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Intermolecular insertion of the carbene ligand of pentacarbonyl tungsten benzylidenes into the M–H bond of transition metal hydrido complexes

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Abstract

The strongly electrophilic carbene complexes [$(CO)_5W{=}C(H)C_6H_4R$-*p*] (**2**) [R = H (**a**), Me (**b**), OMe (**c**)] react with the terminal transition metal hydrides [$(CO)_5MnH$] (**3**) and [$Cp(CO)_3WH$] (**5**) by a formal transfer and insertion of the carbene ligand into the M–H bond (M = Mn, W) to give the benzyl complexes [$(CO)_5MnCH_2C_6H_4R$-*p*] (**4a**–**c**) and [$Cp(CO)_3WCH_2C_6H_4R$-*p*] (**6a**–**c**). Similarly, **6a** is formed when solutions of [$(CO)_5Cr{=}C(H)Ph$] (**7a**) or [$Cp(CO)_2Mn{=}C(H)Ph$] (**8a**) are treated with **5**. The analogous reaction of **2c** with [$Cp^*(CO)_3WH$] (**9**) ($Cp^* = C_5Me_5$) affords [$Cp^*(CO)_3WCH_2C_6H_4OMe$-*p*] (**10**). In contrast, the reactions of **2b** with [Cp_2WH_2] (**11**) and PNP[$(CO)_4FeH$] (**13**) afford binuclear complexes, [$Cp_2W(H)(CH_2C_6H_4Me$-*p*$)W(CO)_5$] (**12**) and PNP[$(CO)_4Fe(CH_2C_6H_4Me$-*p*$)W(CO)_5$] (**14**). Spectroscopic data confirm the existence of a Fe–W bond in the structure of **14** while in complex **12** the $W(CO)_5$ fragment is coordinated to the W–H bond of the second metal center in a three center two electron mode. In contrast to **3**, **5**, **9**, **11**, and **13**, the μ-hydrido complexes [$H_3Mn_3(CO)_{12}$], [$HW_2(CO)_9(NO)$], and $NEt_4[HW_2(CO)_{10}]$ show no comparable reaction with the benzylidene complexes **2**. Kinetic measurements of the reaction of **2c** with **5** reveal second-order kinetics, first-order in the concentrations of the benzylidene complex **2c** and the metal hydride **5**. The activation enthalpy $\Delta H^{\neq}$ is small ($\Delta H^{\neq} = 19 \pm 3$ kJ mol^{-1}), the activation entropy $\Delta S^{\neq}$ strongly negative ($\Delta S^{\neq} = -120 \pm 10$ J mol^{-1} K^{-1}). The kinetic isotope effect for the reaction of **2c** with [$Cp(CO)_3WX$] (X = H, D) is $k^H/k^D = 2.6 \pm 0.4$. The reaction rate increases (a) with increasing electrophilicity of the carbene carbon atom and (b) with decreasing steric demand of the ligands at the metal hydride. The reaction mechanism is discussed on the basis of an associative rate-determining step with an early transition state. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbene complexes; Hydrido complexes; Insertion reactions; Activation parameters; Labeling experiments

1. Introduction

Carbene ligands of transition metal carbene complexes are versatile building blocks in organic synthesis [1]. The transfer of carbene ligands to alkynes, olefins, or imines affords, e.g., carbo- and heterocycles. In addition, transition metal bound carbenes are assumed to be important intermediates in several catalytic processes, e. g. in the Fischer Tropsch Synthesis (FTS) and related reactions.

Thus, the interaction of carbene complexes as model systems with FTS substrates such as hydrogen or carbon monoxide is of fundamental interest. Therefore, reactions of carbene complexes with CO have been investigated in detail [2]. Recently we have shown that CO insertion into the metal carbene bond follows either an intramolecular [3] or an intermolecular pathway [4] depending on the electrophilicity of the carbene complexes. In contrast, there are only few reports on the reactions of carbene complexes with hydrogen [5]. Brady and Pettit observed a dissociative chemisorption of H_2 under heterogeneous FTS reaction conditions [6].

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The reaction was proposed to proceed via formation of metal hydrides. Subsequently, the interest also focused on the interaction of hydrido and carbene ligands in homogeneous systems. The intramolecular coupling of a carbene and a hydrido ligand in carbene hydrido complexes is now well established [7,8]. In contrast, information on intermolecular coupling reactions are rather scarce [9,10].

Nevertheless, based on the results of our investigations on the reaction of benzylidene(pentacarbonyl) complexes with CO [4] we found these carbene complexes also useful precursors to get an insight into the intermolecular mechanisms of carbene–hydrido ligand interaction.

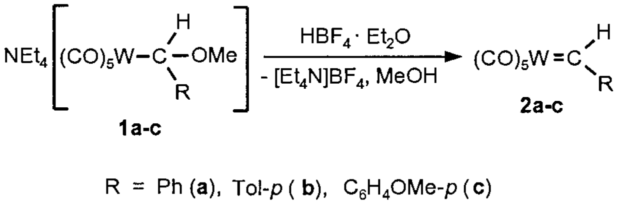
2. Results

2.1. Reactions of benzylidene complexes with transition metal hydrido complexes

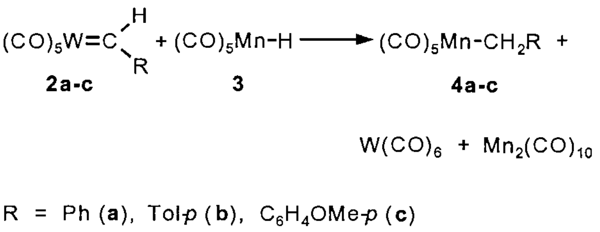
The starting carbene complexes (benzylidene complexes) were generated as shown in Scheme 1. Treatment of solutions of the α-methoxybenzyl tungstates **1a**–**c** [11] (obtained by addition of the hydride of $[HB(O^iPr)_3]^-$ to the carbene carbon of the corresponding methoxycarbene complexes $[(CO)_5W{=}C(OMe)C_6H_4R\text{-}p]$) with $HBF_4 \cdot Et_2O$ at −78°C gave rise to the elimination of methanol and formation of the benzylidene complexes **2a**–**c** [12]. Rapid chromatography of these solutions on silica gel at −70°C afforded solutions of **2a**–**c**. Due to the low thermal stability of these complexes, **2a**–**c** were not isolated in a pure form. Instead, the solutions were immediately used for the subsequent reactions with metal hydrides.

When a solution of $[(CO)_5MnH]$ (**3**) was added to **2a**–**c** in pentane/dichloromethane rapid reactions were observed. Judged by the color change of the solutions from deep red to yellow the reactions were complete within seconds even at −78°C. Workup of the reaction mixtures by column chromatography yielded $[W(CO)_6]$ and $[(CO)_5MnCH_2C_6H_4R\text{-}p]$ (**4a**–**c**) in addition to small amounts of $[Mn_2(CO)_{10}]$ (Scheme 2).

The reactions of **2a**–**c** with $[Cp(CO)_3WH]$ (**5**) proceeded similarly fast giving $[Cp(CO)_3WCH_2C_6H_4R\text{-}p]$ (**6a**–**c**) and $[W(CO)_6]$ (Scheme 3).



Scheme 1.



Scheme 2.

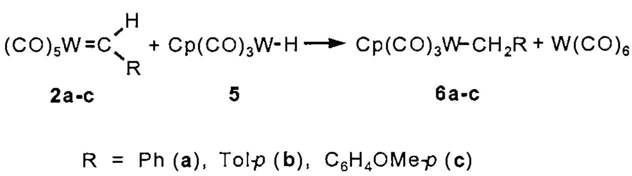
Substitution of the metal ligand fragments $(CO)_5Cr$ or $Cp(CO)_2Mn$ for $(CO)_5W$ in **2a** had no influence on the type of products in the reaction with **5**. Thus, treatment of $[(CO)_5Cr{=}C(H)Ph]$ (**7a**) with **5** afforded **6a** (42%) and $[Cr(CO)_6]$ while the analogous reaction of $[Cp(CO)_2Mn{=}C(H)Ph]$ (**8a**) gave **6a** (4%) and $[CpMn(CO)_3]$. In contrast to **2a**, the less electrophilic carbene complexes $[(CO)_5W{=}C(Ph)C_6H_4OMe\text{-}p]$ and $[(CO)_5W{=}C(OMe)C_6H_4Me\text{-}p]$ either decomposed or remained unchanged when their solutions were stirred with equimolar amounts of **5** at ambient temperature.

