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Syntheses and Reactivity of Functionalized (η^5-Tetramethylcyclopentadienyl) Rhenium Complexes: Molecular Structures of (η^5:η^2-$C_5Me_4CH_2CH_2CH{=}CH_2$)$Re(CO)_2$ and (η^5-$C_5Me_4CH_2$-2-C_4H_3S)$Re(CO)_2(PMe_3)$

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The fulvene complexes (η^6-$C_5Me_4CH_2$)$Re(CO)_2R$ (**1**, R = C_6F_5; **2**, R = I) react at the exocyclic methylene carbon with allylmagnesium chloride or 2-thienyllithium to yield the anionic species $[(\eta^5\text{-}C_5Me_4CH_2L)Re(CO)_2R]^-$ (L = $-CH_2CH{=}CH_2$, -2-C_4H_3S). Further reaction with CH_3I at room temperature affords the methyl complexes (η^5-$C_5Me_4CH_2L$)$Re(CO)_2$(R)(Me) (**3**, R = C_6F_5; **4**, R = I). Protonation of the anionic species with HCl at low temperature gives the hydride complexes *trans*-(η^5-$C_5Me_4CH_2L$)$Re(CO)_2$(R)(H) (**5**, R = C_6F_5; **6**, R = I). Thermolysis of hexane solutions of **6**, under CO atmosphere, produces the tricarbonyl complexes (η^5-$C_5Me_4CH_2L$)$Re(CO)_3$ (**7**) in moderate yields; if the reaction is carried out in the presence of PMe_3, the analogous dicarbonyl phosphine derivatives (η^5-$C_5Me_4CH_2L$)$Re(CO)_2(PMe_3)$ (**9**) are obtained, but no coordination of the lateral functionality is observed. In clear contrast, thermolysis of hexane solutions of the pentafluorophenyl hydride complexes *trans*-(η^5-$C_5Me_4CH_2L$)$Re(CO)_2(C_6F_5)$(H), even under CO atmosphere, yields the chelated complexes (η^5:η^x-$C_5Me_4CH_2L$)$Re(CO)_2$ (**8a**, L = $-CH_2CH{=}CH_2$, $x = 2$; **8b**, L = -2-C_4H_3S, $x = 1$). However, prolonged thermal treatment of **8b** under a CO atmosphere affords the corresponding tricarbonyl complex **7b**. The molecular structures of **8a** and **9b** have been determined. Both molecules exhibit formal three-legged piano-stool structures, with three terminal ligands in **9b** (two CO and one PMe_3), but in the case of **8a**, in addition to the two CO's, the third position corresponds to the η^2-coordination of the butenyl substituent of the η^5-C_5Me_4 ring. Attempts to displace the coordinated sidearm in complex **8a** have been investigated, as well as the photochemical reactions of tricarbonyl complexes **7**.

Introduction

Functionalized cyclopentadienyl complexes of transition metals have attracted significant interest in recent years.[1−4] Jutzi,[1] Siemeling,[3a] and Butenschon[3b] have recently reviewed the chemistry of metal complexes possessing this type of ligand. Although most of the work in this area has been focused on early transition metal complexes for their application as catalysts for olefin polymerization, there are several examples of complexes of the medium and late transition metals.[1,5−9] However, few half-sandwich compounds of this type are known for group 7 metals. For instance, Casey and Wang have reported the preparation of manganese complexes of the type (η^5-C_5H_4L)$Mn(CO)_3$, where L is a haloalkyl or an aminoalkyl chain, which upon irradiation photodissociate a CO ligand to form the chelated species (η^5:η^1-C_5H_4L)$Mn(CO)_2$ by intramolecular coordination of the halide or the amino group to the metal center.[10,11] Several reports dealing with rhenium complexes containing this type of ligand have been published in the past decade. For example, Wang has synthesized and explored the chemistry of the aminorhenium complex (η^5:η^1-$C_5H_4CH_2NHCH_3$)$Re(CO)_2$;[12]

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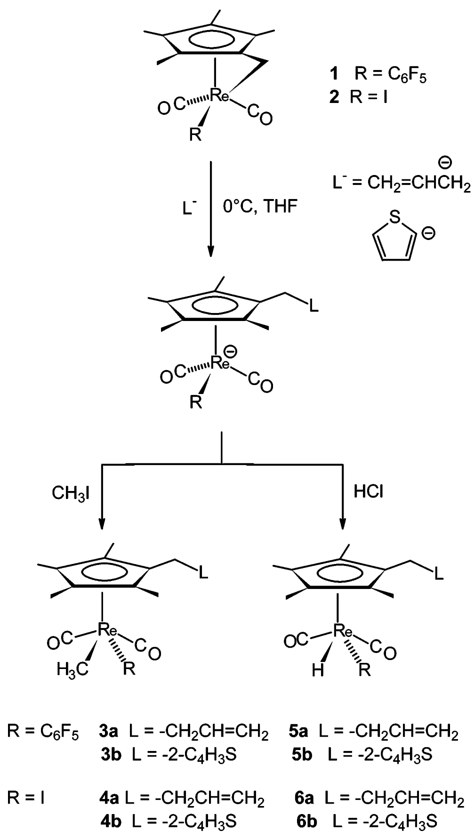
Casey has prepared and used (η^5-C_5H_4L)Re(CO)$_3$ complexes (L = 2-iodoethyl and 2-propenyl), as precursors of chelated metal acyl hydride and hydroxycarbene complexes (η^5:η^1-$C_5H_4CH_2CH_2CO$)Re(CO)$_2$H and (η^5:η^1-$C_5H_4CH_2CH_2COH$)Re(CO)$_2$;[13] Katznellenbogen has developed a general synthetic method for the preparation of substituted Cp rhenium tricarbonyl complexes in order to incorporate the CpRe(CO)$_3$ motif in radiopharmaceuticals.[14]

On the other hand, side chain functionalized tetramethylcyclopentadienyl complexes are by far less abundant than their cyclopentadienyl analogues. Most of the synthetic approaches for the preparation of such kinds of complexes involve the prior synthesis of the target ligand, which is normally prepared by extension of some of the classical methods for the synthesis of pentamethylcyclopentadiene.[15,16] An alternative way to functionalized tetramethylcyclopentadienyl transition metal complexes considers, first, the C−H activation of one of the methyl groups on a parent pentamethylcylopentadienyl complex of the type (η^5-C_5Me_5)ML$_n$, leading to a formal fulvene complex (η^6-$C_5Me_4CH_2$)ML$_n$, and then using the reactivity of the exocyclic methylene carbon to introduce organic functionalities.[17,18] Maitlis has extensively explored this approach with the complex {(η^6-$C_5Me_4CH_2$)RuCl$_2$}$_2$.[18]

In previous publications, we have demonstrated that the rhenium tetramethylfulvene complex (η^6-$C_5Me_4CH_2$)-Re(CO)$_2$(C_6F_5) can be used as a convenient starting material for the preparation of a series of pentamethylcyclopentadienyl complexes.[19] For instance, (η^6-C_5Me_4-CH_2)Re(CO)$_2$(C_6F_5) reacts with HX (X = Cl, Br, I) to yield (η^5-C_5Me_5)Re(CO)$_2$(C_6F_5)X. Ring-substituted cyclopentadienyl complexes (η^5-$C_5Me_4CH_2X$)Re(CO)$_2$(C_6F_5)X (X = Cl, Br, I), [(η^5-$C_5Me_4CH_2OMe$)Re(CO)$_2$(C_6F_5)]$^-$, and the zwitterion (η^5-$C_5Me_4CH_2PMe_3$)Re(CO)$_2$(C_6F_5) can be obtained by reaction of (η^6-$C_5Me_4CH_2$)Re(CO)$_2$(C_6F_5) with halogens (X_2), MeO$^-$ and PMe$_3$, respectively. Very recently, we have found that the new fulvene complexes (η^6-$C_5Me_4CH_2$)Re(CO)$_2$X (X = Cl, Br, I) react at the exocyclic methylene carbon, with hydrogen halides (HX′) and halogens (X′$_2$) to form the mixed-halide complexes *cis*-(η^5-C_5Me_5)Re(CO)$_2$XX′ (X ≠ X′) and *cis*-(η^5-$C_5Me_4CH_2X'$)Re(CO)$_2$XX′, respectively.[20]

