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# Allyl Isomerization Mediated by Cyclopentadienyl Group 6 Metal Compounds

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Reactions at mild temperatures of the acetonitrile adducts $[M(CO)_3(NCMe)_3]$ (M = Mo (**1**), W (**2**)) with various substituted cyclopentadienes in THF give the hydrido derivatives $[MH\{\eta^5\text{-}C_5R_4Si(CH_3)_2\text{-}(CH_2CH{=}CH_2)\}(CO)_3]$ (M = Mo, R = H (**5a**), R = $CH_3$ (**6**), M = W, R = H (**7a**), R = $CH_3$ (**8a**)) and $[MoH\{\eta^5\text{-}C_5R_4R'\}(CO)_3]$ (R = $CH_3$, R′ = H (**16**); R = H, R′ = $SiMe_3$ (**17**)) in isolated yields of 60−70%. THF solutions of derivatives **5a**, **7a**, and **8a** undergo isomerization of the cyclopentadienyl-tethered-allyl unit to give the corresponding methyl-vinyl-dimethylsilyl-$\eta^5$-cyclopentadienyl hydrido compounds $[MH\{\eta^5\text{-}C_5R_4Si(CH_3)_2(CH{=}CHCH_3)\}(CO)_3]$ (M = Mo, R = H (**5b**), M = W, R = H (**7b**), R = $CH_3$ (**8b**)) in final **a**:**b** ratios of ca. 2:1, 2:1, and 1:1, respectively. Solvent polarity seems to be crucial in these transformations. Dehydrogenation and desilylation of **5a** in THF solutions to give the dinuclear derivative $[Mo\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)\}(CO)_3]_2$ (**9**) and $[MoH(\eta^5\text{-}C_5H_5)(CO)_3]$ (**15**), respectively, are processes competitive with the allyl isomerization. Treatment of **5a** and **7a** with equimolar amounts of $ONMe_3$ permits isolation of pure compound **9** and $[W\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)\}\text{-}(CO)_3]_2$ (**10**) in isolated yields of 80−90%. Coordination of the olefin pendant unit to the metal was detectable only by reaction of **5a** and **7a** with $[CPh_3][B(C_6F_5)_4]$ to give the cationic species $[M\{\eta^5\text{-}C_5H_4Si\text{-}(CH_3)_2(CH_2CH{=}CH_2)\}(CO)_3][B(C_6F_5)_4]$ (M = Mo (**18**), W (**19**)). Molecular structure determinations by X-ray diffraction methods for derivatives **8a** and **9** are also reported.

## Introduction

Cyclopentadienyls have been among the most important ligands in organo-transition metal chemistry, as they form a wide range of derivatives whose steric and electronic properties can be easily tailored by varying the ring substituents. This versatility of cyclopentadienyl units can be further enhanced when their substituents bear functionalized side chains, which can act as potential coordinating groups. These variations on the cyclopentadienyl unit open access to ligand architectures with a hemilabile binding profile, which can stabilize otherwise unstable organometallic catalytic intermediates. Other interesting properties that these ligands impart to their metal species include higher catalytic reactivity, introduction of chirality, changing solubility properties, and the possibility to act as anchoring moieties to develop new supported single-site catalysts.[1] Within this context, pendant double bonds attached to cyclopentadienyl rings have already been shown to influence properties of olefin polymerization catalysts generated therefrom.[2] In previous works, we reported the synthesis and chemical behavior of various allyl-dimethylsilyl-$\eta^5$-cyclopentadienyl metallocene-type group 4 and 5 metal compounds.[3] Compared to similar alkyl pendant chains,[2a−c,4] the higher acidity and fluxional character of the silyl substituents could favor coordination of the alkene to the metallic center.[5] Furthermore, the chelating effect of allyl systems tethered to chelating P, N, or S atoms has already been shown to stabilize the otherwise labile π-alkene early transition metal bonds.[6,7] These reasons moved us to undertake similar studies using the allyl-dimethylsilyl-$\eta^5$-cyclopentadienyl ligand with more electron-rich group 6 metal complexes.

Transition metal hydrides are of fundamental importance in organometallic chemistry, particularly due to their involvement as catalysts or proposed intermediates in a wide variety of processes.[8] The hydrido tricarbonyl $\eta^5$-cyclopentadienyl molybdenum and tungsten compounds have been extensively studied and used as convenient precursors for several synthetic

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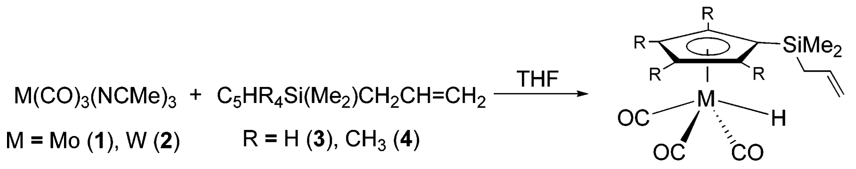
10.1021/om700293a CCC: $37.00

**Scheme 1**



| Compound | Reaction Conditions |
|---|---|
| M = Mo, R = H, **5a** | r.t., 15-30 min |
| M = Mo, R = Me, **6** | r.t, 8-10 hours |
| M = W, R = H, **7a** | r.t, 8-10 hours |
| M = W, R = Me, **8a** | 45ºC, 18-20 hours |

applications.[9] Here we report the synthesis, characterization, and chemical behavior of new hydrido tricarbonyl allyl-dimethyl-silyl-$\eta^5$-cyclopentadienyl molybdenum and tungsten derivatives.

## Results and Discussion

**Hydrido Complexes.** Isolation of the target derivatives was carried out by the typical procedure[9a,b] used to synthesize cyclopentadienyl group 6 metal compounds based on the hydrogen transfer from the cyclopentadiene to the metal carbonyl species [$M(CO)_3(NCMe)_3$] (M = Mo (**1**), W (**2**)). As shown in Scheme 1, treatment of the allylsilylcyclopentadienes **3** and **4** with equimolar amounts of **1** or **2** in THF at mild temperatures gave the cyclopentadienyl derivatives [$MH\{\eta^5\text{-}C_5R_4Si(CH_3)_2(CH_2CH{=}CH_2)\}(CO)_3$] (M = Mo, R = H (**5a**), R = $CH_3$ (**6**), M = W, R = H (**7a**), R = $CH_3$ (**8a**)), respectively, which were isolated as oils in ca. 70% yield and fully characterized by $^1H$ and $^{13}C$ NMR, IR, and elemental analysis. Compared with the typical reaction conditions used to prepare these hydrido cyclopentadienyl group 6 compounds, no refluxing conditions were needed when THF was used as solvent. A probable reason for the milder temperature conditions required in this solvent is the formation of carbonyl molybdenum THF adducts of general formula [$Mo(CO)_3(NCMe)_{3-n}(THF)_n$], with $n = 1-3$, which exist in equilibrium when compound **1** or **2** is dissolved in THF.[10] Noteworthy, this synthetic approach seems to be suitable for a variety of substituted cyclopentadienyl systems.[11−13] Crystals suitable for diffraction structure determination could be obtained from concentrated hexane solutions of **8a**.

The geometry of the tungsten compound **8a** (Figure 1) consists of a distorted tetragonal pyramid based on the three C atoms of the carbonyl groups and one hydride ligand, the angles around the tungsten atom C30−W−H1, C20−W−H1, C20−W−C10, and C10−W−C30 being 75.6(5)°, 74.7(3)°, 81.8(5)°, and 80.8(4)°, respectively. The fifth coordination position is occupied by a cyclopentadienyl ring that is essentially planar, with $W(1)-C_{Cp}$ distances that lie in the range 2.311(8)−2.394(8) Å. The silyl pendant unit shows a high disorder, which hinders a precise determination of the C(7)−C(8) and C(7)−C(6) bond distances. The $W-C_{CO}$ bonds are within the range for this kind of groups, and as it has been previously observed in similar compounds,[14] the carbonyl *trans* to the hydride ligand displays the largest W−C bond length (W(1)−C(10) 1.996(8) Å) of the three.

**Allyl to Prop-1-en-1-yl Isomerization.** During the synthetic studies, we found that, under certain reaction conditions, the isomerization of the allyl pendant group took place. For molybdenum, stirring THF solutions of **1** and the cyclopentadiene ligand **3** at room temperature for more than 4 h and subsequent solvent evaporation gave oily residues with $^1H$ NMR spectra that showed, together with the resonances due to **5a**, a new set of signals that could be assigned to the methyl-vinyl isomer [$MoH\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH{=}CHCH_3)\}(CO)_3$] (**5b**), in a **5a**:**5b** ratio of ca. 2:1 (Scheme 2). Further transformations, observed for longer periods of time, will be discussed later in this article. Selected $^1H$ and $^{13}C$ NMR data assigned to the olefinic pendant unit for both isomers are shown in Table 1.

For tungsten, upon heating the THF reaction mixtures, formation of the corresponding methyl-vinyl isomers [$WH\{\eta^5\text{-}C_5R_4Si(CH_3)_2(CH{=}CHCH_3)\}(CO)_3$] (R = H (**7b**), Me (**8b**)) was detected by $^1H$ NMR spectroscopy. After ca. 12 h at 45 or 70

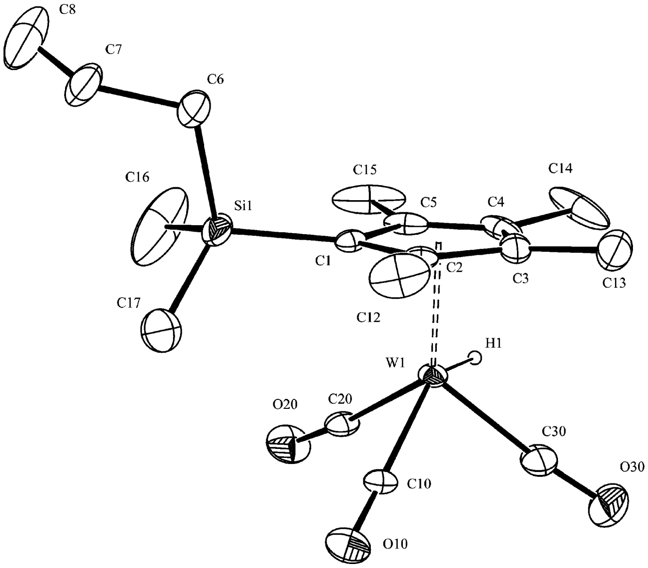


**Figure 1.** Molecular diagram of complex [$WH\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)\}(CO)_3$] (**8a**). Thermal ellipsoids are shown at 20% probability.