The isolated yields of analytically pure compounds **4a**–**c** and **6a**–**c** varied considerably (11–54%, based on the α-methoxybenzyl tungstates **1a**–**c**) depending on workup conditions and the stationary phase used in chromatography. The yields of the benzylidene complexes **2a**–**c** in the synthesis from **1a**–**c** and $HBF_4 \cdot Et_2O$ (Scheme 1) usually are in the range 50–80%. Therefore, the carbene transfer/M–H insertion in the reaction with the hydrido complexes **3** and **5** can be assumed to proceed in most cases almost quantitatively. This assumption is supported by the absence of ν(CO) absorptions in the IR spectra of the reaction mixtures in addition to those derived from the reaction products mentioned above.

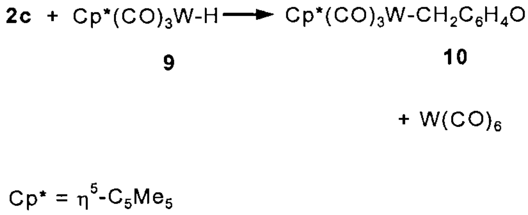
Substitution of the sterically more demanding pentamethylcyclopentadienide for the cyclopentadienide ligand in **5** did not alter the product distribution. The major product in the reaction of **2c** with $[Cp^*(CO)_3WH]$ (**9**) was **10** (Scheme 4). After chromatography, complex **10** was isolated in 53% yield.

All complexes **4a**–**c**, **6a**–**c**, and **10** were identified and characterized by their IR, NMR and mass spectra; their purity was established by elemental analysis.

Complex **2a** also rapidly reacted with $[(CO)_4CoH]$. The IR spectrum of the product mixture indicated the formation of several CO-containing complexes. How-



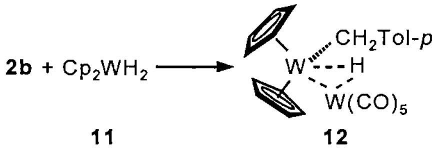
Scheme 3.


$$\mathbf{2c} + \underset{\mathbf{9}}{Cp^*(CO)_3W\text{-}H} \longrightarrow \underset{\mathbf{10}}{Cp^*(CO)_3W\text{-}CH_2C_6H_4OMe\text{-}p} + W(CO)_6$$
$Cp^* = \eta^5\text{-}C_5Me_5$

Scheme 4.

ever, it was not possible to separate the reaction products and characterize them. In contrast, **2b** did not react with $[Cp_2Zr(H)Cl]_n$. When the reaction was monitored by IR spectroscopy complete decomposition of **2b** within 2.3 h and formation of the characteristic thermolysis products of **2b**, namely $[W(CO)_6]$ and $[\{(CO)_5W\}_2\{\mu\text{-}C(H)C_6H_4Me\text{-}p\}]$, was observed. The failure of a reaction between **2b** and the zirconium complex is presumably due to the poor solubility of the zirconium complex in pentane/dichloromethane even at room temperature. As a consequence, the rate of the insertion reaction is rather slow and the competing decomposition dominates.

The reaction of the benzylidene complexes with the dihydrido complex $[Cp_2WH_2]$ (**11**) took a different course than the reactions with the monohydrido species **3**, **5**, or **9**. When **11** was added to a solution of **2b** in pentane/dichloromethane the color of the solution immediately turned yellow and a green-black precipitate (**12**) formed (Scheme 5). The ^{1}H- and ^{13}C-NMR spectra of the precipitate indicated a 1:1 adduct of **2b** and **11**. Purification of the new compound **12** by chromatography or by recrystallization failed since **12** quickly decomposed in solution even at −78°C.

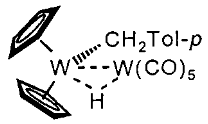


Scheme 5.

When **2b** was employed in a 2-fold excess there was no indication of the transfer of two benzylidene units to one molecule of **11** to form either the known complex $[Cp_2W(CH_2C_6H_4Me\text{-}p)_2]$ [13] or its $W(CO)_5$ adduct. Only complex **12** was isolated independent of whether pentane or polar solvents were used.

Although it was not possible to isolate complex **12** in a pure form, the IR and NMR spectroscopic data allowed one to establish the constitution of **12**. The IR spectrum in the range between 2100 and 1900 cm^{-1} exhibited absorptions at 2067, 1969, and 1926 cm^{-1}. These absorptions are characteristic for a neutral pentacarbonyl metal fragment and are similar to those of $[Cp_2MoH_2 \cdot Mo(CO)_5]$ obtained by reaction of $[Cp_2MoH_2]$ with $[(CO)_5Mo(THF)]$ [14]. The weak absorption at 1970 cm^{-1} can either be assigned to the B_1 mode of the $W(CO)_5$ fragment or to the W–H stretching mode. Although the B_1 mode is formally IR-forbidden for a C_{4v} symmetric $(CO)_5M$ fragment, the band is often observed with low intensity in mononuclear $M(CO)_5$ complexes due to a lowering of the symmetry. The alternative assignment to the W–H stretching vibration is supported by the observation of a W–H stretching mode in the adduct $[Cp_2WH_2 \cdot BCl_3]$ at 1967 cm^{-1} [15].

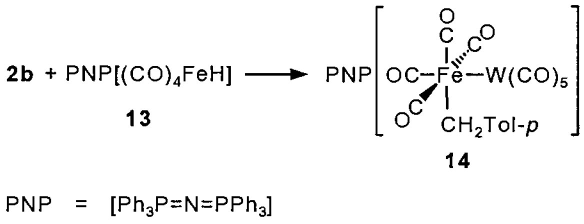
The ^{1}H-NMR spectrum of **12** in [D$_8$]toluene showed resonances at $\delta = -23.42$, 2.23, 2.36, 4.04, 6.50, and 6.91 in a 1:3:2:10:2:2 ratio as expected for a dicyclopentadienyl(hydrido)(*p*-methylbenzyl)tungsten complex. Two sets of satellites of the W–H resonance indicate a bistungsten complex. This conclusion is also confirmed by the strong low-field shift of the methylene protons ($\delta = 2.36$) when compared to the mononuclear derivative $[Cp_2W(H)CH_2C_6H_4Me\text{-}p]$ ($\delta = 0.52$ in [D$_6$]benzene [16]). In contrast, the hydrido signal of **12** ($\delta = -23.42$) is at a significantly higher field than that of $[Cp_2W(H)CH_2C_6H_4Me\text{-}p]$ ($\delta = -11.54$ in [D$_6$]benzene [16]) or of $[Cp_2W(H)_2]$ ($\delta = -12.28$ in [D$_6$]benzene [17]). Similar high-field shifts are characteristic for cationic μ-hydrido complexes [18] such as $[\{Cp(CO)_3W\}_2(\mu\text{-}H)]^+$ ($\delta = -24.77$ in conc. H_2SO_4 [19]). The $^1J(^1H-^{183}W)$ coupling constants ($J = 70.8$ and 36.0 Hz) are in the range usually observed for $^1J(^1H-^{183}W)$ in $[Cp_2W(R)H]$ complexes [18] (e.g., $^1J(^1H-^{183}W) = 73.2$ Hz in $[Cp_2W(H)_2]$ [15] and ca. 72 Hz in $[Cp_2WH_2 \cdot AlEt_3]$ [20]) and in neutral $[(CO)_5W(\mu\text{-}H)ML_n]$ complexes (e.g., $^1J(^1H-^{183}W) = 39.5$ Hz [$L_nM = W(CO)_3(NO)\{P(OMe)_3\}$] [21], 42.5 Hz [$L_nM = Ta(CO)Cp_2$] [22], and 46 Hz [$L_nM = AuPPh_3$] [23]). These NMR spectroscopic data indicate a three-center two-electron H bridge like that in $[Cp_2(CO)Nb(\mu\text{-}H)W(CO)_5]$ [24]. Based on these data and on theoretical considerations, the most likely structure of **12** is that shown in Scheme 5. However, the alternative structure **12A** cannot be completely ruled out.



12A

When a solution of **2b** was treated with the trihydrido complex $[Cp_2NbH_3]$ an as yet unidentified brown precipitate formed insolubly in common organic solvents. There was no indication of an insertion of the benzylidene ligand into the M–H bond of the hydrido complex.

