 26.6 (d, J_{PH} = 18 Hz, CH_2), 97.5 (s, C_5Me_4), 98.6 (s, C_5Me_4), 99.5 (s, C_5Me_4), 128.6 (d, J_{PC} = 7 Hz *Ph*), 130.8 (d, J_{PC} = 11 Hz *Ph*), 136.8 (d, J_{PC} = 15 Hz *Ph*), 133.2 (d, J_{PC} = 19 *Ph*), 197.9 (s, *C*O). $^{31}P\{^1H\}$ NMR δ: -14.7. MS (EI, based on ^{187}Re) m/z: 562 [M^+ – CO], 532 [M^+ – 2CO – 2H].

*(a) From complex **3***

(η^5-$C_5Me_4CH_2PPh_2$)Re(CO)$_3$ (4a). A sample of **3** (10 mg, 0.018 mmol) in benzene-d_6 in an NMR tube was left under a CO atmosphere for 12 h at room temperature. After this time the NMR spectrum showed the complete disappearance of **3** and the presence of **4a**.

(η^5-$C_5Me_4CH_2PPh_2$)Re(PMe_3)(CO)$_2$ (4b). To a solution of complex **3** (30 mg; 0.054 mmol) in benzene-d_6 was added PMe_3 (6 μL, 0.057 mmol, d = 0.735 g/mL; 97%) the reaction was monitored by ^1H NMR spectroscopy. After 5 min at room temperature, the spectrum showed the complete disappearance of the chelated complex **3** and the presence of the **4b**, the reaction mixture was filtered through Celite, the solvent was pumped off and the complex **4b** was isolated as a white solid. Yield 33 mg (0.052 mmol, 96%). IR [hexanes, ν(CO), cm^{-1}]: 1920 (s), 1856 (vs). ^1H NMR (C_6D_6). δ: 1.33 (d, J_{PH} = 9.10 Hz, 9H, PMe_3), 1.86 (s, 6H, C_5Me_4), 1.90 (s, 6H, C_5Me_4), 3.41 (s, 2H, CH_2), 7.11 (m, 6H, *Ph*), 7.44 (m, 4H, *Ph*). $^{13}C\{^1H\}$-NMR (C_6D_6) δ: 11.3 (s, C_5Me_4), 11.0 (s, C_5Me_4), 22.1 (d, J_{PC} = 35 Hz, PMe_3), 27.6 (d, J_{PC} = 18 Hz, CH_2), 94.6 (d, J_{PC} = 19 Hz, C_5M_4), 95.0 (s, C_5Me_4), 96.7 (d, J_{PC} = 2 Hz, C_5Me_4), 128.5 (d, J_{PC} = 7 Hz, Ph), 133.5 (d, J_{PC} = 19 Hz, Ph), 138.6 (d, J_{PC} = 16 Hz, Ph), 206.0 (d, J_{PC} = 8 Hz, *C*O). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: -28.4 (s, PMe_3), -14.3 (s, PPh_2). MS (EI, based on ^{187}Re) m/z : 637 [M^+ – H], 610 [M^+ – CO], 562 [M^+ – PMe_3].

(η^5-$C_5Me_4CH_2PPh_2$)Re(CN^tBu)(CO)$_2$ (4c). To a solution of **3** (30 mg, 0.054 mmol) in benzene-d_6 was added CN^tBu (6 μL, 0.055 mmol, d = 0.795 g/mL, 97%). After 5 min at room temperature, the ^1H NMR spectrum of the reaction mixture showed the complete disappearance of **3** and the presence of **4c**. The reaction mixture was filtered through Celite, the solvent was pumped off and **4c** was isolated as a white solid. Yield 32 mg (0.049 mmol, 91%). IR [hexanes, cm^{-1}] ν(C≡N): 2132 (s); ν(CO): 1928 (s) 1889 (vs). ^1H NMR (C_6D_6) δ: 1.12 (s, 9H, CN^tBu), 1.95 (s, 6H, C_5Me_4), 2.04 (s, 6H, C_5Me_4), 3.44 (s, 2H, CH_2), 7.14 (m, 6H, *Ph*), 7.49 (m, 4H, *Ph*). $^{13}C\{^1H\}$-NMR (C_6D_6) δ: 10.6 (s, CN^tBu), 11.0 (s, C_5Me_4), 11.1 (s, C_5Me_4), 27.3 (d, J_{PC} = 18 Hz, CH_2), 95.3 (d, J_{PC} = 19 Hz, C_5Me_4), 96.7 (s, C_5Me_4), 97.9 (d, J_{PC} = 2 Hz, C_5Me_4), 128.5 (d, J_{PC} = 7 Hz, *Ph*), 133.5 (d, J_{PC} = 19 Hz, *Ph*), 138.57 (d, J_{PC} = 17 Hz, *Ph*), 202.7 (s, *C*O). $^{31}P\{^1H\}$ NMR δ: -13.9 (s, PPh_2). MS (EI, based on ^{187}Re) m/z : 654 [M^+], 617 [M^+ – CO], 562 [M^+ – CN^tBu].