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[11] For comparison with some results described later on this article, we prepared the molybdenum compounds $MoH(C_5HMe_4)(CO)_3$ (**16**) and $MoH(C_5H_4SiMe_3)(CO)_3$ (**17**) following the same procedure as that used for synthesis of hydrido derivatives **5a**−**8a**; see Experimental Section. To the best of our knowledge, neither compound **16** nor **17** had been isolated before (see refs 12 and 13).

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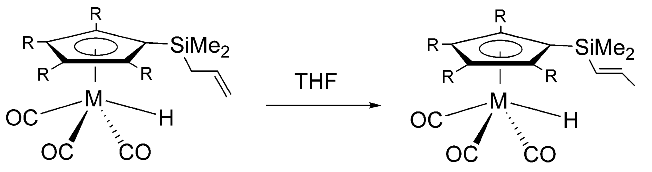
**Scheme 2**



M = Mo, R = H (**5a**)
M = W, R = H (**7a**), R = Me (**8a**)

M = Mo, R = H (**5b**)
M = W, R = H (**7b**), R = Me (**8b**)

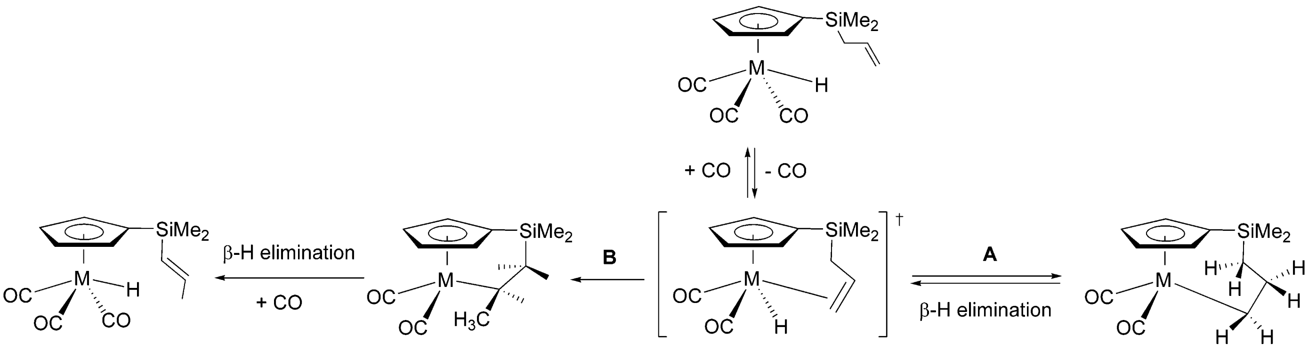
| a:b Ratio | Reaction Conditions |
|---|---|
| **(5a:5b) 2:1** | r.t. 4 hours |
| **(7a:7b) 2:1** | 45°C, > 12 hours |
| **(8a:8b) 1:1** | 70°C, > 12 hours |

**Table 1. Selected $^{1}H$ and $^{13}C$ NMR Shifts ($\delta$ in ppm) of Compounds 5a−b, 7a−b, and 8a−b**

| | Si−CH$_2$ | =CH | =CH$_2$ | | Si−CH= | =CH | −CH$_3$ |
|---|---|---|---|---|---|---|---|
| **5a** | 1.45 (d) | 5.61 (m) | 4.83, 4.87 (both d) | **5b** | 5.97 (dd) | 5.62 (m) | 1.66 (dd) |
| | 24.6 | 134.0 | 114.1 | | 128.3 | 144.6 | 22.5 |
| **7a** | 1.43 (d) | 5.58 (m) | 4.83, 4.87 (both d) | **7b** | 5.96 (dd) | 5.60 (m) | 1.66 (dd) |
| | 24.5 | 133.9 | 114.3 | | 128.8 | 145.5 | 22.4 |
| **8a** | 1.66 (d) | 5.69 (m) | 4.89−4.84 (m)[a] | **8b** | 6.04 (dd) | 6.07 (m) | 1.68 (dd) |
| | 25.3 | 134.4 | 114.2 | | 130.9 | 144.3 | 22.5 |

[a] Unresolved signals.

**Scheme 3**



(**B-1**)

(**A-1**)

°C, **7a**:**7b** and **8a**:**8b** ratios of ca. 2:1 and 1:1, respectively, were reached, which then remained constant even after one week at these temperatures. Complete transformation of the allyl isomers into methyl-vinyl isomers was never observed. The same results were observed from monitoring THF-$d_8$ solutions of pure **5a**, **7a**, or **8a** by $^{1}H$ NMR. As the scale of the reaction was decreased, the time for allyl isomerization was also decreased to ca. 2 h for derivative **5a** and ca. 8 h for the corresponding tungsten species but yielded compounds **5a**, **5b**, **7a**, **7b**, and **8a**, **8b**, respectively, in the final equilibrium isomer ratio as before.

Some examples of octahedral carbonyl group 6 metal compounds with bidentate nitrogen ligands have been reported to be active in alkene isomerization.[6a] In general, the studies of olefin isomerization catalysis in recent decades identified two major families of catalysts, which function by two different reaction mechanisms.[15] The largest family is that of transition metal hydrides, which catalyze C=C bond migration by addition−elimination reactions of an M−H bond. For 18-electron carbonyl derivatives, the process requires a previous dissociation of one CO ligand and subsequent coordination of the olefinic moiety. Migratory insertion can occur in either of the two ways, **A** or **B**, shown in Scheme 3. Addition of the M−H bond to the alkene pendant unit to form the species 3-(dimethylsilylcyclopentadienyl)propyl (**A-1**) is a nonproductive side reaction (path **A**), and only addition to give the transient species 1-methyl-2-(dimethylsilylcyclopentadienyl)ethyl (**B-1**) opens access to the allyl isomerization (path **B**). Subsequent *β*-hydrogen elimination from the silyl-methylene group of **B-1** would produce selectively the observed *trans*-prop-1-en-1-yl pendant unit present in isomers **5b**, **7b**, and **8b**. Selectivity to the *tran*s-isomer formation is a consequence of the required spatial position of the four atoms involved in the addition step of the M−H bond to the alkene, due to the geometry imposed by the chelating character of the cyclopentadienyl-alkene ligand. It should be emphasized that, whatever the mechanism, olefin isomerization is a kinetic phenomenon, and even with some of the more active catalysts, equilibrium mixtures of olefins are formed.

In order to prove the formation of the transient species $[MH\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2\text{-}\eta^2\text{-}CH{=}CH_2)\}(CO)_2]$ with the alkene coordinated to the metal center, compounds **5a** and **7a** were reacted with equimolar amounts of trimethylamine N-oxide, a reagent commonly used to favor elimination of carbonyl ligands from carbonyl transition metal compounds by formation

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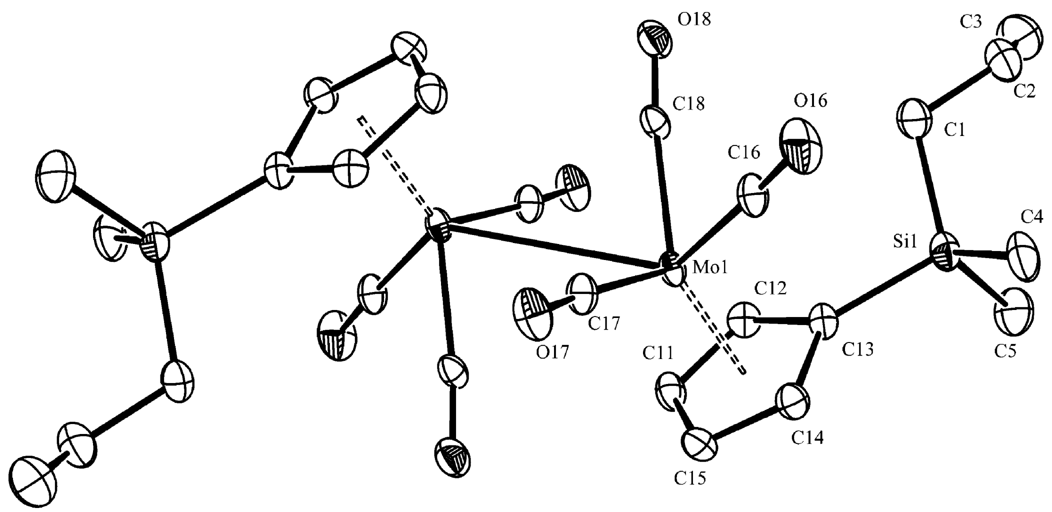
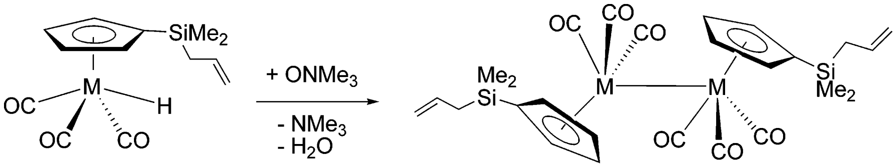


**Figure 2.** Molecular diagram of complex $[Mo\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)\}(CO)_3]_2$ (**9**). Thermal ellipsoids are shown at 30% probability.

