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Insertion reactions of bis(η^5-cyclopentadienyl)-dihydridotungsten with activated olefins and with acetylenes: Tungstenocene alkyl hydrides, olefin and acetylene complexes

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Abstract

Tungstenocene dihydride **1** undergoes insertion of activated olefins at 120 °C to give functional alkyl hydrides $Cp_2WH(\eta^1\text{-}CHXCH_2R)$ (X = CO_2Me, R = H (**2**), CO_2Me (**3**), Ph (**4**); X = CN, R = H (**5**)). In the case of acrylonitrile the olefin complex $Cp_2W(\eta^2\text{-}CH_2CHCN)$ (**8**) may also be formed. Complexes **2** and **3** were oxidized with chloroform to give the corresponding alkyl chloro complexes **17** and **18**. The reaction of **1** with activated acetylenes can produce olefin complexes $Cp_2W(\eta^2\text{-}CH_2{=}CHY)$ (Y = CO_2Me (**6**), COMe (**7**)), but in the case of $CF_3C{\equiv}CH$ alkenyl complexes $Cp_2WX[\eta^1\text{-}C(CF_3){=}CH_2]$ (X = H (**15**), F (**16**)) are formed. Complex **1** also reacts with diphenylacetylene to give an (*E*)-stilbene complex $Cp_2WH[\eta^2\text{-}(E)\text{-}CHPhCHPh]$ (**9**) and a tolan complex $Cp_2W(\eta^2\text{-}C_2Ph_2)$ (**12**); the (*Z*)-stilbene complex **10** is observed as an intermediate. Phenylacetylene likewise gives a styrene complex **11**. Both **12** and **9** can be reversibly protonated at the tungsten centre; the corresponding cations were characterized as PF_6^- derivatives **13** and **14**. In the case of **4** the regiochemistry of the olefin insertion was established by an X-ray structural determination.

Introduction

In a series of pioneering papers, Otsuka and Nakamura studied the insertion reactions of molybdenocene dihydride Cp_2MoH_2 with olefins [1–4] and acetylenes [1,5,6]. Rather surprisingly, little is known about the related chemistry of the analogous tungsten complex Cp_2WH_2 (**1**). This is certainly due to the much lower reactivity of tungstenocene dihydride. For instance, Cp_2MoH_2 readily reacts with C_2Ph_2 at room temperature to give a (*E*)-1,2-diphenylethene $Cp_2Mo[\eta^2\text{-}(E)\text{-}CHPhCHPh]$ [7] and a 1,2-diphenylacetylene complex $Cp_2Mo(\eta^2\text{-}C_2Ph_2)$ [1,7] whereas **1** is reported not to react with C_2Ph_2 in boiling toluene (115 °C, 6 h) [1]. Two early short notes by Green et al. mentioned insertion reactions of **1** with isoprene [8] and diethyl maleate [9], but no details of these experiments have yet been given.

In this paper we show that **1** does indeed undergo many of the insertion reactions

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known for Cp_2MoH_2 when higher reaction temperatures and rather long reaction times are used. A variety of new tungstenocene derivatives **2**–**18** have been obtained, including alkyl hydrides **2**–**5** with functional alkyl groups, olefin complexes **6**–**11**, the diphenylacetylene complex **12**, and miscellaneous other derivatives.

$Cp_2WH(\eta^1\text{-}CHXCH_2R)$

2: $X = CO_2Me$; $R = H$
3: $X = CO_2Me$; $R = CO_2ME$
4: $X = CO_2Me$; $R = Ph$
5: $X = CN$; $R = H$

$Cp_2W(\eta^2\text{-}CHXCHY)$

6: $X = H$; $Y = CO_2Me$
7: $X = H$; $Y = COMe$
8: $X = H$; $Y = CN$
9: $X = Ph$; $Y = Ph$; *E*-isomer
10: $X = Ph$; $Y = Ph$; *Z*-isomer
11: $X = H$; $Y = Ph$

12: $Cp_2W(\eta^2\text{-}C_2Ph_2)$
13: $[Cp_2WH(\eta^2\text{-}C_2Ph_2)]PF_6$
14: $[Cp_2WH\{\eta^2\text{-}(E)\text{-}CHPhCHPh\}]PF_6$

15: $Cp_2WH[\eta^1\text{-}C(CF_3){=}CH_2]$
16: $Cp_2WF[\eta^1\text{-}C(CF_3){=}CH_2]$
17: $Cp_2WCl[\eta^1\text{-}CH(CO_2Me)Me]$
18: $Cp_2WCl[\eta^1\text{-}CH(CO_2Me)CH_2CO_2Me]$

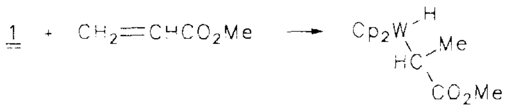
Results

Reactions of Cp_2WH_2 with olefins

There have been few reports on reactions of **1** with olefins [8–10]. With activated olefins charge-transfer absorptions are observed [2,10]. Excitation at the charge-transfer absorption frequency of **1** with maleic anhydride in solution gave the maleic anhydride complex $\mathbf{1} \cdot C_4H_2O_3$ and an equivalent of succinoic anhydride [10]. In a similar manner **1** and fumaronitrile gave a mixture of maleo- and fumaronitrile complexes $\mathbf{1} \cdot [1,2\text{-}C_2H_2(CN)_2]$ and succinonitrile [10].

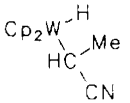
We have investigated the thermal reactions of **1** with activated olefins such as methyl acrylate (Scheme 1). In boiling toluene insertion takes place to give the alkyl hydrido complexes **2**–**5** of tungstenocene in moderate to high yields. In the case of the unsymmetrical olefins ($CH_2{=}CHCN$, $CH_2{=}CHCO_2Me$, (*E*)-$PhCH{=}CHCO_2Me$) the regiochemistry of the insertion is such that the metal atom is found in the α-position to the activating group. Reaction rates decrease in the order $CH_2{=}CHCN > CH_2{=}CHCO_2Me > (Z)\text{-}MeO_2CCH{=}CHCO_2Me > (E)\text{-}PhCH{=}CHCO_2Me \gg (E)\text{-}NCCH{=}CHCN$, with fumaronitrile not reacting at all under these conditions. This is the same order of reactivity as was found for molybdenocene dihydride at temperatures about 100 °C lower [1]. We also note that (*Z*)-1,2-diphenylethene and styrene are completely inactive (120 °C, 10 d).

