

18. (Cycloheptatrienyl)hydridotungsten Complexes

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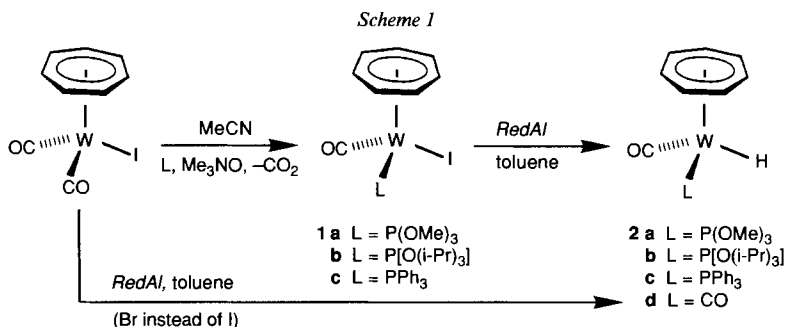
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(19.X.90)

Carbonyl(cycloheptatrienyl)iido(phosphorus donor)tungstens ($[\text{WI}(\text{C}_7\text{H}_7)(\text{CO})\text{L}]$; $\text{L} = \text{P}(\text{OMe})_3$, **1a**; $\text{L} = \text{P}[\text{O}(\text{i-Pr})]_3$, **1b**; $\text{L} = \text{PPh}_3$, **1c**) were prepared from dicarbonyl(cycloheptatrienyl)iidotungsten ($[\text{WI}(\text{C}_7\text{H}_7)(\text{CO})_2]$) *via* a carbonyl-substitution process. Similarly, bromocarbonyl(phosphorus donor)(1,2,4,6-tetramethylcycloheptatrienyl)tungstens ($[\text{WBr}(\text{Me}_4\text{C}_7\text{H}_3)(\text{CO})\text{L}]$; $\text{L} = \text{P}(\text{OMe})_3$, **6a**; $\text{L} = \text{P}[\text{O}(\text{i-Pr})]_3$, **6b**; $\text{L} = \text{PPh}_3$, **6c**) were obtained from the reaction of bromodicarbonyl(1,2,4,6-tetramethylcycloheptatrienyl)tungsten ($[\text{WBr}(\text{Me}_4\text{C}_7\text{H}_3)(\text{CO})_2]$; **4**) with L . The reduction of **1a–c**, **4**, and **6a,b** with sodiumdihydrido-bis(2-methoxyethoxy)aluminium in toluene led to stable hydrido complexes $[\text{WH}(\text{R}_4\text{C}_7\text{H}_3)(\text{CO})\text{L}]$ ($\text{R} = \text{H}$, $\text{L} = \text{P}(\text{OMe})_3$, **2a**; $\text{R} = \text{H}$, $\text{L} = \text{P}[\text{O}(\text{i-Pr})]_3$, **2b**; $\text{R} = \text{H}$, $\text{L} = \text{PPh}_3$, **2c**; $\text{R} = \text{Me}$, $\text{L} = \text{P}(\text{OMe})_3$, **7a**; $\text{R} = \text{Me}$, $\text{L} = \text{P}[\text{O}(\text{i-Pr})]_3$, **7b**; $\text{R} = \text{Me}$, $\text{L} = \text{CO}$, **7d**). Complexes **2a** and **7b** were characterized by X-ray structure analyses.

Introduction. – In recent papers, we have reported about the activating influence of NO ligands on M–H bonds [1–4]. In order to further test the hypothesis that hydride complexes with odd-electron ligands and the odd electron in an antibonding orbital can achieve enhanced reactivity of the transition-metal–hydrogen bond, we focussed on the synthesis of (cycloheptatrienyl)hydridotungsten complexes. Among related systems with VIb transition metal centers, *Green* and coworkers reported the $[\text{MoH}(\text{C}_7\text{H}_7)(\text{dppe})]$ compound ($\text{dppe} = \text{ethane-1,2-diybis[diphenylphosphane]}$) [5], which appeared quite stable at room temperature. Because of that observation, it seemed appropriate to attempt syntheses of heavy-element hydride derivatives preferably with phosphorus-donor substitution in which stable M–H bonds could be expected.