**Scheme 4**



M = Mo (**5a**), W (**7a**)

M = Mo (**9**), W (**10**)

of $CO_2$ and subsequent elimination of $NMe_3$.[16] However, the reactions proceed through a different pathway and afforded, at room temperature, complete transformation of the hydrido derivatives **5a** and **7a** into the dinuclear species $[M\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)\}(CO)_3]_2$ (M = Mo (**9**), W (**10**)), respectively, which can be isolated as solids and fully characterized (Scheme 4). Formation of water and trimethylamine was confirmed by monitoring reactions of **5a** and **7a** with $ONMe_3$ in Young-valved NMR tubes. $^1H$ NMR of the mixture in dichloromethane-$d_2$ or benzene-$d_6$ showed two new singlets at $\delta$ 1.35 ($CD_2Cl_2$) or 0.47 ($C_6D_6$) and $\delta$ 2.22 ($CD_2Cl_2$) or 2.05 ($C_6D_6$), assigned to the water and trimethylamine protons, respectively, together with the formation of **9** and **10** and the disappearance of the proton resonances of $ONMe_3$,[17] **5a**, and **7a**. Red crystals of **9** suitable for a diffractometric analysis (Figure 2) could be obtained from hexane solutions of the molybdenum derivative kept at room temperature over 2−3 days.

The molybdenum compound **9** consists of two $Mo[\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)](CO)_3$ units, disposed in the *anti* conformation and linked by a metal−metal bond, the molecule lying on a crystallographic inversion center. Two independent but chemically equivalent molecules appear in the unit cell. The Mo−Mo bond length (Mo(1)−Mo(1)′ 3.254 and Mo(2)−Mo(2)′ 3.261 Å) agrees well with other metal−metal bond distances found for analogous derivatives of the type $[Mo(\eta^5\text{-}C_5H_4R)(CO)_3]_2$[9a,b,18] and is slightly longer than that reported for $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ (3.235 Å),[18c] probably due to the steric hindrance of the silyl allyl substituent of the cyclopentadienyl ring. The distribution of ligands around each metal center can be described as a distorted tetragonal pyramid based on three C atoms of the carbonyl groups and one molybdenum center of the other $Mo[\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)](CO)_3$ unit, with Mo(1)−Mo(1)′−C(16) and Mo(1)−Mo(1)′−C(18) angles slightly smaller (71.49° and 70.36°, respectively) than those found between carbon atoms of two carbonyl ligands mutually *cis*-disposed (C(16)−Mo(1)−C(17) = 77.2(2)° and C(16)−Mo(1)−C(18) = 77.2(2)°; similar values are observed in the other molecule present in the unit cell). The fifth coordination position is occupied by a cyclopentadienyl ring that is essentially planar, and the $Mo-C_{Cp}$ distances lie in the range 2.331(6)−2.413(6) Å, the C−Mo distance between the C bearing the silyl group and the metal being one of the shortest (2.355(5) and 2.335(6) Å). As expected, the allyl group lies on the opposite side of the cyclopentadienyl ligand of the Mo−Mo bond, while both the terminal C−C distance (C(2)−C(3) 1.28(1) Å) and the C(1)−C(2) (1.514(9) Å) bond lengths agree well with the allyl formulation.

Attempts to prepare corresponding deuterido compounds of the type $[MD\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)\}(CO)_3]$ (M = Mo, W) in order to gain insight into the isomerization mechanism were unsuccessful. Reaction of **1** or **2** with $Li[\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)]$ affords the corresponding $Li[M\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)\}(CO)_3]$ (M = Mo (**11**), W (**12**)) derivatives (Scheme 5), which were isolated and spectroscopically characterized. However, the addition of AcOD, MeOD, or $D_2O$ following a general procedure to synthesize hydrido cyclopentadienyl group 6 species[9] did not afford the desired derivatives but a mixture of different proportions, depending on the reaction conditions, of the corresponding

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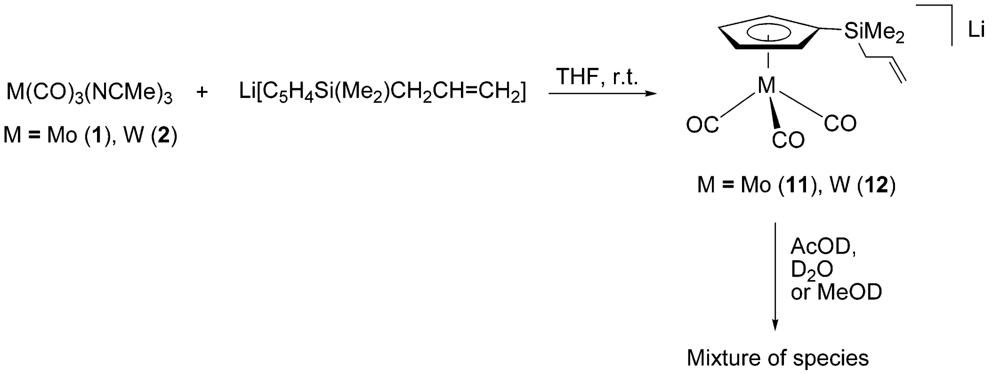
[16] For reactions between carbonyl metal compounds and $ONMe_3$, see the following and references therein: (a) Van Assema, S. G. A.; de Kanter, F. J. J.; Schakel, M.; Lammertsma, K. *Organometallics* **2006**, *25*, 5286. (b) Mathur, P.; Bhunia, A. K.; Kumar, A.; Chatterjee, S.; Mobin, S. M. *Organometallics* **2002**, *21*, 2215. (c) Chin, Y.; Wu, C. H.; Peng, S. M.; Lee, G. H. *Organometallics* **1991**, *10*, 1676. (d) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407.

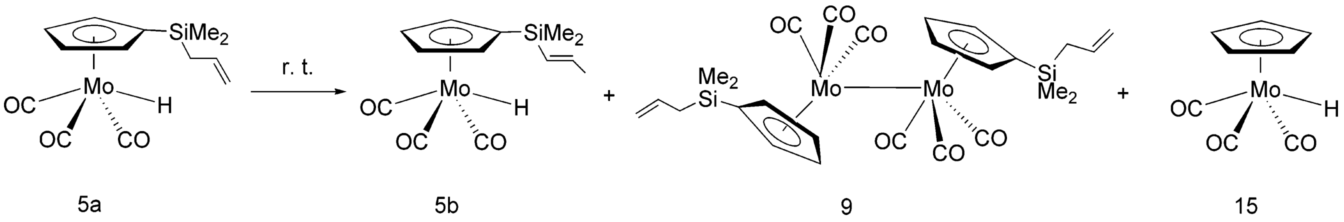
[17] $^1H$ NMR data for $ONMe_3$ (400 MHz, $CD_2Cl_2$): $\delta$ 3.29 (s, $N(CH_3)_3$). $^1H$ NMR (400 MHz, $C_6D_6$): $\delta$ 3.17 (s, $N(CH_3)_3$).

[18] (a) Lin, G.; Wong, W.-T. *J. Organomet. Chem.* **1996**, *522*, 271. (b) Lin, J.; Gao, P.; Li, B.; Xu, S.; Song, H.; Wang, B. *Inorg. Chim. Acta* **2006**, *359*, 4503. (c) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.

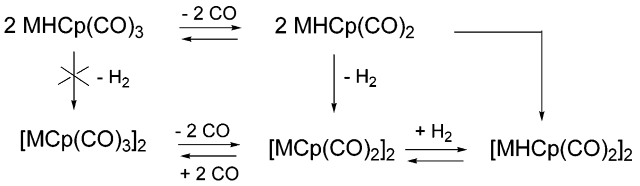
**Scheme 5**



**Scheme 6**



**Scheme 7**



deuteride species [MD{$\eta^5$-$C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)$}(CO)$_3$] (M = Mo, W) together with the desilylated compounds [MD($\eta^5$-$C_5H_5$)(CO)$_3$] (M = Mo, W). Similar behavior of silyl cyclopentadienyl group 6 lithium salts in the presence of acidic protic media has already been observed.[13e]

Following a different approach, chloroform solutions of **5a** or **7a** were stirred at room temperature for 8−12 h to give the corresponding chloride species [MCl{$\eta^5$-$C_5H_4Si(CH_3)_2$-$(CH_2CH{=}CH_2)$}(CO)$_3$] (M = Mo (**13**), W (**14**)) with yields of ca. 80−90%, which were isolated as red solids and fully characterized. Unfortunately, treatment of these chloride monocyclopentadienyl compounds with LiD, $NaBD_4$, $LiAlD_4$, or $LiBEt_3D$ gave product mixtures with $^1$H NMR spectra that indicated reduction of the C=C double bond of the allyl pendant unit.

**Dehydrogenation and Desilylation Reactions.** When THF solutions of **1** and the cyclopentadiene **3** were stirred at room temperature for ca. 8−10 h, in addition to the mixture of isomers **5a** and **5b**, another two sets of signals appeared and allowed their assignment to the dinuclear compound **9** and the unsubstituted cyclopentadienyl compound [MoH($\eta^5$-$C_5H_5$)(CO)$_3$] (**15**),[19a,20] product of a Si−C cleavage process, in a **5a**:**5b**:**9**:**15** ratio of ca. 5:3:1:1 (Scheme 6). After a further 5 days at room temperature, a red solid residue formed, which was isolated in yields of about 35% from the pale-colored solution by filtration and was fully characterized as dinuclear compound **9**. Evaporation of THF from the mother liquor allowed isolation of the pure nonsubstituted cyclopentadienyl derivative **15** as the only organometallic compound present in solution.

Compound **6** decomposes in ca. 12 h in THF solution at room temperature to give the corresponding desilylated compound [MoH($\eta^5$-$C_5HMe_4$)(CO)$_3$][11,12] (**16**) as the only spectroscopically observable organometallic species.

Thermal or photoinduced dehydrogenation of group 6 derivatives of general formula [MH($C_5R_5$)(CO)$_3$] is a very well documented reaction. Alt et al. and others showed that the initial step of these processes involves removal of a carbonyl ligand with formation of highly reactive 16-electron fragments of the type [MH($C_5R_5$)(CO)$_2$] (Scheme 7).[19b−e] However, while **15** undergoes complete photoinduced dehydrogenation in ca. 3 h to give [Mo($C_5H_5$)(CO)$_3$]$_2$ as the major final product, the analogous tungsten hydrido complex is considerably more stable, and after ca. 5 h the extent of reaction is of about 80%.