In the cases of the acrylic and maleic acid esters solely the alkyl hydrido complexes were obtained. No concurrent formation of the corresponding olefinic



Scheme 1

complexes could be observed, either in NMR tube or preparative-scale experiments. However, in the case of the cinnamic acid ester, for which very long reaction times were necessary, the olefinic complex $Cp_2W\{\eta^2\text{-}[(E)\text{-}PhCHCHCO_2Me]\}$ was detected by ^{13}C NMR spectroscopy as a by-product. With acrylonitrile either types of product can be selectively obtained. A small excess of the nitrile affords **5** as the sole identifiable product. With a large excess of acrylonitrile the formation of **5** is faster as expected but the acrylonitrile complex **8** (cf. Ref. 11) is also formed; on prolonged heating the initially high yield of **5** begins to fall, and finally **8** can be obtained as the sole product in high yield (84%). No propionitrile or any other products were detected.



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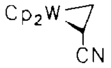

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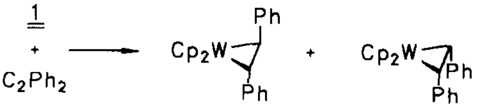
The thermal stability of the alkyl hydrido complexes is remarkably high. The nitrile **5** is unchanged after 50 h at 120 °C in C_6D_6. Under the same conditions the ester **2** slowly decomposes (47% after 16 h) to form propionic acid ester, $Cp_2WD(C_6D_5)$ [12,13], and a presumably dinuclear species that gives a pair of Cp signals at 4.38 and 4.36 ppm like $(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)_2(WHCp)(WMeCp)$ [14]; the acrylic acid ester complex **6** was not formed. In contrast, $Cp_2MoH[\eta^1\text{-}CH(CO_2Me)Me]$ readily decomposes at room temperature, and so can only be identified in solution by NMR spectroscopy [1].

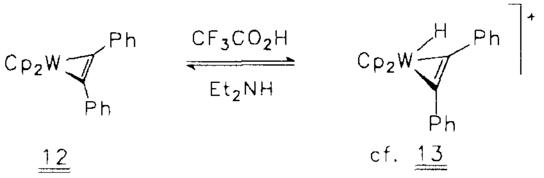
Reactions of Cp_2WH_2 with diphenylacetylene and phenylacetylene

The reaction of **1** with diphenylacetylene sets in above 100 °C. In a NMR-tube experiment we treated **1** with tolan (1/2.6) at 110 °C in C_6D_6, using hexamethylbenzene as an internal standard. The reaction gave the (*E*)-stilbene complex **9** together with a minor amount of the *Z* isomer **10** (typically 7/1 to 10/1) (Scheme 2). The two isomers are readily distinguished by their ^1H NMR spectra since **9** (symmetry C_2) shows one signal for the two cyclopentadienyl rings whereas in **10** (symmetry C_s) the two rings are chemically non-equivalent and hence give a pair of signals. In the later stages of the reaction the concentration of **10** begins to decrease and after 5 h a virtually quantitative amount of **9** is present. Thus it is clear that the *Z* isomer **10** rearranges to the more stable *E* isomer **9**. Such an isomerization is known for $Cp_2Mo[\eta^2\text{-}(Z)\text{-}CHPhCHPh]$ [7], but with the tungsten complex the possibility cannot be excluded that some of the product **9** forms directly. On prolonged heating (1–5 d) **9** undergoes some decomposition, and Cp_2WHPh [8] and the tolan complex **12** appear in the reaction mixture.

With higher temperatures, for instance if the reaction of tolan and **1** is carried out in a melt of the reactants at 150 °C, the product ratio **12**/**9** is higher. Pure tolan



Scheme 2



Scheme 3

complex **12** can readily be obtained since the two complexes can be separated easily by column chromatography. Photolysis of **1** (yellow) is known to give WCp_2 [15,16]; if it is carried out in the presence of tolan in ether complex **12** (red) is formed. However, the photochemical production of **12** is inefficient.

The closely related reaction of **1** with phenylacetylene is accompanied by extensive polymerization of the acetylene and produces the styrene complex **11** in low yield.

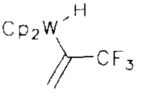
The tolan complex **12** can be protonated, e.g. by CF_3CO_2H in C_6D_6, to give a yellow cation, and addition of Et_2NH reverses the process (Scheme 3). The cation may be precipitated from aqueous solution as hexafluorophosphate **13**. In the same manner the (*E*)-stilbene complex **9** can be reversibly protonated and deprotonated. The corresponding cation (symmetry C_1, showing two cyclopentadienyl signals in the ^1H NMR spectrum) can be characterized as the hexafluorophosphate **14**, and slowly decomposes in solution. Such reactions were first described for the ethylene [17] and the propene [17,18] complexes of tungstenocene.

Reactions of Cp_2WH_2 with activated acetylenes

Metallocene hydrides of Nb, Ta, Mo, W, and Re undergo insertions of activated acetylenes [5,6,19,20], and the mechanism of these reactions has been discussed extensively [5,21]. For **1** insertion reactions have been reported for the most active acetylenes, namely $F_3CC{\equiv}CCF_3$ [5], $MeO_2CC{\equiv}CCO_2Me$ [22], and the cyanoacetylenes $NCC{\equiv}CCN$ and $HC{\equiv}CCN$ [23].