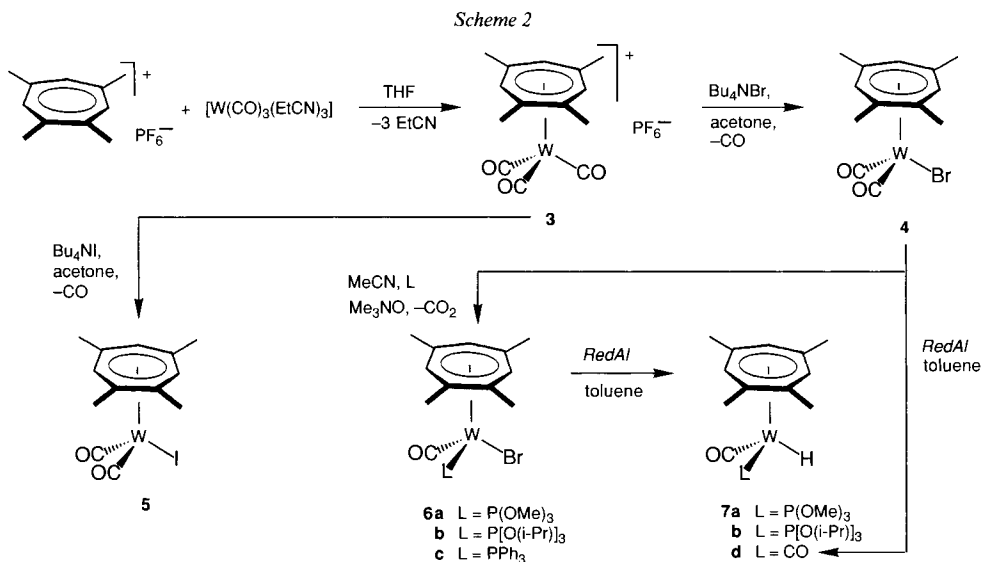
Results and Discussion. – Our goal of finding access to (cycloheptatrienyl)- or (1,2,4,6-tetramethylcycloheptatrienyl)hydridotungsten compounds with either CO or phosphorus donors in the ancillary ligand sphere was pursued by utilizing bromo or iodo derivatives as key intermediates, as shown in *Scheme 1*. In the cycloheptatrienyl series, we



started from $[\text{W}(\text{C}_7\text{H}_7)(\text{CO})_2]$ [6] and its phosphorus-donor substitution products $[\text{W}(\text{C}_7\text{H}_7)(\text{CO})\text{L}]$, with $\text{L} = \text{P}(\text{OMe})_3$ (**1a**), $\text{P}[\text{O}(\text{i-Pr})]_3$ (**1b**), and PPh_3 (**1c**). Complexes **1a** and **1b** were obtained by oxidative decarbonylation of $[\text{W}(\text{C}_7\text{H}_7)(\text{CO})_2]$ with Me_3NO in MeCN in the presence of the ligand L . The triphenylphosphane derivative **1c** was accessible according to a literature procedure [7].

When compounds **1a–c** were treated with sodiumdihydrido-bis(2-methoxyethoxy)-aluminium (*RedAl*) in toluene, the green carbonyl(cycloheptatrienyl)hydrido-(phosphorus donor)tungsten compounds **2a–c** were isolated in a pure state after chromatography. Dicarbonyl(cycloheptatrienyl)hydridotungsten (**2d**) could be detected $^1\text{H-NMR}$ spectroscopically by reacting $[\text{WBr}(\text{C}_7\text{H}_7)(\text{CO})_2]$ with *RedAl*, but due to a fast decomposition process at room temperature, isolation was prevented.

We also developed a synthetic access to carbonylhydrido(phosphorus donor)(1,2,4,6-tetramethylcycloheptatrienyl)tungsten compounds **7a,b** and **7d** (Scheme 2). The route to **7** required the synthesis of tricarbonyl(1,2,4,6-tetramethylcycloheptatrienyl)tungsten hexafluorophosphate (**3**) which was obtained in good yield from tricarbonyltris(propionitrile)tungsten [8] and 1,2,4,6-tetramethylcycloheptatrienylm hexafluorophosphate.