Scheme 1



In this work we report on the reactions of the fulvene complexes (η^6-$C_5Me_4CH_2$)Re(CO)$_2$R (**1**, R = C_6F_5; **2**, R = I) with nucleophiles bearing alkenyl or thienyl groups, leading to the formation of functionalized tetramethylcyclopentadienyl rhenium methyl or hydride complexes: (η^5-$C_5Me_4CH_2L$)Re(CO)$_2$(R)(Me) (**3**, R = C_6F_5; **4**, R = I) and (η^5-$C_5Me_4CH_2L$)Re(CO)$_2$(R)(H) (**5**, R = C_6F_5; **6**, R = I), with L = −$CH_2CH{=}CH_2$, −2-C_4H_3S, respectively. In addition, we show that the hydride complexes **5** and **6** undergo thermal reductive elimination reactions which, depending on the nature of the R group attached to the metal, result in the production of tricarbonyl (or dicarbonyl phosphine) complexes with dangling uncoordinated functionalities, or in the coordination of the lateral function to rhenium to yield the new chelated tetramethylcyclopentadienyl complexes.

Results and Discussion

Syntheses and Reactions of the Fulvene Complexes. The fulvene complexes (η^6-$C_5Me_4CH_2$)Re-(CO)$_2$(R) (**1**, R = C_6F_5; **2**, R = I) were prepared from Cp*Re(CO)$_3$ (Cp* = η^5-C_5Me_5) and Cp*Re(CO)$_2$I$_2$, respectively, according to methods described in the literature.[19,20] Addition of an excess of allylmagnesium chloride or 2-thienyllithium to THF solutions of **1** or **2** provided the anionic rhenium complexes [(η^5-$C_5Me_4CH_2L$)Re(CO)$_2$R]$^-$ (L = −$CH_2CH{=}CH_2$, −2-C_4H_3S) (see Scheme 1). The anionic species were not isolated and were identified by IR spectroscopy. The two promi-

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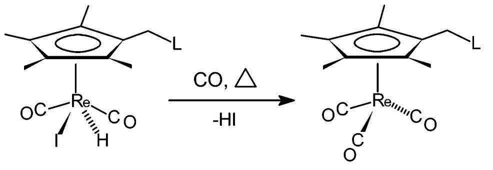
nent absorption bands (ν(CO)), observed in the 1880−1730 cm^{-1} region, are comparable to those reported for analogous anionic compounds.[21,22] Reaction of the anions bearing the 3-butenyl or (2-thienyl)methyl side chains on the tetramethylcylopentadienyl ligand with CH_3I at room temperature yielded the methyl complexes (η^5-$C_5Me_4CH_2L$)Re(CO)$_2$(R)(Me) (**3**, **4**) (Scheme 1). These alkyl complexes were isolated in moderate to good yields (30−65%) as white or pale yellow solids for R = C_6F_5 (**3**) and as yellow-orange solids for R = I (**4**). In all cases, the presence of the methyl groups and the corresponding sidearm of the tetramethylcyclopentadienyl-substituted ligands were inequivocally established by ^{1}H and ^{13}C NMR spectroscopies (see Experimental Section). The stereochemistry of these derivatives was assigned by a combination of IR and ^{13}C NMR spectroscopies and by comparison with analogous complexes.[23] In the case of the methyl iodo complexes, mixtures of *cis* and *trans* isomers were obtained (only the *trans* isomer is shown in Scheme 1), whereas for the methyl pentafluorophenyl complexes, the *trans* isomers were exclusively formed.

On the other hand, the anionic species [(η^5-$C_5Me_4CH_2L$)Re(CO)$_2$R]$^-$ were also reacted in situ with HCl at low temperature to give the hydride complexes *trans*-(η^5-$C_5Me_4CH_2L$)Re(CO)$_2$(R)(H) (**5**, **6**) (see Scheme 1). These compounds showed characteristic CO absorption bands in the 2022−1945 cm^{-1} region in THF solution, similar to those observed in analogous fluoroaryl complexes.[22,24] The slow decomposition of these compounds in THF or hydrocarbon solvents precluded their isolation as pure samples. However, we were able to characterize the complex *trans*-(η^5-$C_5Me_4CH_2CH_2$-$CH{=}CH_2$)Re(CO)$_2$(I)(H) (**6a**) in solution by ^{1}H NMR spectrocopy. As far as we know, the only previous example of a neutral dicarbonylhalohydride complex of rhenium reported in the literature is the complex *trans*-Cp*Re(CO)$_2$(Br)H.[25]

Reactions of the Functionalized Tetramethylcyclopentadienyl Complexes. Both the methyl and the hydrido complexes described above are useful starting materials to explore the potentiality of the lateral function to coordinate to the rhenium center. Considering that the protonation of transition metal methyl complexes has been suggested as one of the best and cleanest methods for the syntheses and isolation of organometallic Lewis acids,[26] we reacted our methyl derivatives with HBF_4, with the aim to form the chelated cationic complexes [η^5:η^x-$C_5Me_4CH_2L$)Re(CO)$_2$(R)]$^+$ (R = C_6F_5, I). However, in no cases could cationic species be detected, and the complexes were recovered unreacted. Attempts to reductively eliminate C_6F_5Me or MeI under several experimental conditions (thermal and photochemical) were also unsuccessful, with complexes remaining intact in most cases.

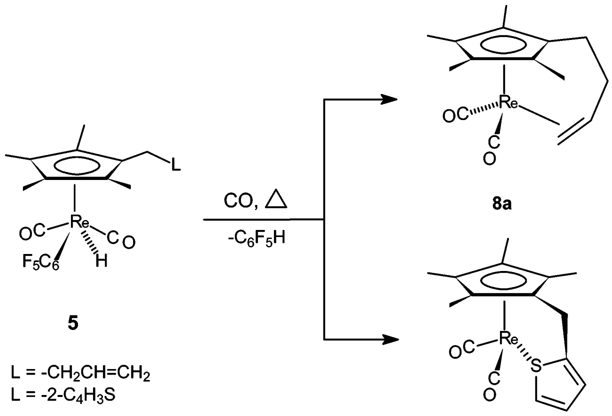
Scheme 2



6

7a L = $-CH_2CH{=}CH_2$
7b L = $-2-C_4H_3S$

Scheme 3



5

L = $-CH_2CH{=}CH_2$
L = $-2-C_4H_3S$

8a

8b

Then, we turned to the hydride complexes. Crude samples of **5** and **6** dissolved in hexanes under a CO atmosphere undergo reductive elimination reactions very easily (25−90 °C). However, the observed product depends on the nature of the group R coordinated to rhenium. Iodo hydride complexes **6** generated the tricarbonyl complexes (η^5-$C_5Me_4CH_2L$)Re(CO)$_3$ **7a**,**b** (L = $-CH_2CH{=}CH_2$, 2-C_4H_3S), which were isolated as pale yellow solids (Scheme 2). The tricarbonyl derivative **7a** has been synthesized very recently by an independent route.[16a] The thiophene derivative **7b** could be obtained in much better yield by an alternative route (vide infra). To demonstrate the elimination of HI from the decomposition reactions of **6a**,**b**, the resulting mixture after the thermolysis of **6a** was extracted with water and then treated with $AgNO_3$, producing quantitative precipitation of AgI. Complexes **7a**,**b** showed CO absorption bands, in hexanes solution, at 2013 and 1923 cm^{-1}, almost identical to those observed for Cp*Re(CO)$_3$. In addition, their ^{1}H, ^{13}C NMR and mass spectra (see Experimental Section) are consistent with the proposed structures. As far as we are aware, no other well-documented thermally induced reductive elimination of hydrogen halide from four-legged piano-stool rhenium complexes has been reported in the literature.[27]