Note: No satisfactory elemental analysis of the complexes **4**, was obtained because of partial oxidation of the lateral phosphine group.

***trans*-[(η^5:η^1-$C_5Me_4CH_2PPh_2$)Re(I)(CO)$_2$]$^+$ I^- (5a).** To a solution of **3** (80 mg, 0.143 mmol) in 15 mL of CH_2Cl_2 was added I_2 (36 mg, 0.143 mmol). An IR spectrum showed the disappearance of CO absorptions due to the starting complex, and the emergence of new absorption bands at 2046 and 1986 cm^{-1}. The solvent was removed under vacuum, and the residue was kept under vacuum. It was dissolved in the minimum amount of CH_2Cl_2, and crystallized by diffusion of a hexanes layer. **5a** was isolated as brownish-red crystals in 63% yield. (73 mg, 0.089 mmol). IR [CH_2Cl_2, ν(CO), cm^{-1}]: 2046 (s) 1986 (vs). ^1H-NMR ($CDCl_3$) δ: 2.39 (s, 6H, C_5Me_4), 2.41 (s, 6H, C_5Me_4), 5.10 (d, J_{PH} = 9.5 Hz, 2H, CH_2), 7.74 (m, 6H, *Ph*), 7.77 (m, 4H, *Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 11.7 (s, C_5Me_4), 12.2 (s, C_5Me_4), 20.0 (d, J_{PC} = 33 Hz, CH_2), 80.7 (d, J_{PC} = 7 Hz, C_5Me_4), 102.0 (s, C_5Me_4), 106.5 (s, C_5Me_4), 124.1 (d, J_{PC} = 58 Hz, C_{ipso} *Ph*), 130.1 (d, J_{PC} = 13 Hz, C_{ortho}, *Ph*), 130.8 (d, J_{PC} = 11 Hz, C_{meta}, *Ph*), 133.3 (d, J_{PC} = 3 Hz, C_{para}, *Ph*), 187.8 (d, J_{PC} = 18 Hz, *C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: –148.1 (s, PPh_2). MS (IES, based on ^{187}Re) m/z : 689 [M^+]; 661 [M^+ – CO]. Anal. Calcd. for $C_{24}H_{24}O_2I_2PRe$: C, 35.37; H, 2.97. Found: C, 36.03; 3.11.

***trans*-[(η^5:η^1-$C_5Me_4CH_2PPh_2$)Re(H)(CO)$_2$]$^+$ BF_4^- (5b).** To a solution of **3** (30 mg, 0.053 mmol) in chloroform-d was added HBF_4 (8 μL; 0.0581 mmol, d = 1.180 g/mL, 54%, in Et_2O). The reaction was monitored by ^1H NMR spectroscopy. After 5 min at 0 °C, the spectrum showed the complete disappearance of **3** and the presence of **5b**. This compound could not be isolated as a pure sample and was only identified *in situ* by spectroscopic techniques. IR [CH_2Cl_2, ν(CO), cm^{-1}]: 2038 (s), 1977 (vs). ^1H-NMR ($CDCl_3$) δ: –6.56 (d, J_{PH} = 20.8 Hz, 1H, Re-*H*), 2.39 (s, 6H, C_5Me_4), 2.42 (s, 6H, C_5Me_4), 4.80 (d, J_{PH} = 10.2 Hz, 2H, CH_2), 7.61 (m, 10H, Ph). $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ: 10.7 (s, C_5Me_4), 12.1 (s, C_5Me_4), 16.4 (d, J_{PC} = 36 Hz, CH_2), 81.4 (s, C_5Me_4), 99,3 (s, C_5Me_4), 103.0 (s, C_5Me_4); 126.2 (d, J_{PC} = 56 Hz, C_{ipso} Ph), 129.9 (d, J_{PC} = 13 Hz, C_{ortho}, Ph), 131.8 (d, J_{PC} = 12 Hz, C_{meta}, Ph); 132.6 (d, J_{PC} = 3 Hz, C_{para}, Ph); 193.0 (d, J_{PC} = 15 Hz, *C*O). $^{31}P\{^1H\}$ ($CDCl_3$) δ: -152.82 (s, PPh_2).