The reaction of the anionic hydrido complex PNP$[(CO)_4FeH]$ (**13**) [PNP = bis(triphenylphospho-

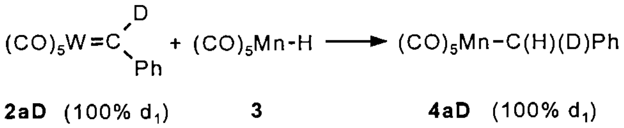


Scheme 6.

ranylidene)ammonium] with the *p*-methylbenzylidene complex **2b** proceeded similarly to the reactions of **2a**–**c**, **7a**, and **8a** with **3**, **5**, and **9**. Addition of a solution of **13** in CH_2Cl_2 to **2b** in CH_2Cl_2 at $-65°C$ instantaneously gave a brown-green reaction mixture. Removal of the solvent and chromatographic workup did not afford a mononuclear alkyl complex similar to **4a**–**c**, **6a**–**c**, and **10** but rather its $W(CO)_5$ adduct $PNP[(CO)_4(CH_2C_6H_4Me\text{-}p)Fe \cdot W(CO)_5]$ (**14**) in 6% yield (Scheme 6). Presumably, complex **14** is formed by insertion of the *p*-methylbenzylidene ligand of **2b** into the Fe–H bond of **13** to give $[(CO)_4Fe(CH_2C_6H_4Me\text{-}p)]^-$ and subsequent addition of the $W(CO)_5$ fragment to the tetracarbonyl(*p*-methylbenzyl)ferrate. An alternative pathway involves initial nucleophilic addition of the anion in **13** to the carbene carbon atom of **2b** to form an ylide complex $[(CO)_5W\{\mu\text{-}C(C_6H_4Me\text{-}p)H\}Fe(H)(CO)_4]^-$ and subsequent fast rearrangement to **14**. On the basis of steric considerations the former pathway seems more likely. In addition, there is no indication for an ylide complex intermediate. Nevertheless, the latter pathway cannot completely be excluded since in other cases **13** has been reported to act as an iron nucleophile [25].

The structure of **14** as a heterobimetallic complex with a Fe–W bond was deduced from the spectroscopic data. The IR and UV–vis spectra agree well with those of the related dinuclear complex $PNP[(CO)_4(H)Fe\text{–}W(CO)_5]$ [26]. The ^{13}C-NMR spectrum exhibits three FeCO resonances ($\delta = 211.1$, 214.4, and 222.2) indicative of a rigid $(CO)_4Fe$ fragment similar to that in $[cis\text{-}(CO)_4FeI_2]$ [27] and $NEt_4[Ph_3AuFe(CO)_4 \cdot W(CO)_5]$ [28]. In contrast, complex **13** [29], $PNP[cis\text{-}(CO)_3\{P(OPh)_3\}FeH]$ [30], and $PNP[(CO)_4(H)Fe\text{–}W(CO)_5]$ [26] show only one ^{13}C-NMR signal for the four iron-bound carbonyl ligands. This was explained by rapid CO exchange ([26]a) and by magnetic and electronic degeneration [30].

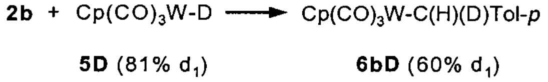
Unlike terminal hydrido complexes, μ-hydrido compounds did not react with the benzylidene complexes **2**. Solutions of **2b** remained unchanged when treated at low temperature with $[H_3Mn_3(CO)_{12}]$, $[HW_2(CO)_9(NO)]$, or $NEt_4[HW_2(CO)_{10}]$. Warming of the mixtures only resulted in decomposition of **2b** giving predominantly $[W(CO)_6]$ and $[\{(Co)_5W\}_2\{\mu\text{-}C(H)C_6H_4Me\text{-}p\}]$.



Scheme 7.

2.2. Mechanistic investigations

The most feasible mechanism for the insertion of the benzylidene ligand of **2a**–**c**, **7a**, and **8a** into the M–H bond of **3**, **5**, **9**, **11**, and **13** is a concerted reaction. Labeling experiments support this assumption. Treatment of the monodeuterated benzylidene complex $[(CO)_5W{=}C(D)Ph]$ (**2aD**, 100% d_1) with **3** gave **4aD** (100% d_1) (Scheme 7). When the analogous reaction of the deuterated benzylidene complex $[(CO)_5W{=}C(D)C_6H_4OMe\text{-}p]$ (**2cD**, 100% d_1) with **3** was quenched with a 100-fold excess of PMe_3 after one half-life only the monodeuterated complex **6cD** and the adduct $[(CO)_5W\text{–}C(D)(PMe_3)C_6H_4OMe\text{-}p]$ were detected. The formation of $[(CO)_5W\text{–}C(H)(PMe_3)C_6H_4OMe\text{-}p]$ by a H/D exchange was not observed. Similarly, the reaction of the deuterido complex $[Cp(CO)_3WD]$ (**5D**, 81% d_1) with **2b** selectively afforded **6bD** (60% d_1) (Scheme 8). Most likely, the small reduction of the degree of deuteration is caused by traces of HBF_4. Small amounts of HBF_4 are usually present in the solutions of the benzylidene complexes when they are obtained by in situ generation (see Scheme 1). HBF_4 presumably reacts with **5D** by H/D exchange to form $[Cp(CO)_3WH]$ which then with **2b** affords undeuterated **6b**.



Scheme 8.

The reaction sequence involving (a) dissociation of H^+ from the terminal metal hydrides $L_nM\text{–}H$, (b) nucleophilic addition of the resulting metallate to the carbene carbon atom in **2a**–**c**, **7a**, and **8a** to form a binuclear carbene-bridged complex and (c) protolytic cleavage of the W–C bond to give the final product can be excluded. Sequential reaction of **2b** with the metallate $NEt_4[(CO)_5Mn]$ and $HBF_4 \cdot Et_2O$ did not afford **4b**.

An alternative mechanism involving (a) heterolytic cleavage of the metal hydride bond to give L_nM^+ and H^-, (b) addition of H^- to the carbene carbon atom to form a benzyl metallate and (c) transfer of the benzyl ligand to L_nM^+ can likewise be excluded. When $NEt_4[(CO)_5W\text{–}CH_2Ph]$ was treated with $[(CO)_5Mn]BF_4$, compound **4a** was not detected among the reaction products.

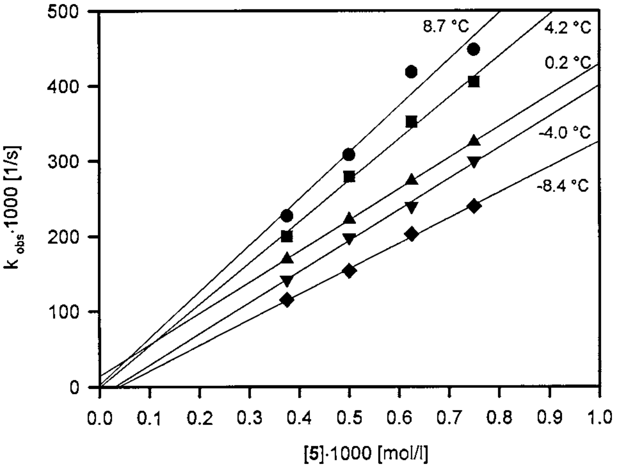


Fig. 1. Plot of k_{obs} versus concentration of complex **5** for the reaction of **2c** with **5** in pentane.

Radical intermediates in the reaction of terminal metal hydrides with benzylidene complexes are also unlikely. Addition of two equivalents of galvinoxyl as a radical scavenger to a solution of **2c** prior to the reaction with **3** did not prevent the formation of **4c** (see Scheme 3).

2.3. Kinetic investigations

Kinetic investigations were performed of the reaction of **2c** with **3** in pentane using stopped-flow techniques and pseudo first-order conditions ($[\mathbf{3}]_0/[\mathbf{2c}]_0 \geq 10$). The progress of the reaction was followed by monitoring the decrease of MLCT absorption of the carbene complex at $\lambda_{max} = 496$ nm as a function of time. Fig. 1 shows plots of k_{obs} (Table 1) versus [**5**] at different temperatures between − 8.4 and 8.7°C.

The reaction of **2c** with **5** follows a second-order rate law first-order in the concentrations of the benzylidene complex **2c** and the hydrido complex **5**. Second-order rate constants k_2 calculated from these plots are (standard deviation in brackets): $k_2 = 340(20)$ l mol^{-1} s^{-1} (at − 8.4°C) 410(20) l mol^{-1} s^{-1} (at − 4.0°C) 420(20) l mol^{-1} s^{-1} (at − 0.2°C) 550(30) l mol^{-1} s^{-1} (at 4.2°C) and 620(90) l mol^{-1} s^{-1} (at 8.7°C). The plot of ln(k_2/T) versus $1/T$ (Fig. 2) yields the activation parameters. The activation enthalpy $\Delta H^{\neq}$ is small (19 ± 3 kJ mol^{-1}), the activation entropy $\Delta S^{\neq}$ strongly negative (− 120 ± 10 J mol^{-1} K^{-1}). The influence of the solvent on the reaction rate is small. When pentane was replaced by polar dichloromethane as the solvent, the reaction accelerated only by about 10% ($k_2 =$ 360(10) l mol^{-1} s^{-1} at − 8.4°C).