A different reaction pathway seems to occur in the thermolysis of the pentafluorophenyl hydride complexes **5a**,**b** (Scheme 3). Under the same experimental conditions described for iodo hydride derivatives, **5a** generated in good yield the chelated tetramethylcyclopentadienyl complex (η^5:η^2-$C_5Me_4CH_2CH_2CH{=}CH_2$)Re(CO)$_2$ (**8a**), instead of the tricarbonyl derivative **7a**. The latter was formed only in trace amounts, as indicated by the IR spectrum of the reaction mixture, although the

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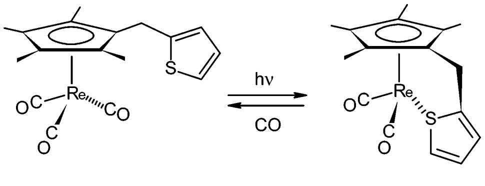
Scheme 4



7b **8b**

reaction was done under a CO atmosphere. When the reaction was carried out under nitrogen (without CO), extensive decomposition occurred: **7a** and **8a** as well as several others carbonyl-containing products were observed by IR spectroscopy.

However, in the case of the thermolysis of the hydride complex with the (2-thienyl)methyl lateral chain, **5b**, the chelated complex (η^5:η^1-$C_5Me_4CH_2(2\text{-}C_4H_3S)$)Re-$(CO)_2$ (**8b**) was observed only as a reaction intermediate, and prolonged heating resulted in the formation of the tricarbonyl complex **7b**. The lability of this type of compound is not surprising since most of the metal-S bound thiophene groups easily dissociate, even when the thiophene is part of a cyclopentadienyl chelated ligand, like in the complex $[(\eta^5:\eta^1\text{-}C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2]^+$.[28] Angelici has explained this behavior in terms of electronic effects.[29] Presumably the electron density provided by the four methyl groups of the cyclopentadienyl ligand in **8b** reduces the Lewis acid character of the Re, which weakens the bond with the electron-donating sulfur atom in the chelated complex **8b**. Nevertheless complex **8b** was obtained by irradiation of complex **7b** in hexanes solution (Scheme 4). Photoextrusion of CO from hexane solutions of complex **5a** also afforded the Re−alkene bonded complex **8a**.

The chelated complexes **8a**,**b** were isolated as solid samples that showed different properties; for instance, **8a** is air stable as a solid and in solution of most organic solvents. In contrast yellow **8b** decompose slowly to **7b** in both solution and solid state. Infrared data for complexes **8a**,**b** are consistent with an increase of the electron density at rhenium from **8a** to **8b**, as expected. The presence of four distinct methyl resonances observed in the ^{1}H and ^{13}C NMR spectra of complex **8a** agrees well with the unsymmetrical nature of the tether alkene coordinated to rhenium and the restricted rotation of the η^5:η^2-tetramethylcyclopentadienyl(butenyl) ligand. This result is in good agreement with the inequivalent resonances measured for the two CO ligands in the ^{13}C NMR spectrum. Further confirmation of the structure of complex **8a** was obtained from an X-ray diffraction study (vide infra). To the best of our knowledge, **8a** is the first complex containing the 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl ligand coordinated in a η^5:η^2 fashion to rhenium. Other metal complexes containing the same ligand reported previously are (η^5:η^2-$C_5Me_4CH_2CH_2CH{=}CH_2$)CoL (L = CO, C_2H_4),[30] $[(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)Ni(PPh_3)]^+$,[30] and $[(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)Ru(\eta^3\text{-}C_3H_5)$.[32]

With the aim of having a more complete view of the thermolysis of the hydrido complexes **5** and **6**, we carried out the reactions in hexanes solution in the presence of an excess of PMe_3. The dicarbonyl trimethylphosphine complexes (η^5-$C_5Me_4CH_2L$)$Re(CO)_2(PMe_3)$ **9** (L = $-CH_2CH{=}CH_2$, **9a**; L = 2-C_4H_3S, **9b**) were formed in good yield from the iodo hydride complexes **6**; however, the thermal reaction of *trans*-(η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$)$Re(CO)_2(C_6F_5)(H)$ (**5a**) afforded a 5:2 mixture of the complexes **8a** and **9a**. The two trimethylphosphine derivatives **9a**,**b** showed almost the same ^{31}P NMR and IR spectra (in the carbonyl region) as those reported for their unsubstituted analogue Cp*$Re(CO)_2PMe_3$,[33] whereas the ^{1}H and ^{13}C NMR spectra clearly showed the presence of the dangling arm of the tetramethylcyclopentadienyl ligand. Additionally, the complex (η^5-$C_5Me_4CH_2$-2-C_4H_3S)$Re(CO)_2(PMe_3)$ (**9b**) was studied by X-ray crystallography (vide infra).

A tentative mechanistic proposal that could explain the formation of the tricarbonyl complexes from the thermolysis of the iodo hydride complexes **6** and the almost exclusive formation of the chelated derivatives from the pentafluorophenyl hydride complexes **5**, in the presence of CO, is shown in Scheme 5.

For the pentafluorophenyl hydride case, we assume an intramolecular reductive elimination of C_6F_5H with formation of an intermediate of the type (η^5-$C_5Me_4CH_2$-$CH_2CH{=}CH_2$)$Re(CO)_2$(η^2-C_6F_5H). Previously, we have demonstrated that the hydrido complex *trans*-Cp*Re-$(CO)_2(2,5\text{-}C_6H_3F_2)H$ converts thermally to the more stable Cp*$Re(CO)_2$(2,3-η^2-1,4-$C_6H_4F_2$).[24] By considering the low stability of the Re-(η^2-arene) moiety with regard to substitution,[34] it is not surprising that the sidearm ligand of the cyclopentadienyl group coordinates intramolecularly to produce the more stable chelated complexes.

On the other hand, an ionic mechanism can be envisaged for the reductive elimination of HI from the iodo hydride complexes. First, we have considered the ionization of the iodide ligand followed by coordination of the sidearm, to form the cationic $[(\eta^5:\eta^x\text{-}C_5Me_4CH_2L)$-$Re(CO)_2H]^+$. Even though we do not have direct experimental evidence for the formation of the chelated cation, we do know that the related complex $[(\eta^5:\eta^1\text{-}C_5Me_4CH_2PPh_2)Re(CO)_2H]^+$ reacts with CO to yield the tricarbonyl complex (η^5-$C_5Me_4CH_2PPh_2$)$Re(CO)_3$.[35]

In an effort to explore the reactivity of the functionalized tetramethylcyclopentadienyl ligands coordinated to rhenium, complexes **8a**,**b** were treated with CO and PMe_3. We found that only the complex containing the weakly chelating thiophene moiety reacted with CO (1 atm of pressure in hexanes solution) to form the tricarbonyl derivative **7b** (Scheme 4), whereas with PMe_3 complex **9b** was obtained in good yield. For complex **7b** the process is reversible under UV irradiation (hexanes solution, room temperature, $\lambda = 300$ nm). Under similar conditions, the phosphine complex **9b** decomposed to unidentified products.