***trans*-[(η^5:η^1-$C_5Me_4CH_2PPh_2$)Re(Me)(CO)$_2$]$^+$ OTf^- (5c).** To a solution of **3** (30 mg, 0.053 mmol) in chloroform-d was added MeOTf (6 μL, 0.054 mmol, d = 1.450 g/mL, 99%). The reaction was monitored by ^1H NMR spectroscopy. After 5 min at room temperature, under argon, the NMR spectrum showed the complete disappearance of **3** and the presence of **5c**. The reaction mixture was concentrated under vacuum to dryness and the residue was dissolved in CH_2Cl_2 and filtered through Celite. The filtrate was evaporated to *ca.* 2 mL and carefully layered with hexanes. Complex **5c** was isolated as a brownish-red solid. Yield: 21 mg (0.029 mmol, 55%) IR [CH_2Cl_2, ν(CO), cm^{-1}]: 2029 (s), 1966 (vs). ^{1}H NMR ($CDCl_3$) δ: 0.90 (d, $J_{HP} = 2.8$ Hz, 3H, Re-*Me*), 1.84 (s, 6H, C_5Me_4), 2.35 (s, 6H, C_5Me_4), 4.81 (d, $J_{PH} = 9.3$ Hz, 2H, CH_2), 7.58 (m, 6H, Ph), 7.63 (m, 4H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: −16.2 (Re-*Me*), 8.3 (s, C_5Me_4), 10.7 (s, C_5Me_4), 19.6 (d, J_{PC} = 36 Hz, CH_2), 79.5 (d, $J_{PC} = 4$ Hz, C_5Me_4), 99.5 (s, C_5Me_4), 103.1 (s, C_5Me_4), 126.3 (d, $J_{PC} = 57$ Hz, C_{ipso} Ph), 129.9 (d, $J_{PC} = 12$ Hz, C_{ortho}, Ph), 131.8 (d, $J_{PC} = 11$ Hz, C_{meta}, Ph), 132.6 (s, C_{para}, Ph); 195.6 (d, $J_{PC} = 16$ Hz, *C*O). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −148.7 (s, *P*Ph$_2$). MS (IES, based on ^{187}Re) *m/z*: 577 [M$^+$], 549 [M$^+$ − CO]. Anal. Calcd. for $C_{24}H_{24}O_2I_2PRe$: C, 35.37; H, 2.97. Found: C, 36.03; H, 3.11.

***trans*-[(η^5:η^1-$C_5Me_4CH_2PPh_2$)Re(Cl)(CO)$_2$]$^+$ BF_4^- (5d).** The hydride complex **5b** was dissolved in chloroform-d and the solution was left for 16 h. The solvent was removed under vacuum and the residue was dissolved in a minimum amount of CH_2Cl_2; then it was filtered through a short Celite column (1 cm). The solvent was pumped off to yield a residue which was crystallised from CH_2Cl_2/hexanes. **5d** was obtained as an orange–red solid (15 mg, 0.022 mmol, 42% yield). IR (CH_2Cl_2, ν(CO), cm^{-1}): 2051 (s) 1989 (vs).^{1}H NMR ($CDCl_3$) δ: 1.93 (s, 6H, C_5Me_4), 2.42 (s, 6H, C_5Me_4), 4.81 (d, $J_{PH} = 10.2$ Hz, 2H, CH_2), 7.63 (m, 6H, Ph). 7.73 (m, 4H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 8.6 (s, C_5Me_4), 10.5 (s, C_5Me_4), 19.9 (d, $J_{PC} = 36$ Hz, CH_2), 81.4 (s, C_5Me_4), 101.6 (s, C_5Me_4); 110.3 (s, C_5Me_4), 124.6 (d, $J_{PC} = 58$ Hz, C_{ipso} Ph), 130.1 (d, J_{PC} = 13 Hz, C_{ortho}, Ph). 131.8 (d, $J_{PC} = 12$ Hz, C_{meta}, Ph), 133.2 (d, J_{PC} = 2 Hz, C_{para}, Ph), 192.2 (d, $J_{PC} = 17$ Hz, *C*O). ^{31}P{^{1}H} ($CDCl_3$) δ: −147.8 (s, *P*Ph$_2$). MS (IES, based on ^{187}Re and ^{35}Cl) *m/z*: 597 [M$^+$], 569 [M$^+$ − CO].