Table 1
Rate constants ($10^3 \cdot k_{obs}$) for the reaction of **2c** with **5** in pentane ($[\mathbf{2c}]_0 = 0.0375$ mM)

Temperature (°C)	$[\mathbf{5}]_0$ (mM)			
	0.375	0.500	0.635	0.750
8.7	0.227(10)	0.308(5)	0.418(10)	0.448(5)
4.2	0.200(3)	0.279(8)	0.352(12)	0.405(4)
0.2	0.169(14)	0.222(5)	0.273(7)	0.325(9)
−4.0	0.142(5)	0.198(5)	0.240(1)	0.300(4)
−8.4	0.115(6)	0.154(3)	0.203(9)	0.240(5)

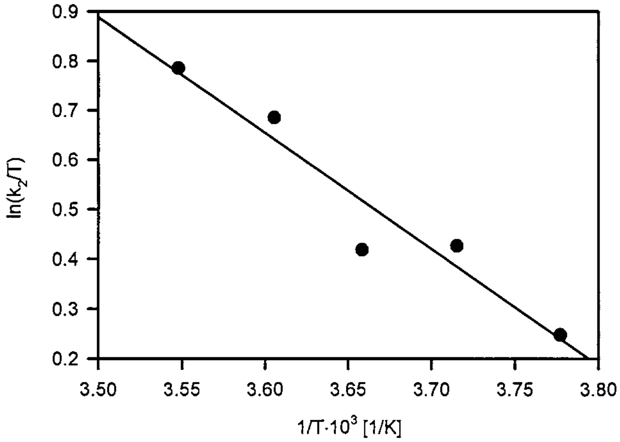


Fig. 2. Plot of ln(k_2/T) versus $1/T$ for the reaction of **2c** with **5** in pentane.

When [Cp(CO)$_3$WH] (**5**) was replaced by the deuteride [Cp(CO)$_3$WD] (**5D**, 75% d$_1$) in the reaction with **2c** in pentane at − 8.4°C a positive kinetic isotope effect of $k_2^H/k_2^D = 2.7 \pm 0.4$ was observed ($k_2^D = 180 \pm 10$ l mol^{-1} s^{-1}).

The influence of the electrophilicity of the carbene carbon atom and of the steric requirements of the spectator ligands in the metal hydride were also determined. Reduction of the electrophilicity of the carbene carbon atom by substitution of OMe for the *p*-methyl substituent in **2b** led to a decrease of the reaction rate in pentane at − 9.5°C by 76%. When the cyclopentadienide ligand in **5** was replaced by the sterically more demanding pentamethylcyclopentadienide in **9** in the reaction with **2c** the reaction rate decreased by 68% ($k_2 = 440(20)$ l mol^{-1} s^{-1} (for **5**), 140(10) l mol^{-1} s^{-1} (for **9**), both in pentane at 3.2°C).

3. Discussion

The strongly electrophilic benzylidene complexes **2a**–**c**, (CO)$_5$Cr=C(H)Ph and Cp(CO)$_2$Mn=C(H)Ph react with a series of terminal hydrido complexes by insertion of the carbene ligand into the metal hydrido bond. In contrast, the reactions of the cationic iron carbene complexes [Cp(CO)$_2$Fe=C(OMe)R]PF$_6$ (R = H, Me, Ph) with [Cp(PPh$_3$)(CO)FeH] afford iron α-alkoxyalkyl complexes [Cp(CO)$_2$Fe=C(OMe)(H)R] by transfer of H$^-$ from the hydride complex to the carbene ligand whereas the phosphine-substituted carbene complexes $[Cp(PPh_3)(CO)Fe{=}C(OMe)R]PF_6$ (R = H, Me) remain unaltered when treated with $[Cp(PPh_3)(CO)FeH]$ [31]. Substitution of [Cp(dppe)FeH] for $[Cp(PPh_3)(CO)Fe–H]$ as the reducing agent leads to dealkylation and formation of $[Cp(PPh_3)(CO)Fe{=}C(O)R]$ [31]. When $[Cp(PEt_3)(CO)Fe{=}C(H)Me]BF_4$ is treated with $[Cp(PR_3)(CO)Fe–H]$ (R = Et, Ph) at − 78°C an instantaneous reaction is observed. However, it was not possible to identify the products [32].

There are many examples for the insertion of unsaturated molecules or fragments into the M–H bond of metal hydrides ([1]b, [33]). Intermolecular insertions of carbene ligands into activated X–H bonds (X = C [34], Si [32,35,36], Ge [36,37], Sn [36,37], P [38], O [39], Se [40], Cl [39], Br [41]) are also well established. However, mechanistic investigations on the latter reactions are very scarce.

Several reaction pathways are conceivable for the insertion of the benzylidene ligand into the M–H bond. On the basis of the mechanistic investigations and of the kinetic results (second-order rate law, strongly negative activation entropy) mechanisms involving a rate-determining CO, H^+, or H^- dissociation or a rate-limiting intramolecular rearrangement can be discarded.

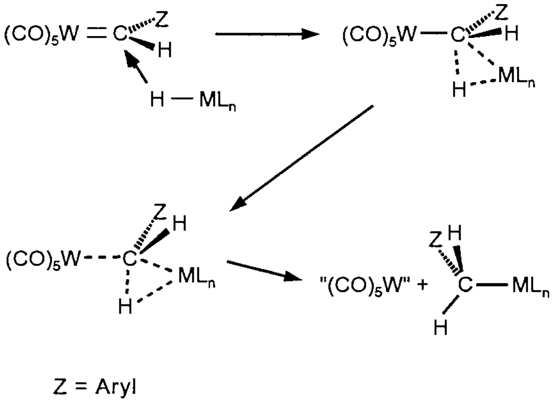
A radical mechanism has to be taken into account as hydrogen atom transfer to unsaturated substrates such as substituted styrenes, anthracenes, allenes, and dienes is an important reactivity pattern exhibited by many transition metal hydrides. The stoichiometric hydrogenation of olefins by metal hydrides has been studied in detail [42]. These reactions follow a second-order rate law and proceed by a stepwise process. The first hydrogen transfer is rate-determining. An inverse isotope effect was found for those hydrogenation reactions that proceed by sequential hydrogen atom transfers from metal hydrides to unsaturated substrates. In addition, H/D exchange between metal deuteride and alkene in the recovered educts and CIDNP effects in the ^{1}H-NMR spectra of the reaction of $[HMn(CO)_5]$ with α-methylstyrene were observed [43].

Similar to these hydrogenations, the reaction of **2c** with **3** follows second-order kinetics. However, several observations do not agree with a radical mechanism. In contrast to these radicalic hydrogenation reactions neither D/H exchange in recovered **2cD** nor 'cage escape' products such as $[Cp(CO)_3W]_2$ and $ArCH_2CH_2Ar$ (derived from the rather long-lived radicals $Cp(CO)_3W^{\bullet}$ and $PhCH_2^{\bullet}$) are observed. Furthermore, the radical scavenger galvinoxyl does not influence the reaction. Instead of an inverse isotope effect a normal isotope effect ($k_2^H/k_2^D = 2.6 \pm 0.4$) is observed in the reaction of **2c** with **3**. Whereas the activation entropies for the hydrogenation of olefins are usually small (e.g. $\Delta S^{\neq} = -12 \pm 1$ cal mol^{-1} K^{-1} for the reaction of $[HMn(CO)_5]$ with $H_2C{=}C(Me)Ph$ [43]) $\Delta S^{\neq}$ for the reaction of **2c** with **3** is strongly negative (-120 ± 10 J mol^{-1} K^{-1}). These observations render a radical mechanism rather unlikely.

IR-spectroscopic studies of metal carbonyl hydrides suggest that the M–H bond is polarized with the negative charge on the hydrogen [44]. The approximate charges on hydrogen are − 0.8 for $[HMn(CO)_5]$ and − 0.75 for $[HCo(CO)_4]$ [45] as derived from the results of X-ray photoelectron spectroscopic studies. Therefore, the most probable pathway involves initial nucleophilic attack of the metal hydride L_nMH on the carbene carbon atom. Interaction of the M–H σ bond with the LUMO of the carbene complex which is predominantly localized on the carbene carbon atom could lead to an elongation of the W–C(carbene) bond and a tilting of the carbene substituent away from the approaching metal hydride. The nucleophilic attack is followed by electrophilic interaction of L_nM with the carbene carbon atom, presumably from the direction opposite to the $(CO)_5W$ fragment. W–C(carbene) bond dissociation then completes the reaction (Scheme 9).

The proposal of a rate-limiting nucleophilic attack of the metal hydride on the carbene carbon is supported by the second-order rate law and by the decrease of the reaction rate when the electrophilicity of the carbene carbon atom (**2b** → **2c**) is reduced.