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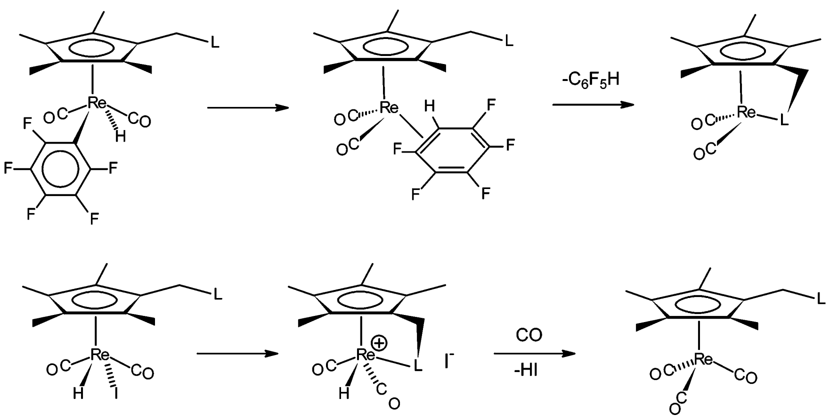
Scheme 5



Attempts to displace thermally the coordinated butenyl sidearm in complex **8a** with excess PMe_3 or CO, even under 2000 psi, were unsuccessful, whereas complete decomposition was observed after UV irradiation. However, the chelated ligand of **8a** can be displaced irreversibly upon oxidative addition of I_2 to the Re(I) center to yield the complex *cis*-(η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$)$Re(CO)_2I_2$. The latter compound was characterized by mass spectrometry, IR, and ^1H NMR spectroscopies. The IR spectrum of this complex shows identical ν(CO) absorption bands to those reported for *cis*-Cp*$Re(CO)_2I_2$.[36]

X-ray Structure of 8a and 9b. Molecular structures of complexes **8a** and **9b** are shown in Figures 1 and 2, respectively. Table 1 collects the most relevant bond distances and angles. Both molecules exhibit analogous three-legged piano-stool structures. In **9b**, three terminal ligands (two carbonyls and a PMe_3) occupy the coordination sphere of the metal together with an η^5-coordination of the $C_5Me_4(CH_2$-2-$C_4H_3S)$ cyclopentadienyl moiety. However, in the case of **8a** an η^5:η^2 chelate bonding mode of a 3-butenyl-functionalized cyclopentadienyl ligand, together with two terminal carbonyl ligands, completes the rhenium coordination.

Only two other transition metal compounds with an alkenyl-substituted C_5Me_4 ring coordinated in an η^5:η^2 bonding mode have been structurally characterized: (η^5:η^2-$C_5Me_4CH_2CH_2CHCH_2$)$Co(Me_3SiCCSiMe_3)$[37] and, very recently, (η^5:η^2-$C_5Me_4CH_2CH_2CHCH_2$)Ru(η^3-C_3H_5).[32] There is also a reduced number of structurally characterized related complexes possessing longer lateral chains, some of them including oxygen atoms in the chelating arms; these are the cases of (η^5:η^2-C_5Me_4-$CH_2(CH_2)_2CHCH_2$)NiBr,[31] [(η^5:η^2-$C_5Me_4CH_2O(CH_2)_n$-$CHCH_2$)$Ru(CO)_2$]$^+$ (n = 1, 2),[38] or (η^5:η^2-$C_5Me_4CH_2O$-$(CH_2)_2CHCH_2$)Ru(CO)(COOMe).[39] The related 1,2-bis(indenyl)ethane complexes [(η^5-C_9H_6)CH_2CH_2(η^2-C_9H_6)]-$M(CO)_2$ (M = Mn, Re) have also been reported, including the X-ray structure of the manganese derivative.[40]

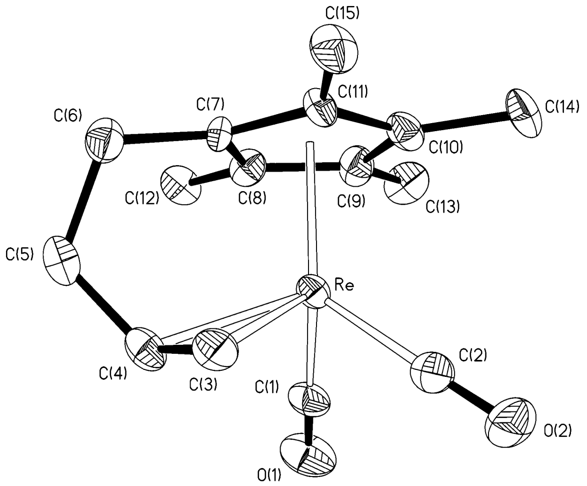


Figure 1. Molecular structure of the chelated complex (η^5:η^2-$C_5Me_4CH_2CH_2CH{=}CH_2$)$Re(CO)_2$ (**8a**) drawn with 50% probability displacement ellipsoids.

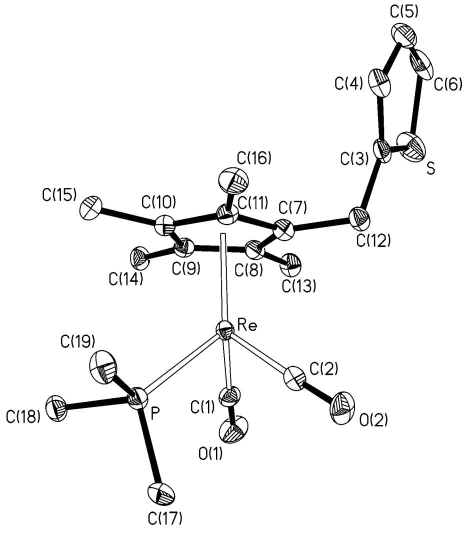


Figure 2. Molecular structure of complex (η^5-$C_5Me_4CH_2$-2-C_4H_3S)$Re(CO)_2(PMe_3)$ (**9b**) drawn with 50% probability displacement ellipsoids.

Unique structural features of **8a** have been sought by comparison with related nonchelated Cp*$Re(CO)_2$(η^2-$(CH_3)_2C{=}CHCOMe$), to our knowledge the only other Cp*$Re(CO)_2$(η^2-olefin) complex studied by X-ray crystallography.[41] In terms of the Re−CO (1.877, 1.912 Å) and Re−C(ring centroid) (1.937 Å) bond distances, the

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 8a and 9b

	8a	**9b**
Re−P		2.3424(8)
Re−C(1)	1.877(6)	1.882(1)
Re−C(2)	1.912(7)	1.891(1)
Re−C(3)	2.298(6)	
Re−C(4)	2.233(6)	
Re−C(7)	2.253(6)	2.273(1)
Re−C(8)	2.282(6)	2.271(1)
Re−C(9)	2.314(7)	2.312(1)
Re−C(10)	2.311(6)	2.343(1)
Re−C(11)	2.298(6)	2.317(1)
Re−centroid($C_5Me_4CH_2L$)	1.937(3)	1.9541(13)
C(1)−O(1)	1.165(7)	1.166(3)
C(2)−O(2)	1.145(7)	1.163(4)
C(3)−C(4)	1.413(11)	1.455(4)
C(4)−C(5)	1.502(9)	1.445(5)
C(5)−C(6)	1.536(8)	1.340(5)
C(6)/C(12)−C(7)	1.479(8)	1.502(4)
P/M#−Re−C(1)[a]	98.41(20)	
P/M#−Re−C(2)	95.63(20)	
C(1)−Re−C(2)	87.4(3)	91.39(13)
Re−C(1)−O(1)	175.2(5)	173.2(3)
Re−C(2)−O(2)	178.4(6)	177.4(3)
C(3)−C(4)−C(5)	123.3(6)	
C(4)−C(5)−C(6)	113.0(5)	
C(5)−C(6)−C(7)	110.9(5)	