With less active acetylenes heating is required to effect reaction. Thus propiolic acid ester $HC{\equiv}CCO_2Me$ and butynone $HC{\equiv}CCOMe$ react with **1** above 60 °C to give the olefin complexes **6** and **7**, respectively (Scheme 4). The initial insertion product, presumed to be an alkenyl hydrido complex, cannot be detected when the progress of the reaction is monitored by ^1H NMR spectroscopy. This is not surprising since when **1** reacts with $MeO_2CC{\equiv}CCO_2Me$ at room temperature the products are the (*Z*)-alkenyl hydrido complex and a mixture of fumaric and maleic acid ester complexes [22]; that is, the rearrangement of the alkenyl hydrido complex to the olefin complex can take place even at room temperature.

The closely related reaction of **1** with trifluoropropyne $HC{\equiv}CCF_3$ again sets in above 60 °C and affords the alkenyl complex **15** and the corresponding fluoro derivative **16**. A similar redox reaction was previously observed for the system $Cp_2NbH_3/CF_3C{\equiv}CCF_3$ [24].



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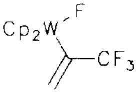

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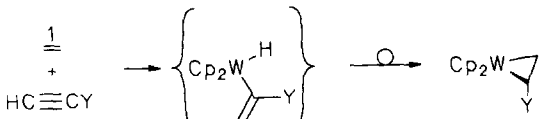

6: Y = CO_2Me

7: Y = COMe

Scheme 4

Miscellaneous synthetic experiments

Halide abstraction from tungstenocene alkyl halogeno complexes Cp_2WClR (R = Et, Pr, ^iPr) provides an interesting route to cationic hydrido olefin complexes $\{Cp_2WH[\eta^2\text{-}(CH_2CHR)]\}^+$ [17,18]. With this in mind we treated the alkyl hydrido complexes **2** and **3** with chloroform as oxidant [25,26] and obtained the corresponding alkyl chloro complexes **17** and **18**. (Closely related derivatives of molybdenocene [11,27] and the compound $Cp_2WCl[\eta^1\text{-}CH(CN)Me]$ [11] have been described previously.) However, in ^1H NMR-tube experiments **17** and **18** were found not to react with $TlPF_6$ in acetone at ambient temperature. Under more forcing conditions (60 ° C, 15 h) decomposition took place.

Characterization

Details of yields and physical properties of the new compounds are given in Tables 1–3 and in the Experimental section. In general the NMR data suffice to establish the structural type of the compounds. Only in case of complex **4** did the spectra not allow simple and unambiguous deduction of the regiochemistry of the insertion. The structure of **4** was thus determined by X-ray crystallography (Tables 4, 5 and Fig. 1). As expected **4** is a bent sandwich complex with the functional alkyl group and a hydrogen atom in the pseudoequatorial plane. The bending angle (i.e. the angle spanned by the perpendiculars of the best cyclopentadienyl planes) is 135.0(3)°.

Cyclic voltammetry for most of the new compounds (Table 3) reveals a nearly reversible oxidation between −0.34 for **9** and 0.21 V vs. SCE for **18**. This oxidation corresponds to the removal of an essentially non-bonding *d* electron from the $2a_1$ orbital of the bent metallocene [30–32]. The half-wave potentials of the olefinic

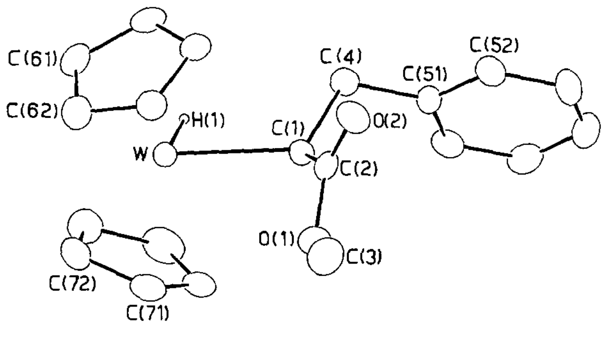

Fig. 1. The molecular structure of **4**.

Table 1

Preparative data and elemental analyses

Complex	Formula	Mol. weight (g/mol)	MS [a]	Analyses (Found (calcd.) (%))		Colour	M.p./Dec. (° C)
				C	H		
2	$C_{14}H_{18}O_2W$	402.15	402	41.65 (41.81)	4.53 (4.51)	orange-red	90/ ≈ 240
3	$C_{16}H_{20}O_4W$	460.20	460	42.04 (41.76)	4.41 (4.38)	orange-red	113/– [b]
4	$C_{20}H_{22}O_2W$	478.25	478	50.28 (50.23)	4.76 (4.64)	yellow-orange	140/ > 200
5	$C_{13}H_{15}NW$	369.12	369	42.68 (42.30)	4.13 (4.10)	yellow	122/ ≈ 245
6	$C_{14}H_{16}O_2W$	400.13	400	41.73 (42.03)	4.17 (4.03)	orange-brown	206–207/238
7	$C_{14}H_{16}OW$	384.13	384	43.63 (43.78)	4.12 (4.20)	red	183–184/ > 215
8	$C_{13}H_{13}NW$	367.10	367	42.70 (42.53)	3.66 (3.57)	red-brown	162/ ≈ 230

9	$C_{24}H_{22}W$	494.29	494	58.22	4.62	red	171–173/– [c]
				(58.32)	(4.49)		
11	$C_{18}H_{18}W$	418.19	418	– [c]	– [c]	dark red	145/ ≈180
				(51.70)	(4.34)		
12	$C_{24}H_{20}W$	492.27	492	58.72	4.23	dark red	157–158/– [c]
				(58.56)	(4.10)		
13	$C_{24}H_{21}F_6PW$	638.25	–	45.03	3.23	light yellow	253/– [d]
				(45.17)	(3.32)		
14	$C_{24}H_{23}F_6PW$	640.26	–	45.10	3.69	light yellow	109–110/– [d]
				(45.02)	(3.62)		
15	$C_{13}H_{13}F_3W$	410.09	410	38.16	3.27	yellow	92–94/– [c]
				(38.08)	(3.20)		
16	$C_{13}H_{12}F_4W$	428.08	428	36.58	2.91	red	180–180.5/– [c]
				(36.48)	(2.83)		
17	$C_{14}H_{17}ClO_2W$	436.59	436	38.59	4.01	dark red	167/– [e]
				(38.52)	(3.93)		
18	$C_{16}H_{19}ClO_4W$	494.65	494	39.67	4.02	reddish-purple	165/– [e]
				(38.85)	(3.87)		

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[a] Parent ion based on most frequent isotopic combination. [b] Darkening >140 °C. [c] Not observed. [d] Melting with dec. [e] No dec. <240 °C.