The strongly negative activation entropy indicates a highly ordered transition state. Steric interactions between the co-ligands do not play a significant role as the reaction rate increases only by a factor of about three when the bulky pentamethylcyclopentadienide ligand in **9** is replaced by the sterically less demanding cyclopentadienide group (in complex **5**). The deuterium isotope effect (2.6 ± 0.4) is indicative of significant M–H(D) bond breaking and still less developed C–H(D) bond formation in the transition state for insertion (early transition state).



Scheme 9.

The insertion of a carbene ligand into the M–H bond of metal hydrides is related to the reactions of complexes **2** with olefins to form cyclopropanes [46,47]. The reaction characteristics for the reaction of **2c** with vinyl acetate are similar to those of the reaction with **5**: small activation enthalpy, strongly negative activation entropy, small solvent effect, similar influence of the substituent at the carbene carbon atom (**2b** react 4.1 times faster with [(CO)$_5$MnH] and 3.8 times faster with vinyl acetate than **2c**). Based on the results of a kinetic study [47] and on HMO calculations performed with the model system $(CO)_5Cr{=}CH_2 + H_2C{=}CH_2$ [48], an associative mechanism with an early transition state was proposed. The calculations indicated that the least-energy pathway involves initial nucleophilic attack of one carbon of the olefin on the carbene carbon followed by an electrophilic attack of the second olefinic carbon on the carbene carbon from the direction opposite to the metal ('backside ring closure'). A similar mechanism was also proposed for the cyclopropanation of olefins by cationic iron carbene complexes $[Cp(CO)LFe{=}C(R)H]^+$ (L = CO, PPh$_3$; R = Me, aryl) [49] and the backside ring closure was verified by labeling studies [50].

4. Experimental section

4.1. General

All manipulations were performed under argon using standard Schlenk techniques. Solvents were dried by refluxing over sodium/benzophenone ketyl or CaH$_2$ and freshly distilled under argon prior to use. To remove water and oxygen, silica gel for flash chromatography (J.T. Baker) and Al$_2$O$_3$ (basic, Merck) was kept in vacuo at room temperature for 4 h and then stored under argon. The complexes **2a**–**c** [12], **3** [51], **5** [51], **7a** [12], **8a** [52], **9** [53], **11** [51], **13** [54], [(CO)$_5$W=C(Ph)C$_6$H$_4$OMe-*p*] [55], [(CO)$_5$W=C(OMe)-C$_6$H$_4$Me-*p*] [56], [(CO)$_4$COH] [57], [(Cp$_2$ZrHCl)$_n$] [58], [Cp$_2$NbH$_3$] [51], [H$_3$Mn$_3$(CO)$_{12}$] [51], [HW$_2$(CO)$_9$(NO)] [59], NEt$_4$[HW$_2$(Co)$_{10}$] [60], NEt$_4$[Mn(CO)$_5$] [61], [(CO)$_5$Mn]BF$_4$ [62], and NEt$_4$[(CO)$_5$WCH$_2$Ph] ([46]a) were synthesized according to literature procedures. The monodeuterated complexes [(CO)$_5$W=C(D)Ph], [(CO)$_5$W=C(D)C$_6$H$_4$OMe-*p*], and [Cp(CO)$_3$WD] were prepared analogously to [(CO)$_5$W=C(H)Ph] [12] and [Cp(CO)$_3$WH] [51], respectively. NMR spectra were recorded with Bruker WM250 or Bruker AC250 spectrometers at room temperature in CDCl$_3$ unless otherwise stated. Chemical shifts are reported relative to TMS. Other instrumentation: IR, Perkin-Elmer 983G or Bio-Rad FTS 60 spectrophotometer; UV–vis, Perkin Elmer Lambda 15; MS, Finnigan MAT 312 (EI, 70 eV); elemental analyses, Heraeus CHN-O-RAPID.

4.2. Generation of carbene complexes **2a**–**c**

The carbene complexes **2a**–**c** were freshly prepared prior to the reactions with the metal hydrides. A typical example is as follows: 3.50 mmol of NEt$_4$[(CO)$_5$WC(H)(OMe)C$_6$H$_4$R-p] (2.01 g (**1a**), 2.06 g (**1b**), 2.12 g (**1c**)) was dissolved in 25 ml of CH$_2$Cl$_2$ and 7.25 mmol of HBF$_4$ (1.00 ml of a 54% solution in Et$_2$O) was rapidly added at −90°C while vigorously stirring the solution. The yellow solution immediately turned deep red. After 1 min, 25 ml of pentane (precooled to −78°C) was added and the solution was chromatographed at −78°C on silica gel. With pentane/CH$_2$Cl$_2$ (3/1 (**2a**), 2/1 (**2b**), 1/1 (**2c**)), the dark red fraction containing **2a**–**c** was eluted and immediately used for the subsequent reactions with metal hydrides.

4.3. Reaction of **2a** with [(CO)$_5$MnH] (**3**)

At −78°C, 0.75 mmol (0.15 g) of **3** was added to a solution of **2a** in pentane/CH$_2$Cl$_2$ (3/1), freshly prepared from 0.35 mmol (0.20 g) of **1a** and 0.72 mmol of HBF$_4$ (0.10 ml of a 54% solution in Et$_2$O). Within seconds the deep red solution turned yellow. The solvent was removed in vacuo. The residue was dissolved in 5 ml of CH$_2$Cl$_2$ and chromatographed at 0°C on silica gel. First, a band containing [(CO)$_6$W] and [(CO)$_{10}$Mn$_2$] was eluted with pentane. Then, **4a** was eluted with pentane/THF (10/1). The solvent was removed in vacuo and the residue recrystallized at −34°C from 2 ml of pentane.

4a: Colorless crystals (24 mg, 24% based on **1a**). All spectroscopic and analytical data agree with reported values [63].

4.4. Reaction of **2b** with [(CO)$_5$MnH] (**3**)

The reaction of 3.00 mmol (0.59 g) of **3** with **2b**, prepared from 1.34 mmol (0.79 g) of **1b** and 2.77 mmol of HBF$_4$ (0.38 ml of a 54% solution in Et$_2$O), and the chromatographic workup were carried out analogously to Section 4.3.

4b: Colorless crystals (80 mg, 20% based on **1b**), m.p. 47°C. IR (pentane/THF 10/1): ν(CO) 2108 w, 2016 vs, 2010 vs, 1990 s cm^{-1}. ^{1}H-NMR: δ 2.26 (s, 3H, CH$_3$), 2.39 (s, 2H, CH$_2$), 6.96–7.00 (m, 2H, C$_6$H$_4$), 7.04–7.08 (m, 2H, C$_6$H$_4$). EI-MS: *m/z* (%) 300 (7) [M$^+$], 160 (84) [M$^+$–5CO], 105 (100) [CH$_2$C$_6$H$_4$CH$_3$-*p*]. Anal. Found: C, 52.15; H, 3.09; C$_{13}$H$_9$MnO$_5$ (300.2) calc.: C, 52.02; H, 3.02.

4.5. Reaction of **2c** with [(CO)$_5$MnH] (**3**)

The reaction of 4.50 mmol (0.88 g) of **3** with **2c**, prepared from 1.80 mmol (1.10 g) of **1c** and 3.77 mmol of HBF$_4$ (0.52 ml of a 54% solution in Et$_2$O), and the chromatographic workup were carried out analogously to Section 4.3.

4c: Colorless crystals (120 mg, 21% based on **1c**). All spectroscopic and analytical data agree with reported values [64].

*4.6. Reaction of **2a** with [Cp(CO)$_3$WH] (**5**)*

At −40°C, a solution of 1.95 mmol (0.65 g) of **5** in 10 ml of CH_2Cl_2 was added to a solution of **2a** in 100 ml of pentane/CH_2Cl_2 (3/1), obtained from 2.14 mmol (1.26 g) of **1a** and 4.43 mmol of HBF_4 (0.61 ml of a 54% solution in Et_2O). The dark red solution immediately turned yellow. Then, 10 g of basic Al_2O_3 was added and the solvent was removed in vacuo. The residue (reaction products adsorbed on Al_2O_3) was placed on top of a column filled with Al_2O_3 and chromatographed at −30°C. First, with pentane [(CO)$_6$W] and then, with pentane/CH_2Cl_2 (5/2), a yellow band containing **6a** was eluted. The solvent of the yellow fraction was removed in vacuo and the residue was recrystallized at −30°C from 2 ml of methanol.

6a: Yellow crystals (0.49 g, 54% based on **1a**), m.p. 86°C. All spectroscopic and analytical data agree with reported values [65].

*4.7. Reaction of **2b** with [Cp(CO)$_3$WH] (**5**)*

The reaction of **2b**, obtained from 2.12 mmol (1.25 g) of **1b** and 4.39 mmol of HBF_4 (0.60 ml of a 54% solution in Et_2O), with 2.12 mmol (0.71 g) of **5** and the chromatographic workup were carried out analogously to Section 4.6.