[a] M# represents the midpoint of the olefinic double bond C(3)−C(4) in **8a**.

molecular parameters of **8a** compare well with those found in $Cp^*Re(CO)_2(\eta^2\text{-}(CH_3)_2C{=}CHCOMe)$[41] (Re−CO 1.851, 1.875 Å and Re−Cp* (centroid) 1.974 Å). The Re−C(olefin) distances are also comparable in the two complexes (2.232 and 2.330 Å vs 2.233 and 2.298 Å in **8a**) as well as the OC−Re−CO and C(olefin)−Re−C(olefin) interbond angles (87.4 and 36.4° vs 87.3 and 36.9°, respectively).

Interestingly, we could not identify a clear reason to justify the asymmetry of the interaction between the olefin and the metal, Re−C(3) vs Re−C(4). In that sense, we could not discern either an electronic delocalization or a source of strain in the bridging arm connecting the η^5-C_5Me_4 ring with the olefin: all the bond distances and angles of the arm seem to be normal for single bonds between sp^3 carbon atoms (see Table 1) and very similar to those observed in the closely related ruthenium complex $(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CHCH_2)Ru(\eta^3\text{-}C_3H_5)$, where a symmetric Ru−olefin interaction has been determined (Ru−C(olefin) 2.167(4) and 2.161(4) Å).[32]

The structure of **9b** resembles that of the related complex $Cp^*Re(CO)_2(PPh_3)$[42] with the sole changes of the substitution of the phosphine (PMe_3 vs PPh_3) and the thiophene presence as a sidearm in the η^5-C_5Me_4 ring. No special bonding parameter, including the Re−P bond length (2.3424(8) in **9b** vs 2.341(10) Å in $Cp^*Re(CO)_2(PPh_3)$), differs significantly in both structures, despite the greater σ-donor capacity of the PMe_3 ligand.

Experimental Section

General Methods. 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. Grignard reagents (Aldrich) were used as received. 2-Thienyllithium was prepared according to literature.[43] The fulvene complexes $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(C_6F_5)$ (**1**) and $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2I$ (**2**) were prepared according to known procedures.[19,20] 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 200 (200 MHz) instrument. All ^1H NMR chemical shifts are referenced using the chemical shifts of residual solvent resonances. ^{13}C NMR chemical shifts were referenced to solvent peaks. Coupling assignments are indicated, where known. Mass spectra were run on a GCMS-QP5050A Shimadzu instrument.

In Situ Preparation of Anionic $[(\eta^5\text{-}C_5Me_4CH_2L)Re(CO)_2R]^-$ Species. The amounts of $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(C_6F_5)$ (**1**) or $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2I$ (**2**) indicated in each case (see below) were dissolved in THF (10−15 mL). Then, 2 equiv of the organolithium or Grignard reagent were added dropwise at 0 °C. After the addition, all reaction mixtures became pale yellow, except that treated with thienyllithium, which became orange. In all cases, strong CO absorption bands were observed in the 1880−1730 cm^{-1} infrared region.[21]

Methyl Complexes 3 and 4. An excess of CH_3I was added to the solution of the corresponding anionic species. The mixtures were stirred at room temperature for 24 h, and then the solvent was removed under vacuum. The solid residue was chromatographed using a short alumina column. Elution with hexanes or the appropiate mixture of solvents (see below) moved the corresponding methyl complex.

***trans*-$(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)Re(CO)_2(C_6F_5)(CH_3)$, 3a.** A 150 mg (0.28 mmol) sample of **1** was reacted. Complex **3a** was isolated as a white solid after crystallization from hexanes. Yield: 108 mg (0.18 mmol), 65%. IR (hexanes, ν(CO), cm^{-1}): 2022(s), 1954(vs). ^1H NMR ($CDCl_3$) δ: 0.81 (s, 3H, Re-CH_3), 1.76 (s, 6H, CH_3), 1.77 (s, 6H, CH_3), 2.10 (m, 4H, −CH_2CH_2−), 5.01 (m, 2H, −CH=CH_2), 5.77 (m, 1H, −C*H*=CH$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: −16.85 (Re-CH$_3$), 9.56 (CH$_3$), 9.62 (CH$_3$), 24.37 (−CH$_2$−), 34.02 (−CH$_2$−), 100.00 (C_5Me$_4$), 100.66 (C_5Me$_4$), 102.48 (C_5Me$_4$), 115.91 (−CH=CH$_2$), 136.96 (−CH=CH$_2$), 196.30 (t, J_{CF} = 4.7 Hz, CO); aromatic carbons of C_6F_5 not seen. MS (EI, based on ^{187}Re) m/z: 600 [M^+], 555 [$M^+ - CO - CH_3 - 2H$]. Anal. Calcd for $C_{22}H_{22}F_5O_2Re$: C, 44.07; H, 3.70. Found: C, 44.15; H, 3.82.

***trans*-$(\eta^5\text{-}C_5Me_4CH_2(2\text{-}C_4H_3S))Re(CO)_2(C_6F_5)(CH_3)$, 3b.** A 150 mg (0.28 mmol) sample of **1** was reacted. Elution with hexanes moved **3b**, which was obtained as a pale yellow solid after evaporation of the solvent. Yield: 104 mg (0.16 mmol), 59%. IR (hexanes, ν(CO), cm^{-1}): 2022(s), 1955(vs). ^1H NMR ($CDCl_3$) δ: 0.88 (s, 3H, Re-CH_3); 1.79 (s, 6H, CH_3), 1.80 (s, 6H, CH_3), 3.56 (s, −CH_2-), 6.72 (m, 1H, C$_4H_3$S), 6.91 (dd, J = 5.1, 3.5 Hz, 1H, C$_4H_3$S), 7.13 (dd J = 5.1, 1 Hz, 1H, C$_4H_3$S). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: −16.71 (Re-CH$_3$); 9.60 (CH$_3$), 9.77 (CH$_3$), 25.27 (−CH$_2$−), 100.02 (C_5Me$_4$), 100.67 (C_5Me$_4$), 100.12 (C_5Me$_4$), 124.04 (C_4H$_3$S), 125.11 (C_4H$_3$S), 139.91 (C_4H$_3$S); 142.09 (C_{ipso}, 2-C$_4$H$_3$S), 195.75 (t, J_{CF} = 6.3 Hz, CO). MS (EI, based on ^{187}Re) m/z: 642 [M^+], 599 [$M^+ - CO - Me$], 404 [$M^+ - 2CO - Me - C_6F_5$]. Anal. Calcd for $C_{23}H_{20}O_2F_5SRe$: C, 43.05; H, 3.14. Found: C, 43.19; H, 3.28.

$(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)Re(CO)_2(I)(CH_3)$, 4a. A 100 mg (0.20 mmol) sample of **2** was reacted. Elution with hexanes afforded the *trans* isomer as a yellow-orange solid (26 mg, 0.046 mmol, 23% yield), whereas elution with hexanes−CH_2Cl_2 (9:1) afforded the *cis* isomer of **4a** (23 mg, 0.04 mmol, 21% yield).