The easier dissociation of a carbonyl ligand from the starting molybdenum hydrido tricarbonyl compounds, as well as the higher reactivity of the coordinatively unsaturated molybdenum species formed compared with those of tungsten, is probably the key to understanding the different behavior observed for complexes **5a** and **7a** or **8a**. Thus, dehydrogenation of derivative **5a** to give **9** seems to be a competitive process with that of isomerization, while no dehydrogenation was evident for the more stable tungsten hydrido derivatives **7a** and **8a**, which need to be heated in order to start the allyl isomerization reaction. When THF solutions of **5a** were stirred in the absence of light, only formation of the desilylation product **15** was detected, which confirms the photoinduced nature of the dehydrogenation and the isomerization reaction, both closely related to the formation of the [MoH{$\eta^5$-$C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)$}(CO)$_2$] species. Moreover, the overall process strongly depends on the solvent used, probably due to stabilization of this 16-electron transient metal species by solvent coordination,[19b−e] and nonpolar solvents slow down not only the dehydrogenation reaction of **5a** but also the transformation of **5a**, **7a**, or **8a** into **5b**, **7b** or

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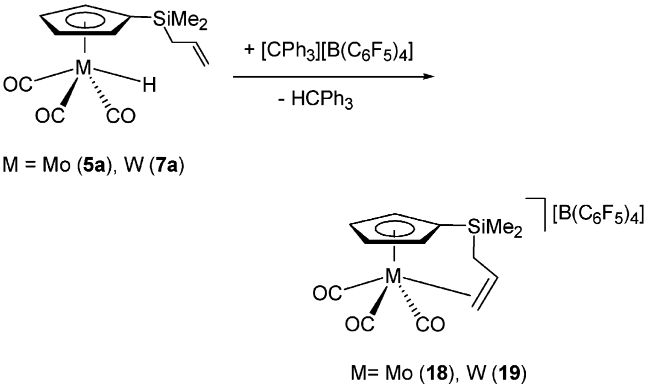
(19) (a) King, R. B. *Organomet. Synth.* **1965**, *1*, 156. (b) Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans.* **1984**, 187. (c) Kubas, G. J.; Wasserman, H. J.; Ryan, R. R. *Organometallics* **1985**, *4*, 2012. (d) Sweany, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 6986. (e) Alt, H. G. J.; Mahmoud, K. A.; Rest, A. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 544.

(20) Structural data for **15**: IR (THF): $\nu$(CO) 2021, 1929 cm$^{-1}$; $\nu$(Mo−H) 1848 cm$^{-1}$. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 4.53 (s, 5H, $C_5H_5$), −5.49 (s, 1H, Mo−H).

**Scheme 8**



**8b**, respectively, which proceeds only to a ca. 5−10% extent in the course of 1 week in benzene-$d_6$ solution under the same temperature conditions used for THF solutions.

Desilylation processes of silyl-substituted cyclopentadienyl transition metal derivatives have already been observed.[5b,13] For group 6 metal species, it has been argued that Si−C cleavage takes place through intermediate species with M−SiR$_3$ bonds, which are remarkably unstable in the presence of polar solvents and decompose to give dinuclear derivatives by M−M bond formation.[13] Reaction of the *ansa*-Me$_2$Si(C$_5$H$_5$)$_2$ cyclopentadiene with [M(CO)$_3$(EtCN)$_3$] (M = Cr, Mo) in refluxing DME afforded [M(C$_5$H$_5$)(CO)$_3$]$_2$ (M = Cr, Mo) as the only organometallic derivative present in solution, while the same procedure allowed synthesis of *ansa*-[{WH(CO)$_3$}$_2${Me$_2$Si(C$_5$H$_5$)$_2$}] from the starting [W(CO)$_3$(EtCN)$_3$] complex.[13d] In order to get a more detailed picture of the desilylation process detected for the molybdenum species, we investigated the composition of THF solutions of **5a** and [MoH(C$_5$H$_4$SiMe$_3$)(CO)$_3$] (**17**),[11,13] by GC-EI-MS. After 1 week at room temperature in the absence of light, solutions of **5a** and **17** produced **15** as the only soluble and nonvolatile organometallic product, as evidenced by $^1$H NMR, MS, and IR. Among these, C$_4$H$_7$OSi(CH$_3$)$_2$(C$_3$H$_5$) (desilylation of **5a**) and C$_4$H$_7$OSi(CH$_3$)$_3$ (desilylation of **17**) were identified by GC-EI-MS (see Experimental Section), which permit the conclusion that the presence of THF plays an important role in desilylation processes, as it has been argued before. When THF solutions of **17** were exposed to solar light, the hydrido compound underwent a competitive dehydrogenation reaction similar to that observed for **5a**, affording a mixture of **15** and the well-known dinuclear compound [Mo($\eta^5$-C$_5$H$_4$SiMe$_3$)(CO)$_3$]$_2$.[13]

**Cationic Species.** Reactions of the silyl-allyl complexes **5a** and **7a** with 1 equiv of [CPh$_3$][B(C$_6$F$_5$)$_4$] allowed us to test the capacity of the alkene pendant unit to coordinate to the metal center. In CD$_2$Cl$_2$, an immediate transformation was observed by $^1$H NMR at −40 °C to give the cationic derivatives [M($\eta^5$-C$_5$H$_4$Si(CH$_3$)$_2$(CH$_2$-$\eta^2$-CH=CH$_2$)(CO)$_3$][B(C$_6$F$_5$)$_4$] (M = Mo (**18**), W (**19**)) accompanied by elimination of HCPh$_3$, which was identified by $^1$H NMR for the resonance observed at $\delta$ 5.54 ppm (Scheme 8). In solution, **18** decomposes at room temperature to a noncharacterized mixture of species, while the tungsten derivative **19** remains unchanged under the same conditions for at least 2−3 days. When the scale of the reactions was increased, treatment of **5a** or **7a** with [CPh$_3$][B(C$_6$F$_5$)$_4$] in dichloromethane at −15 °C for 30 min permitted isolation of red, foamy solids, which were characterized as species **18** and **19**, respectively, which can be stored at 0 °C for several days without any decomposition.

$^1$H and $^{13}$C NMR spectra of cationic compounds **18** and **19** showed important changes when compared with those of neutral derivatives **5a** and **7a**. Disappearance of the $C_2$ symmetry reflected by the nonequivalence of the four cyclopentadienyl protons, the two silicon-methyl groups, and both silicon-methylene protons confirmed the coordination of the olefinic moiety to the metal center. The most notable spectroscopic features are those signals related with the pendant allyl system. The alkene−metal interaction in compounds **18** and **19** was evidenced by the shift of the resonances assigned to =CH and =CH$_2$ protons, as shown in Table 2. Similar displacements were observed in the $^{13}$C NMR spectra, where the signals assigned to the olefinic carbons in compounds **18** and **19** are shifted to high field compared with those found for **5a** and **7a** derivatives, as expected for a higher sp$^3$ character of both carbon atoms, consistent with a $\eta^2$-olefin−M interaction. The values agree well with those reported for related group 6 organometallic complexes.[6,7] Thus, for [Mo($\eta^5$-C$_5$H$_5$)Cl(CO){PPh$_2$(C$_6$H$_4$-$\eta^2$-CH=CHCH$_3$)}],[7a] resonances in the $^{13}$C NMR spectrum (dichloromethane-$d_2$) at $\delta$ 90.44 and 66.0 are assigned to =CH and =CHCH$_3$ carbon atoms, respectively, of the olefin coordinated to the metal center. Analogous chelate coordination of allyldimethylsilyl-$\eta^5$-cyclopentadienyl ligands is known only for group 4 and 5 transition metals. However, depending on the nature of the metal center, the M−olefin bonding situation reflects important differences. For [Zr($\eta^5$-C$_5$H$_5$)($\eta^5$-C$_5$H$_4$Si(CH$_3$)$_2$(CH$_2$-$\eta^2$-CH=CH$_2$)(Bz)][B(C$_6$F$_5$)$_4$], the shift of the signals due to the olefinic carbon atoms compared with those values observed for the noncoordinated olefin of the analogous zirconium neutral derivative ($\delta$ 173.1 and 91.8 for =CH and =CH$_2$ units, respectively, versus $\delta$ 134.9 and 110.0 for the sp$^2$ carbon atoms of the neutral compound [Zr($\eta^5$-C$_5$H$_5$)($\eta^5$-C$_5$H$_4$Si(CH$_3$)$_2$(CH$_2$CH=CH$_2$)(Bz)$_2$]) is consistent with a situation similar to that reported for classical allyl cations with a delocalized electron density in the Zr−C−C system, with a high polarization of the olefin system.[3e,f] In contrast, $^{13}$C NMR resonances (benzene-$d_6$) at $\delta$ 42.2 and 38.1 of the alkene pendant unit in derivative [Nb($\eta^5$-C$_5$H$_5$)($\eta^5$-C$_5$H$_4$Si(CH$_3$)$_2$(CH$_2$-$\eta^2$-CH=CH$_2$)(Bz)] were assigned to =CH and =CH$_2$ groups, in accord with a well-known metallacyclopropane character reported for this type of species.[3d]

**Table 2. Selected $^1$H and $^{13}$C NMR Shifts ($\delta$ in ppm) of Compounds 18 and 19**

| | Si−CH$_2$ | =CH | =CH$_2$ |
|---|---|---|---|
| **18** | 2.08, 2.43 (both dd, 1H) | 6.36 (m, 1H) | 3.69, 4.03 (both d, 1H) |
| | 29.3 | 98.0 | 61.0 |
| **19** | 2.06, 2.84 (both dd, 1H) | 5.95 (m, 1H) | 3.61, 3.94 (both d, 1H) |
| | 29.7 | 97.7 | 56.8 |

## Conclusions

Reaction at mild temperatures of the acetonitrile adducts **1** and **2**, with various substituted cyclopentadiene systems in THF, gives the hydrido derivatives **5a**−**8a**, **16**, and **17**. The method seems to be an entry of general use to substituted cyclopentadienyl hydrido molybdenum and tungsten compounds, with the advantage that no high temperatures are needed. Compounds **5a**, **6**, and **17** undergo Si−C cleavage at room temperature on the silyl-substituted cyclopentadienyl systems both in solution and as pure isolated oils. In the presence of light, a dehydrogenation transformation that takes place with or without any solvent is also detectable by NMR techniques for the molybdenum hydrides **5a** and **17** to give compounds **9** and [Mo($\eta^5$-C$_5$H$_4$SiMe$_3$)(CO)$_3$]$_2$, respectively. Tungsten species are more stable compared with those of molybdenum. The allyl unit present in derivatives **5a**, **7a**, and **8a** isomerizes in THF solution to give the methyl-vinyl system of compounds **5b**, **7b**, and **8b**, respectively. The presumed intermediate species of the isomerization are dicarbonyl hydrido compounds with the alkene unit coordinated to the metal. Unfortunately, attempts to detect or to isolate these through alternative synthetic procedures were unsuccessful, but the capability of the metal centers to $\eta^2$-coordinate the olefin pendant unit was proved in the cationic species **18** and **19**.