6b: Yellow crystals (0.17 g, 18% based on **1b**), m.p. 103°C. IR (pentane): ν(CO) 2016 s, 1933 s, 1927 vs cm^{-1}. ^{1}H-NMR: δ 2.26 (s, 3H, CH_3), 2.96 (s, 2H, CH_2), 5.27 (s, 5H, Cp), 6.95–6.99 (m, 2H, C_6H_4), 7.04–7.08 (m, 2H, C_6H_4). EI-MS: *m*/*z* (%) 438 (2) [M$^+$], 354 (42) [M$^+$−3CO], 105 (100) [$CH_2C_6H_4CH_3$-*p*$^+$]. Anal. Found: C, 43.68; H, 3.23; $C_{16}H_{14}O_3W$ (438.1) calc.: C, 43.86; H, 3.22.

*4.8. Reaction of **2c** with [Cp(CO)$_3$WH] (**5**)*

At −50°C, a solution of 4.49 mmol (1.50 g) of **5** in 10 ml of CH_2Cl_2 was added to a solution of **2c** in 100 ml of pentane/CH_2Cl_2 (1/1), obtained from 3.31 mmol (2.00 g) of **1c** and 6.85 mmol of HBF_4 (0.94 ml of a 54% solution in Et_2O). The solution immediately turned yellow and a yellow-brown precipitate formed. The solution was decanted. When the volume of the solution was reduced in vacuo to a few ml yellow crystals of **6c** formed. Recrystallization of the yellow-brown precipitate from 5 ml of methanol afforded additional crystals of **6c**.

6c: Yellow crystals (0.16 g, 11% based on **1c**), m.p. 107°C. IR (pentane): ν(CO) 2016 s, 1935 s, 1926 vs cm^{-1}. ^{1}H-NMR: δ 0 2.98 (s, 2H, CH_2), 3.76 (s, 3H, OCH_3), 5.27 (s, 5H, Cp), 6.71–6.75 (m, 2H, C_6H_4), 7.07–7.11 (m, 2H, C_6H_4). EI-MS: *m*/*z* (%) 454 (1) [M$^+$], 370 (17) [M$^+$−3CO], 121 (100) [$CH_2C_6H_4OCH_3$-*p*$^+$]. Anal. Found: C, 42.23; H, 3.16; $C_{16}H_{14}O_4W$ (454.1) calc.: C, 42.31; H 3.11.

*4.9. Reaction of [(CO)$_5$Cr=C(H)Ph] (**7a**) with [Cp(CO)$_3$WH] (**5**)*

At −78°C, a solution of 0.33 mmol (0.11 g) of **5** in 15 ml of pentane was added to a solution of **7a**, obtained from 0.28 mmol (0.20 g) of PNP-[(CO)$_5$CrC(H)(OMe)Ph] and 0.58 mmol of HBF_4 (0.08 ml of a 54% solution in Et_2O). The solution turned yellow. Chromatography and recrystallization as described in Section 4.6 gave complex **6a**.

6a: Yellow crystals (50 mg, 42% based on PNP-[(CO)$_5$Cr−C(H)(OMe)Ph]). All spectroscopic and analytical data agree with reported values [65].

*4.10. Reaction of [Cp(CO)$_2$Mn=C(H)Ph] (**8a**) with [Cp(CO)$_3$WH] (**5**)*

At ambient temperature, a green-brown solution of 0.34 mmol (0.09 g) of **8a** in 17 ml of pentane was added to a solution of 0.34 mmol (0.12 mg) of **5** in 17 ml of pentane. The progress of the reaction was followed by IR spectroscopy. The absorptions of **8a** disappeared within 5 min. After a few further min a red-black precipitate formed. The reaction mixture was filtered through a 3 cm-layer of kieselguhr. The filtrate was concentrated in vacuo to a volume of ca. 3 ml and then chromatographed at −20°C with pentane/CH_2Cl_2 (3/1) on flash silica gel. First, a colorless fraction containing [Cp(CO)$_3$Mn] and then a yellow fraction containing **6a** were collected.

6a: Yellow crystals (6 mg, 4% based on **8a**). All spectroscopic and analytical data agree with reported values [65].

*4.11. Reaction of **2c** with [Cp*(CO)$_3$WH] (**9**)*

At −60°C, a solution of 0.25 mmol (0.11 g) of **2c** in 20 ml of CH_2Cl_2 was added to a solution of 0.25 mmol (0.10 g) of **9** in 20 ml of CH_2Cl_2. The solution immediately turned yellow. The solvent was evaporated in vacuo and the residue was chromatographed on Al_2O_3 at 0°C. With pentane/CH_2Cl_2 (10/1) [(CO)$_6$W] was eluted and then with pentane/CH_2Cl_2 (1/1) complex **10**. The solvent was removed in vacuo and the residue recrystallized from pentane/CH_2Cl_2 (40/1).

10: Yellow crystals (0.07 g, 53% based on **1c**), m.p. 149°C. IR (pentane): ν(CO) 2006 s, 1915 vs cm^{-1}.

^{1}H-NMR: δ 2.02 (s, 15H, CH_3), 2.18 (s, 2H, CH_2), 3.74 (s, 3H, OCH_3), 6.67–6.71 (m, 2H, C_6H_4), 7.06–7.10 (m, 2H, C_6H_4). EI-MS: m/z (%) 524 (2) [M^+], 440 (19) [M^+−3CO], 121 (100) [$CH_2C_6H_4OCH_3$-p^+]. Anal. Found: C, 47.90; H, 4.63; $C_{21}H_{24}O_4W$(254.3) calc.: C, 48.11; H, 4.61.

4.12. Reaction of **2b** with [Cp_2WH_2] (**11**)

At −78°C, a solution of 0.79 mmol (0.25 g) of **11** in 25 ml of pentane was added to a solution of **2b** in 100 ml of pentane, obtained from 1.24 mmol (0.73 g) of **1b** and 2.56 mmol of HBF_4 (0.35 ml of a 54% solution in Et_2O). The solution immediately turned yellow and a green-black precipitate formed. The precipitate was washed several times with 10 ml portions of pentane precooled to −78°C. The resulting powder of **12** was dried in vacuo for several hours at −78°C. Due to fast decomposition in solution, it was not possible to recrystallize **12** and obtain the complex in a pure form.

12: Black powder (80 mg, 13% based on **11**). IR (toluene): ν(CO) 2067 w, 1969 w, 1926 s cm^{-1}. ^{1}H-NMR ([D_8]toluene, 238 K): δ −23.42 (1H, W–H–W, ^1J(WH) = 70.8 Hz, ^2J(WH) = 36.0 Hz), 2.23 (s, 3H, CH_3), 2.36 (s, 2H, CH_2), 4.04 (s, 10H, Cp), 6.50–6.53 (m, 2H, C_6H_4), 6.90–6.94 (m, 2H, C_6H_4). ^{13}C-NMR ([D_6]acetone, 238 K): δ −13.8 (CH_2), 20.6 (CH_3), 86.1 (Cp), 128.2, 128.6, 131.6, 153.5 (C_6H_4), 199.2 (*cis*-CO, ^1J(WC) = 129.0 Hz), 199.8 (*trans*-CO). EI-MS: m/z (%) 419 (1) [$Cp_2WCH_2C_6H_4CH_3$-p^+], 352 (4) [$W(CO)_6^+$], 314 (27) [Cp_2W^+], 268 (20) [$W(CO)_3^+$], 106 (82) [$(CH_3)_2C_6H_4^+$].

4.13. Reaction of **2b** with PNP[$(CO)_4FeH$] (**13**)

At −65°C, a solution of 0.96 mmol (0.68 g) of **13** in 50 ml of CH_2Cl_2 was added to a solution of **2b** in 100 ml of CH_2Cl_2, obtained from 2.97 mmol (1.75 g) of **1b** and 6.15 mmol of HBF_4 (0.85 ml of a 54% solution in Et_2O). The solution turned brown-green. The solvent was completely removed in vacuo at −45°C and the residue was dissolved at room temperature in the minimum volume of ether possible. The solution was quickly chromatographed on a 10 cm-layer of basic Al_2O_3. With ether [$(CO)_6W$] was eluted and then, with CH_2Cl_2, the product **14** as a brown-red fraction. The solvent was removed in vacuo at −50°C. The residue was dissolved in a few millilitres of acetone precooled to −30°C. Pentane (precooled to −30°C) was slowly added until the solution got slightly cloudy. When the solution was cooled to −74°C a red-brown precipitate (**14**) formed which was washed with pentane (precooled to −78°C) and dried in vacuo.