***cis* Isomer.** IR (hexanes, ν(CO), cm^{-1}): 2007(s), 1936(s). ^1H NMR (C_6D_6) δ: 1.36 (s, 3H, Re-CH_3), 1.41 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 1.72 (m, 2H,

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$-CH_2-$), 2.02 (m, 2H, $-CH_2-$), 4.83 (m, 2H, $-CH{=}CH_2$), 5.49 (m, 1H, $-CH{=}CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: −17.45 (Re-CH_3), 10.43 (CH_3), 10.64 (CH_3), 10.70 (CH_3), 11.14 (CH_3), 26.26 ($-CH_2-$), 35.55 ($-CH_2-$), 100.37 (C_5Me_4), 101.38 (C_5Me_4), 102.03 (C_5Me_4), 104.50 (C_5Me_4), 105.11 (C_5Me_4), 117.03 ($-CH{=}CH_2$), 137.74 ($-CH{=}CH_2$), 205.56 (*C*O), 209.88 (*C*O). MS (EI, based on ^{187}Re) *m*/*z*: 560 [M^+], 530 [$M^+ - CO - 2H$], 517 [$M^+ - CO - Me$]. Anal. Calcd for $C_{16}H_{22}O_2IRe$: C, 34.50; H, 3.96. Found: C, 34.61; H, 3.78.

trans **Isomer.** IR (hexanes, ν(CO), cm^{-1}): 2019(s), 1955(vs). ^1H NMR (C_6D_6) δ: 0.72 (s, 3H, Re-CH_3); 1.45 (s, 6H, CH_3), 1.55 (s, 6H, CH_3), 1.79 (m, 2H, $-CH_2-$), 1.98 (m, 2H, $-CH_2-$), 4.86 (m, 2H, $-CH{=}CH_2$), 5.50 (m, 1H, $-CH{=}CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: −18.15 (Re-CH_3), 10.92 (CH_3), 10.96 (CH_3), 26.13 ($-CH_2-$), 35.70 ($-CH_2-$), 100.50 (C_5Me_4), 100.79 (C_5Me_4), 102.61 (C_5Me_4), 116.75 ($-CH{=}CH_2$), 138.11 ($-CH{=}CH_2$), 195.34 (*C*O). MS (EI, based on ^{187}Re) *m*/*z*: 560 [M^+], 530 [$M^+ - CO - 2H$], 517 [$M^+ - CO - Me$]. Anal. Calcd for $C_{17}H_{22}O_2IRe$: C, 36.50; H, 3.96. Found: C, 36.47; H, 3.83.

(η^5-$C_5Me_4CH_2$(2-C_4H_3S))Re$(CO)_2$(I)(CH_3), 4b. A 150 mg (0.30 mmol) sample of **2** was reacted. Elution with hexanes (Florisil) afforded the *trans* isomer as a yellow-orange solid (41 mg, 0.07 mmol, 23% yield), whereas elution with hexanes−CH_2Cl_2 (4:1) afforded the *cis* isomer (18 mg, 0.003 mmol, 10% yield).

cis **Isomer.** IR (hexanes, ν(CO), cm^{-1}): 2007(vs), 1936(s). ^1H NMR ($CDCl_3$) δ: 1.28 (s, 3H, Re-CH_3); 1.39 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 3.41 (s, 2H, $-CH_2-$), 6.39 (m, 1H, C_4H_3S), 6.60 (dd, $J = 5.2$, 3.5 Hz, 1H, C_4H_3S), 6.70 (dd, $J = 5.2$, 1 Hz, 1H, C_4H_3S). MS (EI, based on ^{187}Re) *m*/*z*: 602 [M^+], 574 [$M^+ - CO$], 559 [$M^+ - CO - Me$]. Anal. Calcd for $C_{17}H_{20}O_2ISRe$: C, 33.95; H, 3.35; S, 5.33. Found: C, 33.97; H, 3.32; S, 5.07.

trans **Isomer.** IR (hexanes, ν(CO), cm^{-1}): 2019(vs), 1955(s). ^1H NMR ($CDCl_3$) δ: 0.71 (s, 3H, Re-CH_3), 1.30 (s, 6H, CH_3), 1.67 (s, 6H, CH_3), 3.41 (d, $J = 1$ Hz, 2H, $-CH_2-$), 6.35 (m, 1H, C_4H_3S), 6.59 (dd, $J = 5.2$, 3.4 Hz, 1H, C_4H_3S), 6.68 (dd, $J = 5.2$, 1.2 Hz, 1H, C_4H_3S). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: −18.27 (Re-CH_3), 10.61 (CH_3), 11.49 (CH_3), 27.49 ($-CH_2-$), 100.71 (C_5Me_4), 100.88 (C_5Me_4), 101.89 (C_5Me_4), 125.16 (C_4H_3S), 126.35 (C_4H_3S), 127.98 (C_4H_3S), 144.20 (C_{ipso} 2-C_4H_3S), 194.95 (s, *C*O). MS (EI, based on ^{187}Re) *m*/*z*: 602 [M^+], 574 [$M^+ - CO$], 559 [$M^+ - CO - Me$]. Anal. Calcd for $C_{17}H_{20}O_2ISRe$: C, 33.95; H, 3.35; S, 5.33. Found: C, 33.90; H, 3.38; S, 5.40.

Hydride Complexes 5 and 6. Two equivalents of HCl solution (1.0 M in diethyl ether) was added to the solution of the corresponding anionic species at 0 °C. None of the resulting hydrido complexes were isolated and characterized, except for (η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$)Re$(CO)_2$(I)(H), **6a**, which was spectroscopically characterized *in situ*. Instead, the reaction mixtures were concentrated under vacuum, and the resulting residue was exhaustively dried. Hexanes (15 mL) was added, and the mixture was filtered. The salts were washed twice with 2−10 mL portions of hexanes. The yellow filtrate containing the hydrido compounds was bubbled with CO for 5 min, and then the solution was treated as described below for the synthesis of compounds **7**, **8**, and **9**.

***trans*-(η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$)Re$(CO)_2$(I)(H), 6a.** IR (hexanes, ν(CO), cm^{-1}): 2022(s), 1956(vs). ^1H NMR (C_6D_6) δ: −10.93 (s, 1H, Re-*H*), 1.69 (s, 6H, CH_3), 1.73 (s, 6H, CH_3); 1.76 (m, 2H, $-CH_2-$), 2.15 (m, 2H, $-CH_2-$), 4.89 (m, 2H, $-CH{=}CH_2$), 5.46 (m, 1H, $-CH{=}CH_2$).

(η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$)Re$(CO)_3$, 7a. The hexanes solution containing the hydride **6a** (prepared from **2**, 100 mg, 0.20 mmol) was heated under CO at 90 °C for 10 h. The solvent was removed under vacuum, and the solid was chromatographed through a short alumina column. Elution with hexanes moved **7a** (49 mg, 0.11 mmol, 56% yield). IR (hexanes, ν(CO), cm^{-1}): 2014(s), 1923(vs). ^1H NMR (C_6D_6) δ: 1.67 (s, 6H, CH_3), 1.72 (s, 6H, CH_3), 1.82 (m, 2H, $-CH_2$), 2.21 (m, 2H, $-CH_2-$), 4.83 (m, 1H, $-CH{=}CH_2$), 4.92 (m, 1H, $-CH{=}CH_2$), 5.54 (m, 1H, $-CH{=}CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 10.73 (CH_3), 25.36 ($-CH_2-$), 36.10 ($-CH_2-$), 98.49 (C_5Me_4), 98.94 (C_5Me_4); 101.34 (C_{ipso}, C_5Me_4), 115.64 ($-CH{=}CH_2$), 137.21 ($-CH{=}CH_2$), 197.90 (CO). MS (EI, based on ^{187}Re) *m*/*z*: 446 [M^+], 418 [$M^+ - CO$], 405 [$M^+ - CH_2CH{=}CH_2$], 388 [$M^+ - 2CO - 2H$]. Anal. Calcd for $C_{16}H_{19}O_3Re$: C, 43.14; H, 4.30. Found: C, 42.39; H, 3.94.