## Experimental Section

**General Information.** All manipulations were performed at an argon/vacuum manifold using standard Schlenk techniques or in an MBraun MOD system glovebox. Solvents were dried by known procedures and used freshly distilled. $[M(NCMe)_3(CO)_3]$ (M = Mo (**1**), W (**2**))[21] were prepared according to previous reports. The corresponding lithium salt of the cyclopentadienyl ligand, $Li[C_5H_5Si(CH_3)_2(CH_2CH{=}CH_2)]$, was prepared by addition of *n*-BuLi to diethyl ether solutions of the cyclopentadiene system and subsequent precipitation in hexane, according to a modified procedure of previously reported synthesis.[3e,f,22] NMR spectra were recorded in a Bruker 400 Ultrashield. $^1H$ and $^{13}C\{^1H\}$ chemical shifts are reported relative to tetramethylsilane. Coupling constants *J* are given in hertz.

**Preparation of $[MoH\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)\}(CO)_3]$ (5a).** THF (5 mL) was added to a dry mixture of **1** (0.5 g, 1.65 mmol) and $C_5H_5Si(CH_3)_2CH_2CH{=}CH_2$ (0.30 g, 1.81 mmol). Stirring the reaction mixture for 15 min at room temperature gave an orange suspension. The solvent was removed under vacuum, and hexane (2 × 3 mL) was then added to the solid residue, the resulting suspension was filtered, and the orange solution was dried under vacuum to give a red oil. Yield: 0.37 g (65%). Anal. Calcd for $C_{13}O_3H_{16}MoSi$: C, 45.35; H, 4.69. Found: C, 45.51; H, 4.37. IR (THF): $\nu$(CO) 2020, 1930 $cm^{-1}$. $^1H$ NMR (plus COSY plus HMQC, 400 MHz, $C_6D_6$): $\delta$ 5.61 (m, 1H, $^{trans}J_{HH} = 16.8$, $^{cis}J_{HH} = 10.5$, $^3J_{HH} = 8.1$, $=CH$), 4.87 (d, 1H, $^{cis}J_{HH} = 10.5$, $=CH_2$), 4.83 (d, 1H, $^{trans}J_{HH} = 16.8$, $=CH_2$), 4.75, 4.76 (both not resolved, each 2H, $C_5H_4$), 1.45 (d, 2H, $^3J_{HH} = 8.1$, $Si-CH_2$), 0.04 (s, 6H, $SiMe_2$), −5.52 (s, 1H, Mo−H). $^{13}C$ APT NMR (plus HMQC, 100 MHz, $C_6D_6$): $\delta$ 227.0 (−, CO), 134.1 (+, $=CH$), 114.1 (−, $=CH_2$), 98.7 (−, ipso-$C_5H_4$), 95.5, 93.5 (both +, $C_5H_4$), 24.6 (−, $Si-CH_2$), −2.5 (+, $Si(CH_3)_2$).

THF solutions of **5a** kept at room temperature for more than 4 h and subsequent evaporation of the solvent gave an oily, red residue, which was spectroscopically characterized as a mixture of **5a** and the methyl-vinyl isomer $[MoH\{\eta^5\text{-}C_5H_4Si(CH_3)_2CH{=}CHCH_3\}(CO)_3]$ (**5b**), in a **5a**:**5b** ratio of ca. 2:1. $^1H$ and $^{13}C$ NMR of this oil in benzene-$d_6$ allowed assignment of the resonances due to the methyl-vinyl isomer **5b**: $^1H$ NMR (plus COSY, plus HMQC, 400 MHz, $C_6D_6$): $\delta$ 5.97 (dq, 1H, $^{trans}J_{HH} = 18.3$, $^4J_{HH} = 1.8$, $=CHSi$), 5.62 (dq, 1H, $^{trans}J_{HH} = 18.3$, $^3J_{HH} = 6.0$, $=CHMe$), 4.80 (not resolved, 4H, $C_5H_4$), 1.66 (dd, 3H, $^3J_{HH} = 6.0$, $^4J_{HH} = 1.8$, $=CCH_3$), 0.15 (s, 6H, $Si(CH_3)_2$), −5.49 (s, 1H, Mo−H). $^{13}C$ APT NMR (100 MHz, $C_6D_6$,): $\delta$ 227.8 (−, CO), 144.6 (+, $=CH$), 128.3 (+, $=CH-Si$), 95.6, 93.6 (both +, $C_5H_4$), 22.5 (−, $=CCH_3$), −1.5 (+, $Si(CH_3)_2$).

**Preparation of $[MoH\{\eta^5\text{-}C_5Me_4Si(CH_3)_2(CH_2CH{=}CH_2)\}(CO)_3]$ (6).** The same procedure as that used for the synthesis of **5a** was followed, starting from the molybdenum compound **1** (0.6 g, 1.98 mmol) and $C_5Me_4HSi(CH_3)_2CH_2CH{=}CH_2$ (0.38 g, 1.98 mmol). The reaction needs 6−8 h at room temperature to complete. Derivative **6** was obtained as an orange oil, which can be stored for weeks without decomposition at −30 °C. Yield: 0.56 g (71%). Anal. Calcd for $C_{17}O_3H_{24}MoSi$: C, 50.99; H, 6.05. Found: C, 51.32; H, 6.15. IR (THF): $\nu$(CO) 2010, 1922 $cm^{-1}$. $^1H$ NMR (plus COSY plus HMQC, 400 MHz, $C_6D_6$): $\delta$ 5.72 (m, 1H, $^{trans}J_{HH} = 15.0$, $^{cis}J_{HH} = 8.0$, $^3J_{HH} = 8.4$, $=CH$), 4.94 (d, 1H, $^{cis}J_{HH} = 8.0$, $=CH_2$), 4.93 (d, 1H, $^{trans}J_{HH} = 15.0$, $=CH_2$), 1.80, 1.68 (both s, each 6H, $C_5(CH_3)_4$), 1.61 (d, 2H, $^3J_{HH} = 8.4$, $Si-CH_2$), 0.32 (s, 6H, $Si(CH_3)_2$), −5.14 (s, 1H, Mo−H). $^{13}C$ APT NMR (plus HMQC, 100 MHz, $C_6D_6$): $\delta$ 229.7 (−, CO), 134.4 (+, $=CH$), 113.8 (−, $=CH_2$), 111.0, 111.9, 91.7 (all −, $SiC_5(CH_3)_4$), 25.3 (−, $Si-CH_2$), 13.6, 11.0 (both +, $C_5(CH_3)_4$), 0.1 (+, $Si(CH_3)_2$).

**Preparation of $[WH\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)\}(CO)_3]$ (7a).** THF (5 mL) was added to a dry mixture of **2** (1.0 g, 2.56 mmol) and $C_5H_5Si(CH_3)_2CH_2CH{=}CH_2$ (0.42 g, 2.56 mmol). Stirring the reaction mixture for 8 h at room temperature gave an orange suspension. The solvent was removed under vacuum, and hexane (2 × 3 mL) was then added to the solid residue, the resulting suspension was filtered, and the yellow solution was dried under vacuum to give an orange oil. Yield: 0.81 g (72%). Anal. Calcd for $C_{13}O_3H_{16}WSi$: C, 36.12; H, 3.74. Found: C, 36.24; H, 3.98. IR (THF): $\nu$ (CO) 2017, 1922 $cm^{-1}$. $^1H$ NMR (plus COSY plus HMQC, 400 MHz, $C_6D_6$): $\delta$ 5.58 (m, 1H, $^{trans}J_{HH} = 16.8$, $^{cis}J_{HH} = 9.9$, $^3J_{HH} = 7.8$, $=CH$), 4.87 (d, 1H, $^{cis}J_{HH} = 9.9$, $=CH_2$), 4.83 (d, 1H, $^{trans}J_{HH} = 16.8$, $=CH_2$), 4.70, 4.75 (both not resolved, each 2H, $C_5H_4$), 1.43 (d, 2H, $^3J_{HH} = 7.8$, $Si-CH_2$), 0.03 (s, 6H, $Si(CH_3)_2$), −7.24 (s, 1H, W−H). $^{13}C$ APT NMR (plus HMQC, 100 MHz, $C_6D_6$): $\delta$ 217.3 (−, CO), 133.9 (+, $=CH$), 114.3 (−, $=CH_2$), 96.9 (−, $C_5H_4$-ipso), 93.4, 92.4 (both +, $C_5H_4$), 24.2 (−, $Si-CH_2$), −2.5 (+, $Si(CH_3)_2$).