***cis*-(η^5:η^1-$C_5Me_4CH_2PPh_2$)Re(I)$_2$(CO) (6a).** To a solution of **5a** (75 mg, 0.092 mmol) in 15 mL of CH_2Cl_2 was added $Me_3NO{\cdot}2H_2O$ (11 mg, 0.099 mmol) and KI (33 mg, 0.199 mmol). The reaction mixture was stirred at room temperature for 30 min. At this time, the IR spectrum showed the disappearance of the starting complex and one new CO absorption band at 1906 cm^{-1}. The solvent was removed under vacuum and the solid residue was chromatographed on a short Florisil column. Elution with hexanes–CH_2Cl_2 (1 : 4) moved the complex **6a**. The solvent was pumped off, and the red–brown residue was dissolved in the minimum amount of CH_2Cl_2 and crystallized by diffusion of a hexanes layer. Yield: 45 mg (0.0571 mmol, 62%). IR [CH_2Cl_2, ν(CO), cm^{-1}]: 1906 (s). ^{1}H NMR ($CDCl_3$) δ: 2.10 (s, 6H, C_5Me_4), 2.18 (s, 3H, C_5Me_4), 2.52 (s, 3H, C_5Me_4), 4.15 (dd, $J_{PH} = 15.3$ Hz, $J_{HH} = 9.0$ Hz, 1H, CH_2), 4.42 (dd, $J_{PH} = 15.3$ Hz, $J_{HH} = 9.0$ Hz, 1H, CH_2), 7.41 (m, 5H, *Ph*), 7.53 (m, 3H, *Ph*), 7.72 (m, 2H, *Ph*). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 10.9 (s, C_5Me_4), 11.1 (s, C_5Me_4), 11.4 (s, C_5Me_4), 12.9 (s, C_5Me_4), 18.0 (d, $J_{PC} = 32$ Hz, CH_2), 76.4 (d, $J_{PC} = 7$ Hz, C_5Me_4), 91.1 (d, $J_{PC} = 3$ Hz, C_5Me_4), 92.2 (s, C_5Me_4), 104.9 (d, $J_{PC} = 3$ Hz, C_5M_4), 109.1 (s, C_5Me_4), 127–132 (Ph); 217.5 (d, $J_{PC} = 17$ Hz, *C*O). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: -150.5 (s, *P*Ph$_2$). MS (EI, based on ^{187}Re) *m/z*: 788 [M$^+$], 661 [M$^+$ − I]. Anal. Calcd for $C_{23}H_{24}I_2OPRe$: C, 35.04; H, 3.07. Found: C, 34.81; H, 2.95.

(η^5:η^1-$C_5Me_4CH_2PPh_2$)Re(I)(Me)(CO) (6b). To a solution of **5c** (prepared from **3**, 50 mg, 0.089 mmol) in 15 mL of CH_2Cl_2,

Table 2 Crystal data and structure refinement for (η^5:η^1-$C_5Me_4CH_2PPh_2$)Re(CO)$_2$ (**3**) and (η^5:η^1-$C_5Me_4CH_2PPh_2$)Re(I)$_2$CO (**6a**)

	3	**6a**
Empirical Formula	$C_{24}H_{24}O_2PRe$	$C_{23}H_{24}I_2OPRe$
Formula weight	561.60	787.39
Temperature	293 (2) K	298 (2) K
Wavelength	0.71073 Å	0.71073 Å
Cryst. Syst.	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a, (Å)	9.7394 (5)	15.136 (2)
b, (Å)	21.5708 (1)	8.7980 (8)
c, (Å)	10.2864 (5)	17.966 (2)
β (°)	102.685 (1)	103.464 (2)
V. (Å^3)	2108.29 (2)	2326.7 (4)
Z	4	4
D_{calcd}/(g cm^{-3})	1.769	2.248
Absorption coefficient/(mm^{-1})	5.856	7.957
F(000)	1096	1464
Crystal size (mm)	0.43 × 0.25 × 0.25	0.27 × 0.12 × 0.02
θ range for data collection (°)	1.89–28.05	2.01–28.10
Limiting indices	$-12 \le h \le 12, -13 \le k \le 27, -13 \le l \le 13$	$-19 <= h <= 19, -11 <= k <= 11, -22 <= l <= 23$
Reflections collected/unique	12358/4710	16711/5271
Completeness to $\theta = 26.00$	99.9%	99.9%
Min/max transmission	0.555/1	0.556/1
Refinament method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4710/0/253	5271/1/262
Goodness-of-fit on F^2	0.997	1.045
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0221$, $wR2 = 0.0521$	$R1 = 0.0561$, $wR2 = 0.1088$
R indices (all data)	$R1 = 0.0271$, $wR2 = 0.0534$	$R1 = 0.088$, $wR2 = 0.119$
Largest difference peak and hole (e Å^{-3})	0.314 and −0.910	1.690 and −1.097