(η^5-$C_5Me_4CH_2$(2-C_4H_3S)Re$(CO)_3$, 7b. (a) From 5b. The hexanes solution containing the hydride complex **5b** (prepared from **1**, 240 mg, 0.44 mmol) was heated under CO at 50 °C for 4 days. An IR spectrum recorded at this time showed two strong absorption bands at 2014 and 1925 cm^{-1} and minor absorptions at 2060, 1973, and 1874 cm^{-1}. The reaction mixture was concentrated under vacuum to ca. 3 mL, and then it was filtered through a short alumina column (1 cm). **7b** was obtained as a yellow solid after evaporation of the solvent. Recrystallization from hexanes yielded yellow crystals (70 mg, 0.14 mmol, 32%). (**b) From 6b.** The hexanes solution containing the iodo hydride complex **6b** (prepared from **2**, 100 mg, 0.20 mmol) was heated under CO at 70 °C for 4 h and then chromatographed through a Florisil column. Complex **7b** was eluted with hexanes and obtained as a pale yellow solid, after solvent evaporation. It was crystallized from hexanes−CH_2Cl_2 (9:1) to yield 23 mg of a pale yellow microcrystalline powder (0.048 mmol, 24%). IR (hexanes, ν(CO), cm^{-1}): 2014(s), 1925(vs). ^1H NMR ($CDCl_3$) δ: 2.19 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 3.97 (d, 2H, $J = 0.8$ Hz, $-CH_2-$), 6.76 (m, 1H, C_4H_3S), 6.93 (dd, $J = 5.1$, 3.5 Hz, 1H, C_4H_3S), 7.15 (dd, $J = 5.1$, 1.1 Hz, 1H, C_4H_3S). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 10.76 (CH_3), 10.87 (CH_3), 26.27 ($-CH_2-$), 98.92 (C_5Me_4), 99.15 (C_5Me_4), 99.36 (C_5Me_4), 123.84 (C_4H_3S), 124.65 (C_4H_3S), 126,87 (C_4H_3S), 143.73 (C_{ipso}, 2-C_4H_3S), 197.60 (*C*O). MS (EI, based on ^{187}Re) *m*/*z*: 488 [M^+], 460 [$M^+ - CO$], 432 [$M^+ - 2CO$], 404 [$M^+ - 3CO$]. Analysis of this compound did not afford satisfactory C and H values.

(η^5:η^2-$C_5Me_4CH_2CH_2CH{=}CH_2$)Re$(CO)_2$, 8a. The pale yellow filtrate containing **5a**, prepared from **1** (150 mg (0.276 mmol), was heated under CO at 50 °C for 24 h. An IR spectrum recorded at this time showed two strong absorption bands at 1962 and 1892 cm^{-1} and minor absorptions at 2058, 2014, 1994, and 1924 cm^{-1}. The reaction mixture was concentrated under vacuum to ca. 3 mL, and then it was filtered through a short alumina column (2 cm). Elution with hexanes moved **8a**, contaminated with traces of the tricarbonyl complex **7a**. Recrystallization of **8a** from hexanes yielded white crystals (79 mg, 0.18 mmol, 64%). IR (hexanes, ν(CO), cm^{-1}): 1962(vs), 1892(vs). ^1H NMR ($CDCl_3$) δ: 1.66 (dd, 1H, $J = 10.8$, 2.6 Hz, $-CH_2-$); 1.79 (ddd, 1H, $J = 14.6$, 12.8, 6.6 Hz, $-CH_2-$); 1.99 (ddd, 1H, $J = 14.6$, 8.1, 1.2 Hz, $-CH_2-$), 2.07 (s, 3H, CH_3), 2.23 (dd, partially obscured by one methyl resonance, 1H, $-CH_2-$), 2.25 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.89 (m, 1H, $-CH{=}CH_2$), 3.37 (m, 2H, $-CH{=}CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 9.94 (CH_3), 11.09 (CH_3), 11.64 (CH_3), 11.95 (CH_3), 16.17 ($-CH_2-$), 24.40 ($-CH_2-$), 42.29 ($-CH{=}CH_2$), 47.20 ($-CH{=}CH_2$), 93.61 (C_5Me_4), 95.00 (C_5Me_4), 96.01 (C_5Me_4), 99.67 (C_5Me_4), 116.02 (C_{ipso}-C_5Me_4), 207.52 (*C*O), 207.71 (*C*O). MS (EI, based on ^{187}Re) *m*/*z*: 418 [M^+], 388 [$M^+ - CO - 2H$], 360 [$M^+ - 2CO - 2H$]. Anal. Calcd for $C_{15}H_{19}O_2Re$: C, 43.15; H, 4.59. Found: C, 43.06; H, 4.65.

(η^5:η^1-$C_5Me_4CH_2$(2-C_4H_3S)Re$(CO)_2$, 8b. Complex **7b** (40 mg, 0.082 mmol) was dissolved in hexanes (4 mL) in a quartz tube. The solution was irradiated at 35 °C for 1 h ($\lambda = 300$ nm) under N_2. A brown solid was formed, and the solution turned yellow. An IR spectrum of the reaction mixture showed absorption bands due to the starting complex and new bands at 1932 and 1874 cm^{-1}. The mixture was filtered at room temperature and then cooled at 4 °C. Yellow crystals were formed on the walls, which were washed with cold hexanes to yield 8 mg of **8b** (0.02 mmol, 22%). IR (hexanes, ν(CO), cm^{-1}): 1932(s), 1874(s). ^1H NMR ($CDCl_3$) δ: 1.94 (s, 6H, CH_3), 2.10 (s, 6H, CH_3), 3.88 (s, 2H, $-CH_2-$), 6.75 (m, 1H, C_4H_3S), 6.90

(dd, $J = 5.1, 3.4$ Hz, 1H, C_4H_3S), 7.12 (dd, $J = 5.1, 1.1$ Hz, 1H, C_4H_3S). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 10.12 (CH_3), 10.36 (CH_3), 25.85 ($-CH_2-$), 99.64 (C_5Me_4), 100.08 (C_5Me_4), 100.98 (C_5Me_4), 123.74 (C_4H_3S), 124.78 (C_4H_3S), 126,82 (C_4H_3S), 143.21 (C_{ipso}, 2-C_4H_3S), 213.63 (CO). MS (EI, based on ^{187}Re) m/z: 460 [M^+], 404 [$M^+ - 2CO$]. Analysis of this compound did not afford satisfactory C and H values.