14: Red-brown powder (60 mg, 6% based on **13**). IR (CH_2Cl_2): ν(CO) 2060 w, 2006 w, 1946 vs, 1940 sh, 1909 m, 1855 vw, br cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (1g ε): 406 nm (3.488). ^{1}H-NMR (238 K): δ 2.21 (s, 3H, CH_3), 2.35 (s, 2H, CH_2), 6.91–6.94 (m, 2H, C_6H_4), 7.10–7.13 (m, 2H, C_6H_4), 7.48 (m, 24H, *o,m*-H of PNP–Ph), 7.66 (br, 6*p*-H of PNP–Ph). ^{13}C-NMR (238 K): δ 13.3 (CH_2), 21.0 (CH_3), 125.6, 126.5, 127.4, 128.1, 131.0, 131.8, 133.6 (C_6H_4 and Ph), 204.6 (*cis*-WCO, ^1J(WC) = 127.3 Hz), 206.3 (*trans*-WCO), 211.1, 214.4, 222.2 (FeCO). MS (FAB, negative modus): m/z (%) 597 (67) [M^-], 492 (100) [M^-−$CH_2C_6H_4CH_3$-p], 464 (30), 436 (18), 408 (8), 324 (5) [M^-−$CH_2C_6H_4CH_3$-p-nCO] (n = 1, 2, 3, 6), 245 (5) [$(CO)_3FeCH_2C_6H_4CH_3$]. Anal. Found C, 54.98; H, 3.59; N, 1.18; $C_{53}H_{39}FeNO_9P_2W$ (1135.5) calc.: C, 56.06; H, 3.46; N, 1.23. Complex **14** is thermolabile and quickly decomposed at room temperature.

4.14. Mechanistic studies

4.14.1. Reaction of **3** with [$(CO)_5W{=}C(D)Ph$] (**2aD**)

At −70°C, 0.75 mmol (0.15 g) of complex **3** was added to a solution of **2aD**, prepared from 0.35 mmol (0.20 g) of $NEt_4[(CO)_5W{-}C(D)(OMe)Ph]$ (**1aD**) (100% monodeuterated based on the ^{1}H-NMR spectrum). After workup analogously to Section 4.3 [$(CO)_5MnC(H)(D)Ph$] (**4aD**) was recrystallized from 2 ml of pentane.

4aD: Yellow crystals (20 mg, 20% based on **1aD**). ^{1}H-NMR: δ 2.31 (s, 1H, CHD), 6.89 (s, 1H, *p*-H of Ph), 7.09 (s, 4H, *o,m*-H of Ph). Based to the ^{1}H-NMR spectrum **4aD** was 100% monodeuterated at the methylene carbon atom.

4.14.2. Reaction of **5** with [$(CO)_5W{=}C(D)C_6H_4OMe$-p] (**2cD**) and PMe_3

At −80°C, a solution of 0.018 mmol (0.008 g) of **2cD** (100% monodeuterated) was added to a solution of 0.06 mmol (0.02 g) of **5** and thoroughly mixed. After 60 s, 1.84 mmol (0.14 g) of PMe_3 was added. The solution immediately turned yellow. The solvent was removed in vacuo and the residue was analyzed by ^{1}H-NMR spectroscopy. The spectrum showed no proton resonance in the range expected for [$(CO)_5WC(H)(PMe_3)C_6H_4OMe$-$p$]

4.14.3. Reaction of **2b** with [$Cp(CO)_3WD$] (**5D**)

The reaction of 0.047 mmol (0.020 g) of **2b** in 20 ml of CH_2Cl_2 with 0.051 mmol (0.017 g) of **5D** (81% monodeuterated) at −60°C and the chromatographic workup were carried out analogously to Section 4.6. After workup the methylene carbon atom of the resulting product **6bD** was 60% monodeuterated as determined by NMR spectroscopy.

4.14.4. Reaction of **2b** with $NEt_4[(CO)_5Mn]$ and HBF_4

At −60°C, a solution of 0.68 mmol (0.22 g) of $NEt_4[(CO)_5Mn]$ in 10 ml of CH_2Cl_2 was added to a solution of **2b**, obtained from 1.40 mmol (0.80 g) of **lb** and 2.90 mmol of HBF_4 (0.40 ml of a 54% solution in Et_2O). Within 3 min the reaction mixture turned orange and a yellow precipitate formed. Based on the IR spectrum of the solution, the reaction of **2b** with $NEt_4[Mn(CO)_5]$ was complete. The reaction product was unstable and rapidly decomposed at ambient temperature in the IR cuvette. When 2.90 mmol of HBF_4 (0.4 ml of a 54% solution in Et_2O) were added to the mixture at -60°C the yellow compound decomposed. **4b** was not detected among the decomposition products.

4.14.5. Reaction of $[(CO)_5Mn(BF_4)]$ with $NEt_4[(CO)_5WCH_2Ph]$

A solution of 0.21 mmol (0.117 g) of $NEt_4[(CO)_5WCH_2Ph]$ in 10 ml of CH_2Cl_2 was added at ambient temperature to a filtered solution of $[(CO)_5Mn]BF_4$ in 15 ml of CH_2Cl_2, freshly prepared from 0.21 mmol (0.059 g) of $[(CO)_5MnBr]$ and 0.30 mmol (0.059 g) of $AgBF_4$. The mixture turned black and a metallic shiny precipitate formed. The IR spectrum of the solution did not show absorptions due to **4a**.

4.15. Kinetic studies

All reactions were performed with a HI-TECH SFA-11 stopped-flow apparatus using pseudo-first order conditions. The ratio of the hydrido and the carbene complex concentration was at least 10:1. The reactions were followed by continuously monitoring the MLCT absorption of the carbene complex at 496 nm in the UV–vis spectrum for several half-lives. A constant temperature (±0.1°C) was maintained throughout the reaction by an external circulating cryostat.

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References

[1] See e.g. (a) K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert, K. Weiss (Eds.), Transition Metal Carbene Complexes, Verlag Chemie, Weinheim, 1983. (b) L.S. Hegedus, Transition Metals in the Synthesis of Complex Organic Molecules, University Science Books, 1994.

[2] Recent review: G.L. Geoffroy, S.L. Bassner, Adv. Organomet. Chem. 28 (1988) 1.

[3] H. Fischer, Angew. Chem. 95 (1983) 913; Angew. Chem., Int. Ed. Engl. 22 (1983) 874.

[4] H. Fischer, H. Jungklaus, J. Schmid, J. Organomet. Chem. 368 (1989) 193.

[5] C.P. Casey, S.M. Neumann, J. Am. Chem. Soc. 99 (1977) 1651.

[6] (a) R.C. Brady III, R. Pettit, J. Am. Chem. Soc. 102 (1980) 6181. (b) R.C. Brady III, R. Pettit, J. Am. Chem. Soc. 103 (1981) 1287.

[7] (a) T. Ziegler, L. Versluis, V. Tschinke, J. Am. Chem. Soc. 108 (1986) 612. (b) E.A. Carter, W.A. Goddard III, J. Am. Chem. Soc. 109 (1987) 579. (c) E.A. Carter, W.A. Goddard III, Organometallics 7 (1988) 675.

[8] See e.g. (a) M.J. Winter, Polyhedron 8 (1989) 1583. (b) V.A. Osborn, C.A. Parker, M.J. Winter, J. Chem. Soc. Chem. Commun. (1986) 1185. (c) M.J. Winter, S. Woodward, J. Organomet. Chem. 361 (1989) C18. (d) R.S. Threlkel, J.E. Bercaw, J. Am. Chem. Soc. 103 (1981) 2650. (e) C.E. Davey, R. Devonshire, M.J. Winter, Polyhedron 8 (1989) 1863. (f) J.C. Green, M.L.H. Green, C.P. Morley, Organometallics 4 (1985) 1302.

[9] W.A. Herrmann, H. Biersack, B. Balbach, M.L. Ziegler, Chem. Ber. 117 (1984) 95.

[10] P.J. Brothers, W.R. Roper, Chem. Rev. 88 (1988) 1293.

[11] C.P. Casey, S.W. Polichnowski, H.E. Tuinstra, L.D. Albin, J.C. Calabrese, Inorg. Chem. 17 (1978) 3045.

[12] (a) C.P. Casey, T.J. Burkhardt, J. Am. Chem. Soc. 96 (1974) 7808. (b) H. Fischer, S. Zeuner, K. Ackermann, J. Chem. Soc. Chem. Commun. (1984) 684.

[13] M. Berry, K. Elmitt, M.L.H. Green, J. Chem. Soc. Dalton Trans. (1979) 1950.

[14] B. Deubzer, H.D. Kaesz, J. Am. Chem. Soc. 90 (1968) 3276.

[15] M.P. Johnson, D.F. Shriver, J. Am. Chem. Soc. 88 (1966) 301.