Table 2

^{1}H NMR data [a]

Complex	Cp rings	Other groups	Solvent
2	4.29 (d) [b]; 4.25 (d) [b]	3.49 (s, OMe); 2.25 (qm [c], CH), 1.57 (d, Me), ^3J 6.8 Hz; −11.32 (s br, ^1J(WH) 81.7 Hz, WH)	C_6D_6
3	4.27 (d) [d]; 4.18 (d) [b]	3.45 (s, OMe); 3.1–2.3 m ($CHCH_2$); −11.69 (s, ^1J(WH) 80.0 Hz, WH)	C_6D_6
4	4.29 (s)	7.37–7.04 (m, Ph); 3.79–2.37 (m, $CHCH_2$); 3.39 (s, OMe); −11.34 (s, ^1J(WH) 79.9 Hz, WH)	C_6D_6
5	4.24 (s); 4.07 (s)	1.49 (q, CH), 1.32 (d, Me), ^3J 5.7 Hz; −11.43 (s, ^1J(WH) 81.3 Hz, WH)	C_6D_6
6	4.14 (s); 3.88 (s)	3.56 (s, OMe); 2.13 (dd, H_c), 1.49 (dd, H_b), 0.93 (dd, H_a), $^3J_{ac}$ 9.0, $^3J_{bc}$ 10.8, $^2J_{ab}$ 7.1 Hz	C_6D_6
7	4.05 (s); 3.87 (s)	2.17 (d, Me); 2.20 (ddq, H_c), 1.51 (dd, H_b), 0.91 (dd, H_a), $^3J_{ac}$ 8.2, $^3J_{bc}$ 11.2, $^3J_{ab}$ 6.8 Hz, ^4J(Me, H_c) 0.45	C_6D_6
8	4.13 (s); 3.67 (s)	0.91–0.52 (m, $CHCH_2$)	C_6D_6
9	3.89 (s) [e]	7.32–7.12 (m, $2H_o$, $2H_m$); 7.0 (t, ^3J 7.0 Hz, $2H_p$); 3.40 (s, ^2J(WH) 6.5 Hz, 2CH)	
10 [f]	4.03 (s); 3.73 (s)	3.2 (s, 2CH)	C_6D_6
11	3.89 (s); 3.67 (s)	7.1–6.8 (m, Ph); 2.89 (dd, H_c), 1.36 (dd, H_b), 0.92 (dd, H_a), $^3J_{ac}$ 9.6, $^3J_{bc}$ 11.9, $^3J_{ab}$ 6.9 Hz	C_6D_6
12 [g]	4.25 (s)	7.93 (d, $4H_o$), 7.36 (t, $4H_m$), 7.14 (t, $2H_p$), ^3J 7.7 Hz	C_6D_6
13 [g]	5.95 (d) [b]	8.01–7.95 (m, $4H_o$); 7.65–7.38 (m, $4H_m$, $2H_p$); −2.82 (s, ^1J(WH) 52.2 Hz, WH)	CD_3COCD_3
14 [g]	5.55 (d) [h]; 5.37 (d) [h]	7.63–7.07 (m, 2Ph); 4.82 (d, CH), 4.66 (d, CH), ^3J 14.8 Hz; −5.50 (s, ^1J(WH) 48.2 Hz, WH)	CD_3COCD_3
15	4.12 (d) [d]	6.59 (m, CH_2); −11.94 (s br, WH)	$C_6D_5CD_3$
16	4.62 (d) [i]	6.21 (m, CH); 6.05 (m, CH)	$C_6D_5CD_3$
17	5.16 (s); 5.13 (s)	3.61 (s, OMe); 2.64 (q, CH), 1.32 (d, Me), ^3J 6.8 Hz	C_6D_6
18	5.26 (s); 5.13 (s)	3.63 (s, OMe); 3.60 (s, OMe); 3.1–2.6 (m, $CHCH_2$)	$CDCl_3$

[a] $\delta(^1H)$ (ppm) relative to internal TMS, 80 MHz. [b] ^3J 0.5 Hz. [c] Small unresolved couplings. [d] J 0.6 Hz. [e] ^2J(WH) 8.6 Hz. [f] Data from reaction mixture; Ph groups hidden by signals of **9**. [g] Recorded at 270 MHz. [h] ^3J 0.4 Hz. [i] ^3J(HF) 1.5 Hz.

Table 3

Cyclovoltammetric data [a]

Complex	$E_{1/2}$ (mV)	ΔE_p (mV)	i_a/i_c	Ref.
Cp_2WMe_2	−448			[28]
Cp_2WEt_2	−383			[28]
2	−150	80	1.2	
Cp_2WH_2	0			[10]
3	28	95	1.1	
4 [b]	75	90	1.8	
17	130	80	1.0	
18	210	60	1.0	
Cp_2WCl_2	300			[29]
9 [c]	−343	75	1.5	
12 [d]	−285	70	1.1	
6	−239	72	1.5	
7	−220	80	1.2	
8	−45	51	1.1	
A [e]	−30	80	1.9	

[a] Measured in acetonitrile/NBu_4HSO_4 vs. SCE. Scan rate 20 mV/s. [b] Scan rate 50 mV/s. [c] Measured in acetonitrile/NBu_4PF_6. [d] A second irreversible oxidation occurs at −95 mV. [e] A = $Cp_2W[\eta^2\text{-}(E)\text{-}CH(CO_2Me){=}CHCO_2Me]$ [22].