Heating THF solutions of **7a** at 45 °C for ca. 1 day with subsequent evaporation of the solvent gave an oily yellow residue, which was spectroscopically characterized as a mixture of **7a** and the methyl-vinyl isomer $[WH\{\eta^5\text{-}C_5H_4Si(CH_3)_2CH{=}CHCH_3\}(CO)_3]$ (**7b**) in a **7a**:**7b** ratio of ca. 2:1, which allowed identification by NMR techniques the set of signals corresponding to derivative **7b**: $^1H$ NMR (plus COSY, plus HMQC, 400 MHz, $C_6D_6$): $\delta$ 5.97 (dq, 1H, $^{trans}J_{HH} = 18.3$, $^4J_{HH} = 1.8$, $=CHSi$), 5.60 (dq, 1H, $^{trans}J_{HH} = 18.3$, $^3J_{HH} = 6.3$, $=CHMe$), 4.76 (not resolved, 4H, $C_5H_4$), 1.66 (dd, 3H, $^3J_{HH} = 6.3$, $^4J_{HH} = 1.8$, $=CCH_3$), 0.14 (s, 6H, $Si(CH_3)_2$), −7.21 (s, 1H, W−H). $^{13}C$ APT NMR (100 MHz, $C_6D_6$,): $\delta$ 217.6 (−, CO), 144.9 (+, $=CH$), 128.8 (+, $=CH-Si$), 97.8 (+, ipso-$C_5H_4$), 93.5, 92.5 (both +, $C_5H_4$), 22.4 (−, $=CCH_3$), −1.6 (+, $Si(CH_3)_2$).

**Preparation of $[WH\{\eta^5\text{-}C_5Me_4Si(CH_3)_2(CH_2CH{=}CH_2)\}(CO)_3]$ (8a).** THF (5 mL) was added to a dry mixture of **2** (0.5 g, 1.28 mmol) and $C_5Me_4HSi(CH_3)_2CH_2CH{=}CH_2$ (0.24 g, 1.28 mmol). Stirring the reaction mixture for 12 h at 45 °C gave a dark orange suspension. The solvent was removed under vacuum, and hexane (2 × 3 mL) was then added to the residue. The resulting orange-brown suspension was filtered and the solution dried under vacuum to give a dark orange oil. Yield: 0.42 g (67%). Anal. Calcd for $C_{17}O_3H_{24}WSi$: C, 41.81; H, 4.96. Found: C, 42.30; H, 5.01. IR (THF): $\nu$(CO) 2007, 1914 $cm^{-1}$. $^1H$ NMR (plus COSY plus HMQC, 400 MHz, $C_6D_6$): $\delta$ 5.69 (m, 1H, $^{trans}J_{HH} = 16.4$, $^{cis}J_{HH} = 8.8$, $^3J_{HH} = 7.6$, $=CH$), 4.89−4.84 (m not resolved, 2H, $=CH_2$), 1.89, 1.72 (both s, each 6H, $C_5(CH_3)_4$), 1.66 (d, 2H, $^3J_{HH} = 7.6$, $Si-CH_2$), 0.30 (s, 6H, $Si(CH_3)_2$), −6.66 (s, 1H, W−H). $^{13}C$ APT NMR (plus HMQC, 100 MHz, $C_6D_6$): $\delta$ 221 (−, CO), 134.4 (+, $=CH$), 114.1 (−, $=CH_2$), 110.0, 108.7, 90.5 (all −, $SiC_5(CH_3)_4$), 25.3 (−, $Si-CH_2$), 13.8, 11.1 (both +, $C_5(CH_3)_4$), 0.3 (+, $Si(CH_3)_2$).

Heating THF solutions of **8a** at 70 °C for ca. 1 day with subsequent evaporation of the solvent gave an oily, yellow residue, which was spectroscopically characterized as a mixture of **8a** and

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[21] Edelmann, F.; Behrens, P.; Behrens, S.; Behrens, U. *J. Organomet. Chem.* **1986**, *310*, 333.

[22] Spectroscopic data for $Li[C_5H_4SiMe_2(CH_2CH{=}CH_2)]$: $^1H$ NMR (plus HMQC, 400 MHz, THF-$d_8$): $\delta$ 5.90 (not resolved, 2H, $C_5H_4$), 5.85 (m, 1H, $=CH$), 5.82 (not resolved, 2H, $C_5H_4$), 4.70 (second order system, 2H, $=CH_2$), 1.60 (dd, 1H, $^3J_{HH} = 12$, $^{gem}J_{HH} = 1.2$, $Si-CH_2$), 0.90 (s, 6H, $SiMe_2$). $^{13}C$-APT NMR (plus HMQC, 100 MHz, THF-$d_8$): $\delta$ 137.9 (+, $=CH$), 111.6 (+, $C_5H_4$), 110.9 (−, $=CH_2$), 106.7 (+, $C_5H_4$), 106.4 (−, $C_5H_4$-ipso), 27.1 (−, Si-$CH_2$), −1.3 (+, $SiMe_2$).

the methyl-vinyl isomer [WH{$\eta^5$-$C_5Me_4Si(CH_3)_2CH{=}CHCH_3$}(CO)$_3$] (**8b**) in a **8a**:**8b** ratio of ca. 1:1, which allowed identification by NMR techniques the set of signals corresponding to derivative **8b**: $^1$H NMR (plus COSY plus HMQC, 400 MHz, $C_6D_6$): $\delta$ 6.07 (dq, 1H, $^{trans}J_{HH}$ = 18.4, $^3J_{HH}$ = 6.4, =CH(Me)), 6.04 (dq, 1H, $^{trans}J_{HH}$ = 18.4, $^4J_{HH}$ = 1.2, SiCH=), 1.94, 1.74 (both s, each 6H, $C_5(CH_3)_4$), 1.68 (dd, 3H, $^3J_{HH}$ = 6.4, $^4J_{HH}$ = 1.2, =C(CH$_3$)), 0.37 (s, 6H, Si(CH$_3$)$_2$), −6.63 (s, 1H, W−H). $^{13}$C APT NMR (plus HMQC, 100 MHz, $C_6D_6$): $\delta$ 221 (−, CO), 144.3 (+, =CH(Me)), 130.9 (+, SiC=), 110.2, 108.8, 91.0 (all −, Si*C*$_5$(CH$_3$)$_4$), 22.5 (−, =C(*C*H$_3$)), 13.7, 11.2 (both +, SiC$_5$(*C*H$_3$)$_4$), 0.7 (+, Si(CH$_3$)$_2$).

**Preparation of [Mo{$\eta^5$-$C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)$}(CO)$_3$]$_2$ (9).** Toluene (5 mL) was added to a dry mixture of **5a** (0.5 g, 1.42 mmol) and trimethylamine oxide (0.10 g, 1.42 mmol). Stirring the reaction mixture for 2 h at room temperature gave a red solution. Solvent was removed under vacuum and the residue washed with hexane (2 × 3 mL) and dried under vacuum to give a red solid. The same results were obtained when dichloromethane was used as solvent. Yield: 0.90 g (89%). Anal. Calcd for $C_{26}O_6H_{14}Mo_2Si_2$: C, 45.48; H, 4.40. Found: C, 44.70; H, 4.41. IR (THF): $\nu$(CO) 1954, 1913 cm$^{-1}$. $^1$H NMR (plus COSY plus HMQC, 400 MHz, $C_6D_6$): $\delta$ 5.66 (m, 1H, $^{trans}J_{HH}$ = 16.4, $^{cis}J_{HH}$ = 10.7, $^3J_{HH}$ = 7.8, =CH), 5.07, 4.92 (both not resolved, each 2H, $C_5H_4$), 4.90 (d, 1H, $^{cis}J_{HH}$ = 10.7, =CH$_2$), 4.87 (d, 1H, $^{trans}J_{HH}$ = 16.4, =CH$_2$), 1.55 (d, 2H, $^3J_{HH}$ = 7.8, Si−CH$_2$), 0.19 (s, 6H, Si(CH$_3$)$_2$). $^{13}$C APT NMR (plus HMQC, 100 MHz, $C_6D_6$): $\delta$ 226.3 (−, CO), 133.8 (+, =CH), 114.1 (−, =CH$_2$), 99.4 (−, $C_5H_4$-ipso), 95.6, 99.5 (both +, $C_5H_4$), 24.6 (−, Si−CH$_2$), −2.6 (+, Si(CH$_3$)$_2$).

**Preparation of [W{$\eta^5$-$C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)$}(CO)$_3$]$_2$ (10).** An analogous procedure to that described for **9** was followed for the synthesis of derivative **10**, starting from a solution of **7a** (1.0 g, 2.29 mmol) and trimethylamineoxide (0.17 g, 2.29 mmol). Yield: 1.72 g (75%). Anal. Calcd for $C_{26}O_6H_{14}W_2Si_2$: C, 36.21; H, 3.51. Found: C, 36.43; H, 3.55. IR (THF): $\nu$(CO) 1952, 1910 cm$^{-1}$. $^1$H NMR (plus COSY plus HMQC, 400 MHz, $C_6D_6$): $\delta$ 5.64 (m, 1H, $^{trans}J_{HH}$ = 16.9, $^{cis}J_{HH}$ = 10.2, $^3J_{HH}$ = 8.1, =CH), 5.16, 4.91 (both not resolved, each 2H, $C_5H_4$), 4.89 (d, 1H, $^{cis}J_{HH}$ = 16.8, =CH$_2$), 4.86 (d, 1H, $^{trans}J_{HH}$ = 10.2, =CH$_2$), 1.52 (d, 2H, $^3J_{HH}$ = 8.1, Si−CH$_2$), 0.18 (s, 6H, Si(CH$_3$)$_2$). $^{13}$C APT NMR (plus HMQC, 100 MHz, $C_6D_6$): $\delta$ 215.1 (−, CO), 133.9 (+, =CH), 114.4 (−, =CH$_2$), 95.0 (−, $C_5H_4$-ipso), 99.4, 93.5 (both +, $C_5H_4$), 24.6 (−, Si−CH$_2$), −2.6 (+, Si(CH$_3$)$_2$).