[16] N.J. Cooper, M.L.H. Green, R. Mahtab, J. Chem. Soc. Dalton Trans. (1979) 1557.

[17] M.L.H. Green, J.A. McCleverty, L. Pratt, G. Wilkinson, J. Chem. Soc. (1961) 4854.

[18] See P. Legzdins, J.T. Martin, F.W.B. Einstein, A.C. Willis, J. Am. Chem. Soc. 108 (1986) 7971 and literature cited therein.

[19] A. Davison, W. McFarlane, L. Pratt, G. Wilkinson, J. Chem. Soc. (1962) 3653.

[20] A. Storr, B.S. Thomas, Can. J. Chem. 49 (1971) 2504.

[21] R.A. Love, H.B. Chin, T.F. Koetzle, S.W. Kirtley, B.R. Whittlesey, R. Bau, J. Am. Chem. Soc. 98 (1976) 4491.

[22] J.C. Leblanc, J.F. Reynoud, C. Moise, J. Organomet. Chem. 244 (1983) C24.

[23] M. Green, A.G. Orpen, I.D. Salter, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1984) 2497.

[24] B. Balbach, S. Baral, H. Biersack, W.A. Herrmann, J.A. Labinger, W.R. Scheidt, F.J. Timmer, M.L. Ziegler, Organometallics 7 (1988) 325.

[25] M.Y. Darensbourg, C.E. Ash, S.C. Kao, R. Silva, J. Springs, Pure Appl. Chem. 60 (1988) 131.

[26] (a) L. Arndt, T. Delord, M.Y. Darensbourg, J. Am. Chem. Soc. 106 (1984) 456. (b) L.W. Arndt, M.Y. Darensbourg, T. Delord, B.T. Bancroft, J. Am. Chem. Soc. 108 (1986) 2617.

[27] L. Vancea, W.A.G. Graham, J. Organomet. Chem. 134 (1977) 219.

[28] L.W. Arndt, M.Y. Darensbourg, J.P. Fackler Jr., R.J. Lusk, D.O. Marler, K.A. Youngdahl, J. Am. Chem. Soc. 107 (1985) 7218.

[29] K.H. Whitmire, T.R. Lee, J. Organomet. Chem. 282 (1985) 95.

[30] C.E. Ash, C.M. Kim, M.Y. Darensbourg, A.L. Rheingold, Inorg. Chem. 26 (1987) 1357.

[31] T. Bodnar, S.J. LaCroce, A.R. Cutler, J. Am. Chem. Soc. 102 (1980) 3292.

[32] E. Scharrer, M. Brookhart, J. Organomet. Chem. 497 (1995) 61.

[33] A. Dedieu, Transition Metal Hydrides, VCH, New York, 1992.

[34] See e.g. (a) M.F. Semmelhack R. Tamura, J. Am. Chem. Soc. 105 (1983) 6750. (b) H Fischer, J. Schmid, R. Märkl, J. Chem. Soc. Chem. Commun. (1985) 572. (c) A. Wienand, H.-U. Reissig, Tetrahedron Lett. 29 (1988) 2315. (d) A. Wienand, H.-U. Reissig, Angew. Chem. 102 (1990) 1156; Angew. Chem., Int. Ed. Engl. 29 (1990) 1129. (e) A. Wienand, H.-U. Reissig, Organometallics 9 (1990) 3133.

[35] (a) E.O. Fischer, K.H. Dötz, J. Organomet. Chem. 36 (1972) C4. (b) J.A. Connor, P.D. Rose, J. Organomet. Chem. 24 (1970) C45. (c) J.A. Connor, J.P. Day, R.M. Turner, J. Chem. Soc. Dalton Trans. (1976) 108.
[36] (a) J.A. Connor, P.D. Rose, R.M. Turner, J. Organomet. Chem. 55 (1973) 111. (b) J.A. Connor, J.P. Day, R.M. Turner, J. Chem. Soc. Chem. Commun. (1973) 578.
[37] J.A. Connor, J.P. Day, R.M. Turner, J. Chem. Soc. Dalton Trans. (1976) 283.
[38] F.R. Kreissl, E.O. Fischer, C.G. Kreiter, H. Fischer, Chem. Ber. 106 (1973) 1262.
[39] U. Schubert, E.O. Fischer, Chem. Ber. 106 (1973) 3882.
[40] E.O. Fischer, V. Kiener, Angew. Chem. 79 (1967) 982; Angew. Chem., Int. Ed. Engl. 6 (1967) 961.
[41] E.O. Fischer, G. Kreis, Chem. Ber. 106 (1973) 2310.
[42] For reviews see e. g. (a) J. Halpern, Pure Appl. Chem. 58 (1986) 575. (b) D.C. Eisenberg, J.R. Norton, Isr. J. Chem. 31 (1991) 55. (c) R.M. Bullock, Comments Inorg. Chem. 12 (1991) 1. (d) R.G. Pearson, Chem. Rev. 85 (1985) 41. (e) R.M. Bullock, E.G. Samsel, J. Am. Chem. Soc. 112 (1990) 6886 and literature cited therein.
[43] R.L. Sweany, J. Halpern, J. Am. Chem. Soc. 99 (1977) 8335.
[44] R.L. Sweany, J.W. Owens, J. Organomet. Chem. 255 (1983) 327.
[45] H.-W. Chen, W.L. Jolly, J. Kopf, T.H. Lee, J. Am. Chem. Soc. 101 (1979) 2607.
[46] (a) C.P. Casey, S.W. Polichnowski, J. Am. Chem. Soc. 100 (1978) 7565. (b) C.P. Casey, S.W. Polichnowski, A.J. Shusterman, C.R. Jones, J. Am. Chem. Soc. 101 (1979) 7282. (c) M.P. Doyle, J.H. Griffin, V. Bagheri, R.L. Dorow, Organometallics 3 (1984) 53. (d) H. Fischer, J. Hofmann, Chem. Ber. 124 (1991) 981. (e) H. Fischer, E. Mauz, M. Jaeger, R. Fischer, J. Organomet. Chem. 427 (1992) 63.
[47] H. Fischer, M. Jaeger, J. Organomet. Chem. 456 (1993) 205.
[48] M. Jaeger, M.-H. Prosenc, C. Sontag, H. Fischer, New J. Chem. 19 (1995) 911.
[49] Reviews: (a) M.P. Doyle, Chem. Rev. 86 (1986) 919. (b) M. Brookhart, W.B. Studabaker, Chem. Rev. 87 (1987) 411.
[50] (a) M. Brookhart, Y. Liu, Organometallics 8 (1989) 1569. (b) C.P. Casey, L.J. Smith, Organometallics 8 (1989) 2288. (c) M. Brookhart, Y. Liu, J. Am. Chem. Soc. 113 (1991) 939. (d) C.P. Casey, L.J. Smith Vosejpka, Organometallics 11 (1992) 738.
[51] G. Brauer, Handbuch der Präparativen Anorganischen Chemie, vol. 3, 3rd ed., Enke, Stuttgart, 1981.
[52] C. Troll, Diploma Thesis, Universität Konstanz, 1988.
[53] R.B. King, A. Fronzaglia, Inorg. Chem. 5 (1966) 1837.
[54] M.Y. Darensbourg, D.J. Darensbourg, H.L.C. Barros, Inorg. Chem. 17 (1978) 297.
[55] E.O. Fischer, W. Held, F.R. Kreißl, A. Frank, G. Huttner, Chem. Ber. 110 (1977) 656.
[56] E.O. Fischer, A. Schwanzer, H. Fischer, D. Neugebauer, G. Huttner, Chem. Ber. 110 (1977) 53.
[57] H.W. Sternberg, I. Wender, R.A. Friedel, M. Orchin, J. Am. Chem. Soc. 75 (1953) 2717.
[58] P.C. Wailes, H. Weigold, J. Organomet. Chem. 24 (1970) 405.
[59] J.P. Olsen, T.F. Koetzle, S.W. Kirtley, M. Andrews, D.L. Tipton, R. Bau, J. Am. Chem. Soc. 96 (1974) 6621.
[60] R.G. Hayter, J. Am. Chem. Soc. 88 (1966) 4376.
[61] W. Hieber, G. Wagner, Z. Naturforsch. 12b (1957) 478.
[62] S.P. Schmidt, J. Nitschke, W.C. Trogler, Inorg. Synth. 26 (1986) 113.
[63] D. Drew, M.Y. Darensbourg, D.J. Darensbourg, J. Organomet. Chem. 85 (1975) 73.
[64] M.J. Nappa, R. Santi, J. Halpern, Organometallics 4 (1985) 34.
[65] D.S. Ginsley, C.R. Bock, M.S. Wrighton, Inorg. Chim. Acta 23 (1977) 85.