Table 4

Non-hydrogen atoms and hydride atom coordinates for **4**

Atom	x	y	z	B_{eq} [a]
W	0.84444(2)	0.17831(2)	0.08986(1)	2.268(4)
O(1)	0.5906(3)	0.3504(5)	0.0458(2)	3.64(9)
O(2)	0.5704(3)	0.1834(6)	−0.0630(3)	4.1(1)
C(1)	0.7375(4)	0.3255(7)	−0.0137(3)	2.8(1)
C(2)	0.6260(4)	0.2776(7)	−0.0151(3)	3.0(1)
C(3)	0.4889(5)	0.2901(9)	0.0562(4)	4.7(2)
C(4)	0.7643(5)	0.3126(8)	−0.0968(3)	3.6(1)
C(51)	0.7184(4)	0.4609(8)	−0.1507(3)	3.0(1)
C(52)	0.6305(5)	0.4353(8)	−0.2109(3)	3.6(1)
C(53)	0.5888(5)	0.5714(9)	−0.2611(4)	4.5(2)
C(54)	0.6355(5)	0.733(1)	−0.2523(4)	4.8(1)
C(55)	0.7236(5)	0.7602(9)	−0.1922(4)	4.5(1)
C(56)	0.7639(5)	0.6250(8)	−0.1422(4)	3.9(1)
C(61)	0.9137(5)	−0.0924(8)	0.0958(4)	3.8(1)
C(62)	0.8278(5)	−0.0884(7)	0.1362(4)	3.9(1)
C(63)	0.7335(5)	−0.0564(7)	0.0794(3)	3.2(1)
C(64)	0.7604(5)	−0.0456(7)	0.0042(3)	3.2(1)
C(65)	0.8707(5)	−0.0673(7)	0.0153(4)	3.6(1)
C(71)	0.7958(6)	0.3303(8)	0.1929(4)	4.2(1)
C(72)	0.8856(6)	0.2249(9)	0.2219(4)	4.4(2)
C(73)	0.9694(6)	0.2848(9)	0.1889(4)	5.0(2)
C(74)	0.9310(6)	0.4312(8)	0.1407(4)	5.2(2)
C(75)	0.8256(5)	0.4570(8)	0.1460(3)	4.3(1)
H(1)	0.926(6)	0.24(1)	0.043(5)	5(2) [b]

[a] The anisotropic thermal parameters are given in the form of their isotropic equivalents; in 10^4 pm^2. [b] The hydridic hydrogen atom was refined isotropically.

Table 5

Selected bond distances (pm) for **4**

W-C(1)	231.0(5)	W-H(1)	153(9)
C(1)-C(2)	148.6(8)	O(2)-C(2)	121.3(7)
O(1)-C(2)	135.3(7)	O(1)-C(3)	144.5(7)
C(1)-C(4)	155.0(8)	C(4)-C(51)	150.7(8)

Ph group C(51-56)		Cp rings	C(61-65)	C(71-75)
$C-C_{min}$	137(1)	$W-C_{min}$	221.8(6)	224.4(6)
$C-C_{max}$	139(1)	$W-C_{max}$	237.1(5)	237.6(6)
$C-C_{av}$	138.3	$W-C_{av}$	229.3	230.3
		$C-C_{min}$	139.8(9)	137.0(9)
		$C-C_{max}$	143.5(9)	142(1)
		$C-C_{av}$	141.6	140.8

complexes and of the dialkyl derivatives (cf. **9** and Cp_2WMe_2, **6** and **2**) are rather similar, in accord with the cyclopropane formulation of metallocene olefin complexes (see in particular a discussion of NMR data for molybdenocene complexes [33]).

Discussion

This paper gives the first detailed account of thermal insertion reactions of **1** with activated olefins. In a short note the reaction of **1** with diethyl maleate [9] was reported to give (at 50 °C [12]; misprint?) the alkyl hydrido complex $Cp_2WH[\eta^1$-$CH(CO_2Et)CH_2CO_2Et]$ (cf. **3**) and the fumaric acid ester complex $Cp_2W[\eta^2$-(E)-$CH(CO_2Et)$=$CHCO_2Et]$. The same note also reported the slow thermal decomposition of the alkyl hydrido complex in benzene (120 °C, 6 h) to give Cp_2WHPh (10%), fumarate complex, **1**, and diethyl succinate [9]. The apparent inconsistencies with our work seem to arise from differences in the experimental conditions used; unfortunately details of those used in the earlier work were not given.

The tungstenocene alkyl hydrido complexes **2**–**5** belong to the rare class of *cis*-alkyl hydrido metal complexes [34]. They are thermally more stable than Cp_2WHMe (slow decomposition at 60 °C), for which the reductive elimination of CH_4 has been studied in detail [34,35].

Tungstenocene olefin complexes are rare. Examples include the complexes of ethylene [17,36–38], propene [17,18], complexes **9**–**11** described in the present paper, and some complexes of olefins containing functional groups. Compounds of the last type can be made by one of three routes. (i) Thermal reaction of **1** and activated olefins give olefin complexes when sufficiently high reaction temperatures and long reaction times are used; an example is the synthesis of the diethyl fumarate complex [9] and of the acrylonitrile complex **8**. (ii) The same overall reaction can be induced photochemically, as recently demonstrated by the syntheses of the maleic anhydride complex and of the maleo/fumarodinitrile complexes [10]. (iii) Insertion of activated acetylenes into **1** followed by rearrangement; this is the route used here to give complexes **6** and **7**, and in earlier work to give dimethyl maleate and dimethyl fumarate complexes [22].

Very little is known about tungstenocene acetylene complexes. Prior to our preparation of the tolan complexes **12** and **13** only the two 2-butyne complexes $Cp_2W(\eta^2\text{-}C_2Me_2)$ [36,39] and $[Cp_2WMe(\eta^2\text{-}C_2Me_2)]PF_6$ [40] had been described.