**Desilylation Reactions of [MoH{$\eta^5$-$C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)$}(CO)$_3$] (5a) and [MoH{$\eta^5$-$C_5H_4Si(CH_3)_3$}(CO)$_3$] (17).** THF solutions of **5a** or **17** were stirred at room temperature for 1 week or 24 h, respectively, in the absence of light. Evaporation of the solvent gave oily, pink residues, which were washed with hexane to afford white precipitates, which were identified in both cases by $^1$H NMR and IR as MoH($\eta^5$-$C_5H_5$)(CO)$_3$. IR (THF): $\nu$(CO) 2021, 1929 cm$^{-1}$; $\nu$(Mo−H) 1848 cm$^{-1}$. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 4.53 (s, 5H, $C_5H_5$), −5.49 (s, 1H, Mo−H). Aliquots of the THF solutions were also studied by GC-IE-mass spectrometry. MS(GC-EI) for desilylation of **5a**: 3.23 min: *m/z* 172 (58%, [$C_9H_{20}OSi$]$^+$), 132 (31%, [$C_6H_{16}OSi$]$^+$), 41 (100%, [$C_3H_5$]$^+$); 5.62 min: *m/z* 248 (24%, [$MoC_8H_6O_3$]$^+$), 164 (91%, [$MoC_5H_5$]$^+$), 98 (71%, [Mo]$^+$), 65 (71%, [$C_5H_5$]$^+$). MS(GC-EI) for desilylation of **17**: 5.61 min: *m/z* 248 (24%, [$MoC_8H_6O_3$]$^+$), 164 (91%, [$MoC_5H_5$]$^+$), 98 (71%, [Mo]$^+$), 65 (71%, [$C_5H_5$]$^+$); 10.56 min *m/z* 132 (33%, [$C_6H_{16}OSi$]$^+$), 118 (53%, [$C_5H_{14}OSi$]$^+$), 73 (100%, [$C_4H_8O$]$^+$), 75 (99%, [$C_3H_{10}Si$ + H]$^+$), 57 (40%, [$C_3H_5O$]$^+$), 43 (90%, [$C_2H_3O$]$^+$).

**Preparation of Li[Mo{$\eta^5$-$C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)$}(CO)$_3$] (11).** THF (5 mL) was added at 0 °C to a dry mixture of **1** (0.5 g, 1.65 mmol) and Li[$C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)$] (0.28 g, 1.65 mmol). After addition of the solvent, the mixture was stirred 15 min at this temperature and then a further 1 h at room temperature. During this time, the reaction suspension changed to give an orange solution. The solvent was removed under vacuum and the oily residue washed twice with hexane (2 × 3 mL) and dried under vacuum to give a yellow foam. Yield: 0.51 g (86%). $^1$H NMR (plus HMQC, 400 MHz, THF-$d_8$): $\delta$ 5.82 (m, 1H, $^{trans}J_{HH}$ = 17.1, $^{cis}J_{HH}$ = 9.9, $^3J_{HH}$ = 8.1, =CH), 4.77 (d, 1H, $^{cis}J_{HH}$ = 9.9, =CH$_2$), 4.72 (d, 1H, $^{trans}J_{HH}$ = 17.1, =CH$_2$), 5.07 (not resolved, 4H, $C_5H_4$), 1.65 (d, 2H, $^3J_{HH}$ = 8.1, Si−CH$_2$), 0.12 (s, 6H, Si(CH$_3$)$_2$). $^{13}$C APT NMR (plus HMQC, 100 MHz, $C_6D_6$): $\delta$ 236.2 (−, CO), 137.9 (+, =CH), 112.0 (−, =CH$_2$), 94.0, 88.9 (both +, $C_5H_4$), 86.6 (−, $C_5H_4$-ipso), 26.8 (−, Si−CH$_2$), −1.5 (+, Si(CH$_3$)$_2$).

**Preparation of Li[W{$\eta^5$-$C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)$}(CO)$_3$] (12).** The same procedure as that described for compound **11** was followed for the synthesis of **12**, starting from **2** (0.35 g, 0.90 mmol) and Li[$C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)$] (0.15 g, 0.90 mmol). Compound **12** was obtained as a yellow, foamy solid. Yield: 0.51 g (86%). $^1$H NMR (plus HMQC, 400 MHz, THF-$d_8$): $\delta$ 5.92 (not resolved, 1H, =CH$_2$), 4.83 (not resolved, 1H, =CH), 5.11, 5.09 (both not resolved, each 2H, $C_5H_4$), 1.65 (d, 2H, $^3J_{HH}$ = 8.0, Si−CH$_2$), 0.13 (not resolved, 6H, Si(CH$_3$)$_2$). $^{13}$C APT NMR (plus HMQC, 100 MHz, $C_6D_6$): $\delta$ 227.3 (−, CO), 136.7 (+, =CH), 112.0 (−, =CH$_2$), 92.2, 87.6 (both +, $C_5H_4$), 86.6 (−, ipso-$C_5H_4$), 26.5 (−, Si−CH$_2$), −1.7 (+, Si(CH$_3$)$_2$).

**Preparation of [MoCl{$\eta^5$-$C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)$}(CO)$_3$] (13).** A chloroform (5−10 mL) solution of **5a** (1.0 g, 2.84 mmol) was stirred at room temperature for 8 h. Volatiles were removed from the resulting dark red mixture, and the solid residue was washed twice with hexane (2 × 3 mL) and dried under vacuum to give a red powder. Yield: 0.86 g (80%). Anal. Calcd for $C_{13}O_3H_{15}MoClSi$: C, 41.23; H, 3.99. Found: C, 41.00; H, 3.86. IR ($CH_2Cl_2$): $\nu$(CO) 2054, 1974 cm$^{-1}$. $^1$H NMR (plus COSY plus HMQC, 400 MHz, $CDCl_3$): $\delta$ 5.74 (m, 1H, $^{trans}J_{HH}$ = 18.3, $^{cis}J_{HH}$ = 9.0, $^3J_{HH}$ = 8.1, =CH), 4.89 (d, 1H, $^{cis}J_{HH}$ = 9.0, =CH$_2$), 4.88 (d, 1H, $^{trans}J_{HH}$ = 18.3, =CH$_2$), 5.75, 5.35 (both not resolved, each 2H, $C_5H_4$), 1.72 (d, 2H, $^3J_{HH}$ = 8.1, Si−CH$_2$), 0.27 (s, 6H, Si(CH$_3$)$_2$). $^{13}$C APT NMR (plus HMQC, 100 MHz, $CDCl_3$): $\delta$ 224.0 (−, CO), 133.3(+, =CH), 114.6 (−, =CH$_2$), 104.6, 96.5 (both +, $C_5H_4$), 24.2 (−, Si−CH$_2$), −2.9 (+, Si(CH$_3$)$_2$).

**Preparation of [WCl{$\eta^5$-$C_5H_4Si(CH_3)_2CH_2CH{=}CH_2$}(CO)$_3$] (14).** An analogous procedure to that described for **13** was followed, starting from a chloroform solution of **7a** (1.0 g, 2.29 mmol), which was stirred at room temperature for at least 16 h to complete the transformation. Yield: 0.71 g (66%). Anal. Calcd for $C_{13}O_3H_{15}WClSi$: C, 33.46; H, 3.24. Found: C, 33.55; H, 3.07. IR ($CH_2Cl_2$): $\nu$(CO) 2046, 1952 cm$^{-1}$. $^1$H NMR (plus COSY plus HMQC, 400 MHz, $CDCl_3$): $\delta$ 5.75 (m, 1H, $^{trans}J_{HH}$ = 18.6, $^{cis}J_{HH}$ = 9.6, $^3J_{HH}$ = 7.8, =CH), 4.90 (d, 1H, $^{cis}J_{HH}$ = 9.6, =CH$_2$), 4.89 (d, 1H, $^{trans}J_{HH}$ = 18.6, =CH$_2$), 5.75, 5.40 (both not resolved, each 2H, $C_5H_4$), 1.74 (d, 2H, $^3J_{HH}$ = 7.8, Si−CH$_2$), 0.30 (s, 6H, Si(CH$_3$)$_2$). $^{13}$C APT NMR (plus HMQC, 100 MHz, $CDCl_3$): $\delta$ 230.8, 218.8 (both −, CO), 133.2 (+, =CH), 114.7 (−, =CH$_2$), 102.7, 94.5 (both +, $C_5H_4$), 24.3 (−, Si−CH$_2$), −2.9 (+, Si(CH$_3$)$_2$).

**Preparation of [MoH($\eta^5$-$C_5HMe_4$)(CO)$_3$] (16).** The same procedure as that used for the synthesis of **5a** or **6** was followed, starting from the molybdenum compound **1** (0.5 g, 1.65 mmol) and $C_5H_2Me_4$ (0.22 g, 1.80 mmol). The reaction is completed in 2 h at room temperature. Derivative **11** was obtained as an orange oil. Yield: 0.38 g (68%). Anal. Calcd for $C_{12}O_3H_{14}Mo$: C, 47.70; H, 4.67. Found: C, 48.12; H, 4.68. IR (THF): $\nu$(CO) 2011, 1922 cm$^{-1}$; $\nu$(Mo−H) 1850 cm$^{-1}$. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 4.64 (s, 1H, $C_5H$), 1.62, 1.61 (both s, each 6H, $C_5(CH_3)_4$), −5.06 (s, 1H, Mo−H). $^{13}$C APT NMR (plus HMQC, 100 MHz, $C_6D_6$): $\delta$ 230.0 (−, CO), 104.7, 107.4, (both −, ipso-*C*$_5$(CH$_3$)$_4$), 88.4 (+, *C*$_5$H), 12.7, 11.0 (both +, C$_5$(*C*H$_3$)$_4$).