(η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$)Re(CO)$_2$(PMe$_3$), 9a. Complex **6a**, prepared in situ from 100 mg (0.20 mmol) of **2**, was reacted with an excess of PMe_3 (0.4 mL, 1.0 M THF solution). After stirring for 10 min at room temperature, the IR spectrum showed the complete disappearance of **6a** and the presence of two strong absorption bands at 1911 and 1844 cm^{-1}. Solvent was pumped off, and the light brown oily residue was extracted with hexanes (3 × 5 mL) and filtered through a short alumina column. The solution was concentrated to ca. 3 mL and kept at −10 °C overnight, to yield 62 mg of **9a** as a tan oily solid (0.13 mmol, 63%). IR (hexanes, ν(CO), cm^{-1}): 1924(s), 1860(s). ^1H NMR (C_6D_6) δ: 1.22 (d, $J = 8.9$ Hz, 9H, PMe_3), 1.84 (s, 6H, CH_3), 1.90 (s, 6H, CH_3), 2.02 (m, 2H, $-CH_2-$), 2.39 (m, 2H, $-CH_2-$), 4.95 (m, 2H, $CH{=}CH_2$), 5.70 (m, 2H, $CH{=}CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: 12.05 (CH_3), 12.11 (CH_3), 23.34 (d, $J = 34$ Hz, PMe_3), 27.41 ($-CH_2-$), 37.44 ($-CH_2-$), 96.69 (C_5Me_4), 96.78 (C_5Me_4), 99.98 (C_5Me_4), 116.08 ($CH{=}CH_2$), 139.11 ($CH{=}CH_2$), 206.97 (d, $J = 7.6$ Hz, CO). ^{31}P NMR (C_6D_6) δ: −27.9 (s). MS (EI, based on ^{187}Re) m/z: 494 [M^+], 453 [$M^+ - CH_2CH{=}CH_2$], 436 [$M^+ - 2CO$].

(η^5-$C_5Me_4CH_2$(2-C_4H_3S)Re(CO)$_2$(PMe$_3$), 9b. Following the same procedure described for **9a**, this complex was prepared from **2** (100 mg, 0.20 mmol). **9b** was isolated as a white solid after crystallization from hexanes at −10 °C. Yield: 64 mg (0.12 mmol, 60%). IR (hexanes, ν(CO), cm^{-1}): 1920(s), 1856(vs). ^1H NMR (C_6D_6) δ: 1.22 (d, $J = 8.9$ Hz, 9H, PMe_3), 1.78 (s, 6H, CH_3), 1.97 (s, 6H, CH_3), 3.79 (d, $J = 1$ Hz, 2H, $-CH_2-$), 6.53 (m, 1H, C_4H_3S), 6.65 (dd, $J = 5.2, 3.5$, 1H, C_4H_3S), 6.73 (dd, $J = 5.2, 1.2$, 1H, C_4H_3S). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: 11.94 (CH_3), 12.25 (CH_3), 23.32 (d, $J = 34$, PMe_3), 28.16 ($-CH_2-$), 97.16 (C_5Me_4), 97.48 (C_5Me_4), 97.85 (C_5Me_4), 124.57 (C_4H_3S), 125.44 (C_4H_3S), 127.62 (C_4H_3S), 146.33 (C_{ipso}-C_4H_3S), 206.75 (d, $J = 8.4$ Hz, CO). ^{31}P NMR (C_6D_6) δ: −28.3 (s). MS (EI, based on ^{187}Re) m/z: 536 [M^+], 521 [$M^+ - Me$], 508 [$M^+ - CO$]. Anal. Calcd for $C_{19}H_{26}O_2PSRe$: C, 42.60; H, 4.89. Found: C, 41.54; H, 4.43.

***cis*-(η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$)Re(CO)$_2$I$_2$.** To a solution of **8a** (19 mg, 0.046 mmol) in 4 mL of CH_2Cl_2 was added 2 mL of a $I_2-CH_2Cl_2$ solution (23 mg of I_2 in 4 mL of CH_2Cl_2). An IR spectrum showed the disappearance of the starting complex and new absorption bands at 2022 and 1946 cm^{-1}. The solvent was removed under vacuum, and the residue was kept under vacuum for 30 min. It was dissolved in the minimum amount of CH_2Cl_2 and crystallized by diffusion of a hexanes layer. Yield: 8 mg (0.012 mmol, 26%) of brownish-red crystals. IR (CH_2Cl_2, ν(CO), cm^{-1}): 2022(vs), 1953(s). ^1H NMR ($CDCl_3$) δ: 2.20 (m, 2H, $-CH_2-$), 2.23 (s, 6H, CH_3), 2.26 (s, 6H, CH_3), 2.40 (m, 2H, $-CH_2-$), 5.06 (m, 2H, $-CH{=}CH_2$), 5.78 (m, 1H, $-CH{=}CH_2$). MS (EI, based on ^{187}Re) m/z: 672 [M^+], 644 [$M^+ - CO$], 545 [$M^+ - I$], 517 [$M^+ - I - CO$].

Structural Determination of Complexes 8a and 9b. Crystals of **8a** and **9b** suitable for X-ray diffraction studies were obtained by recrystallization from hexanes solutions 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 colorless (**8a**) or a white crystal (**9b**) was glued to a glass fiber and mounted on a Bruker SMART APEX diffractometer, equipped with a CCD area detector. Data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and low-temperature equipment (173 K for **8a** and 100 K for **9b**). Cell constants for **8a** were obtained from the least-squares refinement of three-dimensional centroids of 4481 reflections in the range 4.80° ≤ 2θ ≤ 57.06° and from 5767 reflections in the region 5.04° ≤ 2θ ≤ 56.76° for **9b**. Data were measured through the use of CCD recording of ω rotation frames (0.3° each). All data were corrected for Lorentz and polarization effects. Absorption corrections were applied using the SADABS routine.[44] Both data were integrated with the Bruker SAINTPLUS program.[45]

Table 2. Crystallographic Data for Complexes 8a and 9b

	8a	**9b**
formula	$C_{15}H_{19}O_2Re$	$C_{19}H_{26}O_2PSRe$
MW	417.50	535.63
a, Å	9.100 (3)	10.2133 (6)
b, Å	13.557 (4)	12.0658 (7)
c, Å	10.900 (3)	16.1707 (9)
β, deg	93.394 (5)	90
V, Å^3	1342.4 (6)	1992.7 (2)
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_12_12_1$
Z	4	4
θ min−max, deg	2.8−28.8	2.1−28.4
ρ_{calcd}, g/cm^3	2.066	1.785
μ, mm^{-1}	9.043	6.291
no. measd reflns	8704	13078
no. indep reflns	3196	4635
no. of params	196	317
no. of restraints	0	0
GOF	1.050	1.096
μ, mm^{-1}	9.043	6.291
F(000)	800	1048
transm coeff	0.120−0.497	0.190−0.271
R(int)	0.0677	0.0156
$R(F)$ ($F^2 \geq 2\sigma(F^2)$)	0.0448	0.0148
$R_w(F^2)$ (all data)	0.1190	0.0382

Both structures were solved by Patterson, completed by difference Fourier techniques, and refined by full-matrix least-squares on F^2 (SHELXL-97)[46] with initial isotropic, but subsequent anisotropic thermal parameters. Hydrogens in **8a** were included in calculated positions and refined riding on carbon atoms with free isotropic displacement parameters; those of the coordinated olefin were refined from observed positions as free isotropic atoms. In the case of **9b**, all hydrogens were introduced from observed positions and refined as isotropic atoms. Atomic scattering factors were used as implemented in the program.[45]

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Supporting Information Available: Bond lengths and interbond angles, anisotropic displacement coefficients, and all atom coordinates and thermal parameters for complexes **8a** and **9b** in both CIF and tabular formats. ^1H NMR spectra for compounds **6a**, **7b**, **8b**, **9a**, and *cis*-(η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$)Re(CO)$_2$I$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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