Experimental

Reactions were carried out under dinitrogen by Schlenk techniques. Hexane was distilled from Na/K alloy; toluene, ether, and THF were distilled from sodium benzophenone ketyl. Dioxygen in solvents was removed by repeated distillation under dinitrogen. Alumina for chromatography (Woelm, N-Super O) was degassed *in vacuo* at 300 °C and deactivated with water (7%). Melting points were determined under dinitrogen and are uncorrected. NMR spectra were recorded on a Bruker WP-80 SY (^1H) or a Bruker WH-270 (^{13}C) instrument. Cyclic voltammetry was performed with a PAR Model 173 potentiostat and a Model 175 programmer. Cyclic voltammograms were recorded with a trielectrode cell containing a Pt working electrode, a Pt auxiliary electrode, and a SCE reference electrode and in acetonitrile solution ($\approx 10^{-3}$ *M*) with $(NBu_4)PF_6$ (≈ 0.1 *M*) as the supporting electrolyte.

Bis(η^5-cyclopentadienyl)hydrido{η^1-[1-(methoxycarbonyl)ethyl]}tungsten (2)

A solution of **1** (1.42 g, 4.49 mmol) and methyl acrylate (3.80 g, 44.9 mmol) in toluene (20 ml) was stirred at 120 °C for 3 h. After removal *in vacuo* of all volatiles the residue was dissolved in ether. Filtration to remove some black material, reduction of the volume to 30 ml, and cooling to −50 °C gave, after 2 d, **2** (1.42 g, 79%) as orange-red, slightly air-sensitive crystals.

^{13}C-NMR (δ (ppm), vs. int. TMS, $J(^{13}C-^1H)$ (Hz), 67.88 MHz, C_6D_6): 80.75 (dquin, 181, 6.5, Cp); 80.46 (dquin, 181, 6.5, Cp); 186.80 (s, CO); 49.58 (q, 144, OMe); 26.78 (q, 123, Me); −7.21 (d, 128, CH). IR (KBr): ν(WH) 1890m, ν(CO) 1660s cm^{-1}.

Bis(η^5-cyclopentadienyl)hydrido{η^1-[1,2-bis(methoxycarbonyl)ethyl]}tungsten (3)

A solution of **1** (2.0 g, 6.34 mmol) and dimethyl maleate (4.7 g, 15.5 mmol) in toluene (60 ml) was stirred at 120 °C for 15 h. Removal of some black material and reduction of the volume to 20 ml gave crystals of dimethyl fumarate. The supernatant solution was evaporated to dryness. The residue was recrystallized from ether to give **3** (1.62 g, 56%) as orange-red, slightly air-sensitive crystals. The reaction mixture can also be worked up by chromatography on alumina with toluene to elute the dimethyl fumarate and toluene–ether (1/1) to elute **3**.

^{13}C-NMR (δ (ppm), vs. int. TMS, $J(^{13}C-^1H)$ (Hz), 67.88 MHz, C_6D_6): 81.05 (dquin), 181, 6.5, Cp); 80.37 (dquin, 181, 6.5, Cp); 185.38 (s, CO); 175.35 (s, CO); 50.67 (q, 145, OMe); 49.84 (q, 145, OMe); 46.67 (t, 127, CH_2); −5.15 (dt, 134, 5, CH). IR (KBr): ν(WH) 1830m br, ν(CO) 1725s, 1670s cm^{-1}.

Bis(η^5-cyclopentadienyl)hydrido{η^1-[1-(methoxycarbonyl)-2-phenylethyl]}tungsten (4)

A solution of **1** (0.63 g, 1.99 mmol) and methyl cinnamate (4.30 g, 26.5 mmol) in toluene (15 ml) was stirred at 120 °C for 11 d. The mixture was worked up by chromatography on alumina with hexane to elute unconsumed starting materials and toluene–ether (1/1) to elute a brown product. Crystallization from ether (50 ml) at −50 °C gave, after 7 d, **4** (0.33 g, 35%) as yellow-orange crystals.

^{13}C-NMR (δ (ppm), vs. int. TMS, $J(^{13}C-^{1}H)$ (Hz), 67.88 MHz, C_6D_6): 80.84 (dm 181, Cp); 80.50 (dm, 181, Cp); 185.4 (s, CO); 157.9 (s, C_{ipso}); 49.61 (q, 144,OMe); 48.41 (t, 128, CH_2); 3.41 (dd, 130, 5.4, CH); Ph, partially hidden by solvent signal. IR (KBr): ν (WH) 1911s, ν(CO) 1671s cm^{-1}.

Bis(η^5-cyclopentadienyl)hydrido[η^1-(1-cyanoethyl)]tungsten (5)

A solution of **1** (0.60 g, 1.89 mmol) and acrylonitrile (0.13 g, 2.45 mmol) in toluene (20 ml) was stirred at 120 °C for 1 h. Removal of all volatiles and redissolution of the residue in toluene, followed by filtration, concentration, and cooling to −50 °C gave, after 2 d, **5** (0.43 g, 62%) as yellow crystals.

^{13}C-NMR (δ (ppm), vs. int. TMS, $J(^{13}C-^{1}H)$ (Hz), 67.88 MHz, C_6D_6): 81.29 (dquin, 181, 6.5, Cp), 80.73 (dquin, 181, 6.5, Cp); 133.67 (d, 4.7, CN); 27.45 (qd, 125.5, 8, Me); −31.2 (dq, 133, 6, CH). IR (KBr): ν(CN) 2190s, ν(WH) 1940m br cm^{-1}.

Bis(η^5-cyclopentadienyl)(η^2-acrylonitrile)tungsten (8)

A solution of **1** (1.31 g, 4.15 mmol) and acrylonitrile (2.2 g, 41.5 mmol) in toluene (40 ml) was stirred at 120 °C for 15 h. Work-up as for **5** and crystallization from toluene at −20 °C afforded **8** (1.28 g, 84%) as red-brown, somewhat air-sensitive crystals.