**Preparation of [MoH($\eta^5$-$C_5H_4SiMe_3$)(CO)$_3$] (17).** The same procedure as that used for the synthesis of **5a**, **6**, or **11** was followed, starting from the molybdenum compound **1** (0.80 g, 2.64 mmol) and $C_5H_5SiMe_3$ (0.36 g, 2.64 mmol). The reaction needs 4−6 h at room temperature to complete. Derivative **17** was obtained as a pink oil, which can be stored for weeks without any decomposition at −30 °C. In the absence of light, this oil evolves within hours at room temperature, both pure or in solution, into a mixture of **17** and $[Mo(\eta^5\text{-}C_5H_4SiMe_3)(CO)_3]_2$; see ref 13.Yield: 0.62 g (73%). Anal. Calcd for $C_{11}O_3H_{14}MoSi$: C, 41.51; H, 4.43. Found: C, 41.81; H, 4.88. IR: $\nu$(CO) 2011, 1940 cm$^{-1}$; $\nu$(Mo−H) 1890 cm$^{-1}$. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 4.76, 4.73 (both m, each 2H, $C_5H_4$), 0.03 (s, 9H, $Si(CH_3)_3$), −5.51 (s, 1H, Mo−H). $^{13}$C APT NMR (plus HMQC, 100 MHz, $C_6D_6$): $\delta$ 227.8 (−, CO), 100.6 (−, ipso-$C_5H_4$), 95.2, 93.4 (both +, $C_5H_4$), −0.25 (+, $Si(CH_3)_2$).

**Preparation of $[Mo\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2\text{-}\eta^2\text{-}CH{=}CH_2)\}(CO)_3][B(C_6F_5)_4]$ (18).** Dichloromethane (5 mL) was added to a dry mixture of **5a** (0.25 g, 0.73 mmol) and triphenylmethylpentafluorophenylboron (0.67 g, 0.73 mmol) at −30 °C, and the mixture stirred for 30 min. Volatiles were removed from the resulting red dark solution, and the oily residue was washed twice with cold hexane (2 × 3 mL) and dried under vacuum to give a red powder. Yield: 0.68 g (92%). Anal. Calcd for $C_{37}O_3H_{15}MoSiF_{20}B$: C, 43.47; H, 1.48. Found: C, 43.60; H, 1.70. IR ($CH_2Cl_2$): $\nu$(CO) 2070, 1984 cm$^{-1}$. $^1$H NMR (plus COSY plus HMQC, 400 MHz, 273 K, $CD_2Cl_2$): $\delta$ 6.50, 6.38, 5.86, 5.50 (all s, each 1H, $C_5H_4$), 6.09 (m, 1H, $^{trans}J_{HH} = 14.8$, $^{cis}J_{HH} = 8.9$, $^3J_{HH} = 5.5$, $^3J_{HH} = 10.1$, =CH), 4.03 (d, 1H, $^{trans}J_{HH} = 14.8$, =$CH_2$), 3.69 (d, 1H, $^{cis}J_{HH} = 8.9$, =$CH_2$), 2.89 (dd, 1H, $^2J_{HH} = 13.7$, $^3J_{HH} = 5.5$, Si−$CH_2$), 2.10 (dd, 1H, $^2J_{HH} = 13.7$, $^3J_{HH} = 10.0$, Si−$CH_2$), 0.68, 0.40 (both s, each 3H, $Si(CH_3)_2$). $^{13}$C APT NMR (plus HMQC, 100 MHz, 273 K, $CD_2Cl_2$): $\delta$ 223.222 (−, *cis*-CO), 210.8 (−, *trans*-CO), 149.6, 146.5, 139.8, 137.8, 136.5, 134.6 (all −, $B(C_6F_5)_4$), 115.9 (−, ipso-$C_5H_4$), 103.9, 102.0, 89.2 (all +, $C_5H_4$), 98.0 (+, =CH), 61.0 (−, =$CH_2$), 29.3 (−, Si−$CH_2$), 0.7, −4.6 (both +, $Si(CH_3)_2$). $^{19}$F NMR (376 MHz, 273 K, $CD_2Cl_2$): $\delta$ 134.7 (*o*, *m*-$C_6F_5$), 165.5 (*p*-$C_6F_5$), 170.0 (*o*, *m*-$C_6F_5$).

**Preparation of $[W\{\eta^5\text{-}C_5H_4Si(CH_3)_2(CH_2\text{-}\eta^2\text{-}CH{=}CH_2)\}(CO)_3][B(C_6F_5)_4]$ (19).** Dichloromethane (5 mL) was added to a dry mixture of **7a** (0.40 g, 0.92 mmol) and triphenylmethylpentafluorophenylboron (0.84 g, 0.92 mmol) at −30 °C, and the mixture stirred for 15 min. The dark red solution was then allowed to warm to room temperature and stirred for a further 1 h. Dichloromethane was evaporated under reduced pressure and the oily residue washed twice with hexane (2 × 3 mL) and dried under vacuum to give a red powder. Yield: 0.97 g (95%). Anal. Calcd for $C_{37}O_3H_{15}WSiF_{20}B$: C, 40.03; H, 1.36. Found: C, 40.33; H, 1.42. IR ($CH_2Cl_2$): $\nu$(CO) 2066, 1968 cm$^{-1}$. $^1$H NMR (plus COSY plus HMQC, 400 MHz, 298 K, $CD_2Cl_2$): $\delta$ 6.41, 6.21, 5.80, 5.44 (all s, each 1H, $C_5H_4$), 5.95 (m, 1H, $^{trans}J_{HH} = 14.7$, $^{cis}J_{HH} = 8.4$, $^3J_{HH} = 5.1$, $^3J_{HH} = 9.6$, =CH), 3.94 (d, 1H, $^{trans}J_{HH} = 14.7$, =$CH_2$), 3.61 (d, 1H, $^{cis}J_{HH} = 8.4$, =$CH_2$), 2.84 (dd, 1H, $^2J_{HH} = 14.4$, $^3J_{HH} = 5.1$, Si−$CH_2$), 2.06 (dd, 1H, $^2J_{HH} = 14.4$, $^3J_{HH} = 9.3$, Si−$CH_2$), 0.63, 0.39 (both s, each 3H, $Si(CH_3)_2$). $^{13}$C APT NMR (plus HMQC, 100 MHz, 298 K, $CD_2Cl_2$): $\delta$ 208.9 (−, *CO*), 149.8, 146.5, 139.6, 137.9, 136.5, 134.6 (all −, $B(C_6F_5)_4$), 130.7 (+, =CH), 111.2 (−, ipso-$C_5H_4$), 102.3, 100.0, 97.7, 88.5 (all +, $C_5H_4$), 56.9 (−, =$CH_2$), 30.0 (−, Si−$CH_2$), 1.4, −4.4 (both +, $SiMe_2$).). $^{19}$F NMR (376 MHz, 298 K, $CD_2Cl_2$): $\delta$ 134.7 (*o*, *m*-$C_6F_5$), 165.5 (*p*-$C_6F_5$), 170.0 (*o*, *m*-$C_6F_5$).

**X-ray Structure Determination of Derivatives 8a and 9.** Suitable single crystals of **8a** and **9** for the X-ray diffraction study were both grown from hexane solutions. A crystal was selected, covered with perfluorinated ether, and mounted on a Bruker-Nonius Kappa CCD single-crystal diffractometer equipped with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). Data collection was performed at 200(2) K. Multiscan[23] absorption correction procedures were applied to the data. The structures were solved, using the WINGX package,[24] by direct methods (SHELXS-97) and refined by using full-matrix least-squares against $F^2$ (SHELXL-97).[25] In the structure of **8a** some carbon atoms show positional disorder. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were geometrically placed and left riding on their parent atoms. The hydride atom was located using the Hydex routine within the WINGX package, and its position was not refined. Full-matrix least-squares refinements with 253 parameters were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features.

For compound **9**, all non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms. The complex crystallizes with two independent but chemically equivalent molecules in the unit cell, for which two independent halves of the molecules are present in the asymmetric unit (the other half in each case being generated by the crystallographic inversion center). Full matrix least-squares refinements with 325 parameters were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final electron density maps showed peaks > 1.000 near the Mo center (e Å$^{-3}$).

Crystal data: $C_{17}H_{24}O_3SiW$, $M_w$ 488.30, colorless/prism (0.38 × 0.28 × 0.25 mm$^3$), monoclinic, space group $P2_1/n$, $a = 7.1721(9)$ Å, $b = 17.954(4)$ Å, $c = 15.3349(19)$ Å, $\alpha = 90°$, $b = 96.236(13)°$, $\gamma = 90°$, $V = 1963.0(6)$ Å$^3$, $Z = 4$, $D_{calc} = 1.652$ g cm$^{-3}$, $F(000) = 952$, $T = 200$ K; $\mu = 5.954$ mm$^{-1}$; 42 907 measured reflections ($\theta$ range: 3.65−27.50°), 4470 unique ($R_{int} = 0.0609$). R1/wR ($2I > 2\sigma(I)$) = 0.0465/0.1029 (3450 observed reflections, $I > 2\sigma(I)$) and R1/wR2 (all data) = 0.0682/0.1124; data/restrains/parameters = 4470/0/253; GoF = 1.080. Largest peak and hole = 1.679 and −1.835 e Å$^3$. $C_{17}H_{24}O_3SiW$, $M_w$ 686.56, red/prism (0.31 × 0.30 × 0.18 mm$^3$), triclinic, space group $P\bar{1}$, $a = 7.5130(15)$ Å, $b = 12.397(3)$ Å, $c = 16.679(3)$ Å, $\alpha = 73.33(3)°$, $b = 88.68(3)°$, $\gamma = 87.76(3)°$, $V = 2517.4(4)$ Å$^3$, $Z = 2$, $D_{calc} = 1.536$ g cm$^{-3}$, $F(000) = 694$, $T = 200$ K; $\mu = 0.959$ mm$^{-1}$; 29 773 measured reflections ($\theta$ range: 3.60−25°), 5173 unique ($R_{int} = 0.0510$); R1/wR2 ($I > 2\sigma(I)$) = 0.0528/0.1304 (3834 observed reflections, $I > 2\sigma(I)$) and R1/wR2 (all data) = 0.0735/0.1391; data/restrains/parameters 5173/0/325; GOF(on $F^2$) = 0.995. Largest peak and hole = +2.738 and −0.881 e Å$^3$ ($R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$).

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**Supporting Information Available:** Tables of crystallographic data and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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