was added KI (30 mg, 0.181 mmol) and $Me_3NO{\cdot}2H_2O$ (11 mg, 0.135 mmol). The reaction mixture was stirred at room temperature for 1 h. After this time, the IR spectrum showed the disappearance of the starting complex and one new absorption band at 1885 cm^{-1}. The solvent was removed under vacuum. The solid residue was chromatographed on a short Florisil column. Elution with hexanes–CH_2Cl_2 (1:4) moved the complex **7b**. The solvent was pumped off, and the orange residue was dissolved in the minimum amount of CH_2Cl_2 and recrystallized by diffusion of a hexanes layer. Yield: 21.9 mg (0.032 mmol, 47%). IR [CH_2Cl_2, ν(CO), cm^{-1}]: 1885 (s). ^1H NMR ($CDCl_3$) δ: 1.25 (s, 3H, Re-*Me*), 1.47 (s, 3H, C_5Me_4), 1.61 (s, 3H, C_5Me_4), 2.06 (s, 3H, C_5Me_4), 2.49 (s, 3H, C_5Me_4), 4.1 (dd, $J_{PH} = 15.0$ Hz, $J_{HH} = 8.1$ Hz, 1H, CH_2), 4.25 (dd, $J_{PH} = 15.0$ Hz, $J_{HH} = 8.1$ Hz, 1H, CH_2), 7.33 (m, 5H, *Ph*), 7.48 (m, 3H, *Ph*), 7.72 (m, 2H, *Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: -7.8 (d, $J_{PC} = 12$ Hz, Re-*Me*), 7.5 (s, C_5Me_4), 8.5 (s, C_5Me_4), 11.3 (s, C_5Me_4), 11.4 (s, C_5Me_4), 20.9 (d, $J_{PC} = 27$ Hz, CH_2), (overlap, C_5Me_4), 87.5 (d, $J_{PC} = 3$ Hz, C_5Me_4), 89.5 (s, C_5M_4), 100.3 (d, $J_{PC} = 2$ Hz, C_5Me_4), 103.7 (d, $J_{PC} = 3$ Hz, C_5Me_4), 127.6–132.8 (Ph); 219.8 (d, $J_{PC} = 15$ Hz, *C*O). $^{31}P\{^1H\}$ ($CDCl_3$) δ: −154.8 (s, *P*Ph_2). MS (EI, based on ^{187}Re) *m*/*z*: 661 [M^+ − Me], 648 [M^+ − CO]. Calcd for $C_{24}H_{27}OPIRe$: C, 42.70; H, 4.03. Found: C, 41.59; H, 3.89.

Structure determination of complexes 3 and 6a

Crystals of **3** and **6a** suitable for X-ray diffraction studies were obtained by recrystallization from CH_2Cl_2/hexanes diffusion at room temperature by slow cooling to −18 °C. A summary of crystal data, data collection, and refinement parameters for the structural analyses is given in Table 2. A pale yellow (**3**) or red–brown crystal (**6a**) was glued to a glass fiber and mounted on a Bruker SMART APEX diffractometer, equipped with a CCD area detector. Data collection was collected with SMART-NT.[30] Both data sets were integrated with the Bruker SAINTPLUS program[31] and absorption corrections were applied using the SADABS routine. The structures were solved by Patterson, completed by difference Fourier techniques, and refined by full-matrix least squares on F^2 (SHELXL-97)[32] with initial isotropic, but subsequent anisotropic thermal parameters. Hydrogens in **3** and **6a**, were introduced from observed positions and refined as isotropic atoms.

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