^{13}C-NMR (δ (ppm), vs. int. TMS, $J(^{13}C-^{1}H)$ (Hz), 67.88 MHz, C_6D_6): 81.69 (dquin, 181, 6, Cp); 79.02 (dquin, 180, 6, Cp); −2.01 (t, 152, CH_2); −17.36 (d, 158, CH); CN, not observed. IR (KBr): ν(CN) 2170s cm^{-1}.

Bis(η^5-cyclopentadienyl){η^2-[(E)-1,2-diphenylethylene]}tungsten (9)

A solution of **1** (1.87 g, 5.91 mmol) and 1,2-diphenylethyne (1.05 g, 5.91 mmol) in toluene (15 ml) was stirred at 110 °C for 15 h. The mixture was filtered to remove black material and then worked up by chromatography on alumina. Elution with hexane–THF (10/1) developed a red band giving a dark red solution of **12** (50 mg, 2%) and elution with toluene–THF (10/1) developed the orange main band. The eluate was dried with Na_2SO_4, concentrated, and cooled to −20 °C to give **9** (1.71 g, 61%) as red crystals.

^{13}C-NMR (δ (ppm), vs. int. TMS, $J(^{13}C-^{1}H)$ (Hz), 67.88 MHz, C_6D_6): 80.3 (dm, 180, J(WC) 8, 2Cp); 19.0 (d, 143, J(WC) 32, 2CH=); Ph: 153.4 (t, 7, $2C_i$); 128.1 (d) and 127.8 (d, 157, $4C_o$ and $4C_m$, partially obscured by solvent signals); 123.0 (dt, 157, 8, $2C_p$).

Bis(η^5-cyclopentadienyl)[η^2-(1,2-diphenylethyne)]tungsten (12)

(a) A melt of tolan (4.08 g, 22.9 mmol) and **1** (2.415 g, 7.64 mmol) was stirred at 150 °C for 2 h. The mixture was worked up by chromatography on alumina. Hexane–toluene (1/1) was used to elute a yellow forerun of unidentified material. Elution with pure toluene followed by crystallization from hexane gave **12** (0.87 g, 23%). Further elution with toluene–THF (10/1) and crystallization from toluene–hexane (1/1) afforded **9** (1.29 g, 56%).

(b) A Schlenk tube (Duran glass) was charged with **1** (1.00 g, 3.2 mmol), tolan (1.69 g, 9.5 mmol), and ether (100 ml). The solution was stirred and irradiated by means of a mercury lamp (TQ 150, Original Hanau, 150 W) for 93 h. Chromatographic work-up as above produced a yellow and an orange forerun, a yellow band of unconsumed **1** (0.41 g, 41%), and a red band of **12** (250 mg, 16%).

^{13}C-NMR (δ (ppm), vs. int. TMS, $J(^{13}C-^{1}H)$ (Hz), 67.88 MHz, C_6D_6): 80.3 (dm, 179, 2Cp), 126.3 (t, 5, 2C≡); Ph: 138.1 (t, 7, $2C_i$); 131.6 (dt, 158, 7, $4C_o$); 128.4 (dd, 158, 8, $4C_m$); 126.6 (dt, 161, 7, $2C_p$). IR (KBr); ν(C≡C) 1736m cm^{-1}.

Bis(η^5-cyclopentadienyl)[η^2-(phenylethylene)]tungsten (11)

A solution of **1** (1.80 g, 5.7 mmol) and phenylacetylene (2.1 ml, 20 mmol) in toluene (40 ml) was heated under reflux for 15 h. Removal of all volatiles followed by chromatography of the residue on alumina first with hexane as eluent then with toluene–THF (10/1) gave a brown band which upon crystallization afforded **11** (0.24 g, 10%, not always reproducible) as a dark red powder.

^{13}C-NMR (δ (ppm), vs. int. TMS, $J(^{13}C-^{1}H)$ (Hz), 67.88 MHz, C_6D_6): 78.68 (dquin, 179, 6.5, Cp); 77.88 (dquin, 179, 6.5, Cp); 18.44 (d, 145, CH); −3.30 (t, 148, CH_2); Ph, 129.5–126.0, not resolved.

{Bis(η^5-cyclopentadienyl)[η^2-(1,2-diphenylethyne)]hydridotungsten} hexafluorophosphate (13)

A Schlenk tube was charged with **12** (142 mg, 0.29 mmol) in toluene (5 ml), NH_4PF_6 (0.33 g, 2.0 mmol), and CF_3CO_2H (0.5 ml) in water (30 ml) and thoroughly shaken. A light yellow precipitate formed. This was collected, washed with water and ether, and dried. Recrystallization from CH_2Cl_2–ether gave **13** (127 mg, 69%) as light yellow needles.

[Bis(η^5-cyclopentadienyl){η^2-[(E)-1,2-diphenylethylene)]}hydridotungsten]hexafluorophosphate (14)

The procedure used to make **13** was used but starting from **9** (173 mg, 0.35 mmol), NH_4PF_6 (0.29 g, 1.8 mmol), and CF_3CO_2H (0.1 ml) gave **14** (145 mg, 65%) as a light yellow powder; it decomposes slowly in acetone or CH_2Cl_2 solutions.

Bis(η^5-cyclopentadienyl)[η^2-(methyl acrylate)]tungsten (6)

A solution of **1** (2.43 g, 7.69 mmol) and methyl propiolate (0.82 ml, 9.2 mmol) in toluene (30 ml) was kept at 110 ° C for 15 h followed by chromatographic work-up on alumina. Hexane/THF (10/1) eluted ≈ 50 mg of an unidentified by-product ($m/z = 448$) and toluene–THF (10/1) developed an orange product band. Crystallization from ether–hexane at −20 ° C gave **6** (0.58 g, 19%) as orange-brown, slightly air-sensitive, crystals.

^{13}C-NMR (δ (ppm), vs. int. TMS, $J(^{13}C-^{1}H)$ (Hz), 67.88 MHz, C_6D_6): 79.8 (dquin, 181, 7, Cp); 79.0 (dquin, 180, 7, Cp); 50.3 (q, 145, OMe); 7.5 (d, 150, CH); −1.1 (t, 150, CH_2); CO, not observed. IR (KBr): ν(CO) 1715s, 1210s cm^{-1}.

Bis(η^5-cyclopentadienyl)(η^2-butynone)tungsten (7)

A solution of **1** (2.46 g, 7.78 mmol) and butynone (0.64 g, 9.3 mmol) in toluene (25 ml) was kept at 110 ° C for 15 h then filtered, then subjected to chromatography on alumina. Elution with toluene–THF (10/1) gave a yellow forerun, immediately followed by the red product band. Crystallization from toluene–hexane at −20 ° C gave **7** (1.0 g, 30%) as dark red, slightly air-sensitive crystals.

^{13}C-NMR (δ (ppm), vs. int. TMS, $J(^{13}C-^{1}H)$ (Hz), 67.88 MHz, C_6D_6): 80.5

(dquin, 180, 6, Cp); 78.9 (dquin, 179, 6, Cp); 29.8 (q, 126, Me); 22.7 (d, 146, CH); -1.8 (t, 150, CH_2); CO, not observed. IR (KBr): ν(CO) 1610s cm^{-1}.

*Bis(η^5-cyclopentadienyl)hydrido{η^1-[1-(trifluoromethyl)vinyl]}tungsten (**15**) and bis(η^5-cyclopentadienyl)fluoro{η^1-[1-(trifluoromethyl)vinyl]}tungsten (**16**)*

An ampoule was charged with toluene (15 ml) and **1** (1.0 g, 3.12 mmol), then at $-80\,^\circ C$ with $CF_3C\equiv CH$, prepared from $CF_3CCl{=}CCl_2$ (7.5 g, 38 mmol) and zinc [41]. The ampoule was cooled with liquid nitrogen, sealed and kept at 90 °C for 50 h. Removal of the volatiles was followed by chromatography on alumina. Elution with pentane–CH_2Cl_2 (2/1) gave a yellow band; crystallization from pentane afforded **15** (92 mg, 7%) as yellow crystals. Elution with CH_2Cl_2–THF (2/1) gave a brown-black band containing unidentified material (50 mg). Elution with THF gave a red band; crystallization from toluene gave **16** (214 mg 16%) as red crystals, moderately soluble in toluene.

15: ^{19}F-NMR (75.26 MHz, toluene-d_8): $\delta(^{19}F)$ -63.20 ppm, vs. $CFCl_3$. IR (KBr): ν(WH) 1938w, ν(C=C) 1585w, ν(CF) 1237vs cm^{-1}.

16: ^{19}F-NMR (75.26 MHz, toluene-d_8): $\delta(^{19}F)$ -495.02br (WF), -56.51br (CF_3) ppm, vs. $CFCl_3$. IR (KBr): ν(C=C) 1582w, ν(CF) 1234vs cm^{-1}.

*Chlorobis(η^5-cyclopentadienyl){η^1-[1-(methoxycarbonyl)ethyl]}tungsten (**17**)*

Chloroform (10 ml) was added to a solution of **2** (2.12 g, 5.27 mmol) in ether (200 ml). The mixture was kept at ambient temperature for 15 h during which **17** (1.75 g, 75%) separated as dark red crystals, insoluble in ether.

^{13}C-NMR (δ (ppm), vs. int. TMS, $J(^{13}C-^{1}H)$ (Hz), 67.88 MHz, C_6D_6): 93.07 (dquin, 183, 6.5, Cp); 92.41 (dquin, 183, 6.5, Cp); 187.29 (s, CO); 49.84 (q, 145, OMe); 18.76 (q, 127, Me); -2.31 (d, 132, CH). IR (KBr): ν(CO) 1672s cm^{-1}.

*Chlorobis(η^5-cyclopentadienyl){η^1-[1,2-bis(methoxycarbonyl)ethyl]}tungsten (**18**)*

A solution of **3** (0.33 g, 0.72 mmol) in $CHCl_3$ (10 ml) was kept at ambient temperature for 15 h. Removal of the solvent followed by crystallization from CH_2Cl_2/ether gave **18** (0.28 g, 81%) as reddish-purple, air-stable crystals.

IR (KBr): ν(CO) 1726s, 1672s cm^{-1}.

*Determination of the structure of **4***

A single crystal of dimensions 0.3 · 0.1 · 0.1 mm was grown from a solution of **4** in toluene/hexane. Both geometry and intensity data were collected on an Enraf Nonius CAD4 diffractometer using Mo-K_α radiation with a graphite crystal monochromator (λ 70.93 pm). Crystal data: $C_{20}H_{22}O_2W$; M 478.3 g mol^{-1}, monoclinic, space group: $P2_1/c$ (No. 14), a 1297.1(2), b 764.6(3), c 1727.0(4) pm, β 102.27(1)°, V 1.674(1) nm^3, Z 4, d_c 1.899 g cm^{-3}, μ(Mo-K_α) 70.6 cm^{-1}, $F(000)$ 928. 3709 reflections were recorded at 20 °C by the ω scan method ($2 \leqslant \theta \leqslant 26°$). An empirical absorption correction was applied using psi scan data [42]. The structure was solved by Patterson and difference Fourier methods [43]. In the final full-matrix refinement, non-hydrogen atoms were refined with anisotropic thermal parameters, the tungsten-bonded H(1) was refined isotropically, and all other hydrogen atoms were included riding in standard positions (C–H 98 pm); a secondary extinction correction was applied [44]. Refinement converged at R 0.026, R_w 0.032 (statistical weights) with 213 refined parameters for 2664 unique reflections with $I > 2\sigma(I)$. A final difference Fourier map showed a local maximum of 0.8 e $Å^{-3}$ close to the tungsten atom. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technischen Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55266, the names of the authors, and the journal reference.

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