Complex **3** was then easily converted to the green halide derivatives **4** and **5** by a carbonyl/halide exchange process in acetone. As described in Scheme 1, we then succeeded in achieving a Me_3NO -induced phosphorus-donor substitution in **4** to yield complexes **6a–c**. Treatment of **4** and **6a,b** with *RedAl* in toluene led to **7a,b** and **7d** under mild conditions. Several attempts to transform **6c** under various conditions to hydrido-(triphenylphosphine)tungsten species **7c** were not met with success.

The structures of compounds **1–7** were all consistent with their spectroscopic data (see Table 1). The hydride complexes **2a–c** and **7a,b** showed quite remarkable NMR features. First of all, $\text{H}(\text{ring})$, $\text{C}(\text{ring})$, or CH_3 resonances appeared like those in **6a–c** at different chemical shifts or were in a few cases accidentally isochronous (see Table 1). Secondly, in

Table 1. ^1H - and ^{13}C -NMR spectra of Compounds 1–7

	^1H -NMR			^{13}C -NMR				
	δ [ppm] (group)		J [Hz] (multiplicity)		δ [ppm] (group)	J [Hz] (multiplicity)		
1a ^a)	5.21	(7H _{ring})	2.6	(<i>d</i>)	226.4	(CO)	20.1	(<i>d</i>)
	3.6	(3CH ₃ O)	11.1	(<i>d</i>)	87.8	(7C _{ring})	1.8	(<i>d</i>)
					53.2	(3CH ₃ O)		(<i>m</i>)
1b ^b)	5.21	(7H _{ring})	2.6	(<i>d</i>)	229.2	(CO)	20.1	(<i>d</i>)
	4.6	(3CHO)		(<i>m</i>)	87.8	(7C _{ring})		(<i>s</i>)
	1.26	(6CH ₃)	14.1, 6.1	(<i>dd</i>)	70.6	(3CHO)	6.1	(<i>d</i>)
2a ^b)	4.85	(7H _{ring})	2.8, 1.2	(<i>dd</i>)	23.9	(6CH ₃)	11.9, 3.4	(<i>dd</i>)
	3.3	(3CH ₃ O)	11.5	(<i>d</i>)	228.8	(CO)	18.6	(<i>d</i>)
	-4.82	(W,H)	84 J (W, H)		83.5	(7C _{ring})		(<i>s</i>)
			51 J (P, H)		51.7	(3CH ₃ O)		(<i>m</i>)
			1.2 J (H(ring), H)					
2b ^b)	4.91	(7H _{ring})	2.8, 1.2	(<i>dd</i>)	231.8	(CO)	17.1	(<i>d</i>)
	4.7	(3CHO)		(<i>m</i>)	83.6	(7C _{ring})		(<i>s</i>)
	1.17	(6CH ₃)	6.4	(<i>t</i>)	69.1	(3CHO)	3.3	(<i>d</i>)
	-4.61	(W,H)	83 J (W, H)		23.8	(6CH ₃)	2.9	(<i>d</i>)
			48 J (P, H)					
		1.2 J (H(ring), H)						
2c ^b)	7.6, 7.0	(3C ₆ H ₅)		(<i>m</i>)	233.9	(CO)	12.6	(<i>d</i>)
	4.67	(7H _{ring})	2.2, 1.3	(<i>dd</i>)	139.0	(C ₆ H ₅)	42.8	(<i>d</i>)
	-3.44	(W,H)	83 J (W, H)		134.5	(C ₆ H ₅)	11.2	(<i>d</i>)
			40 J (P, H)		130.0	(C ₆ H ₅)	1.9	(<i>d</i>)
		1.3 J (H(ring), H)		84.3	(7C _{ring})		(<i>s</i>)	
2d ^b)	4.52	(7H _{ring})		(<i>d</i>) ^d				
	-4.68	(W,H)		(<i>d</i>) ^d				
3 ^c)	6.345	(H _{ring})		(<i>s</i>)	200.8	(3CO)		(<i>s</i>)
	6.339	(H _{ring})		(<i>s</i>)	113.4, 100.2	(7C _{ring})		(<i>s</i>)
	6.176	(H _{ring})		(<i>s</i>)	98.4			
	3.02	(2CH ₃)		(<i>s</i>)	25.6	(2CH ₃)		(<i>s</i>)
	2.84	(2CH ₃)		(<i>s</i>)	24.5	(2CH ₃)		(<i>s</i>)
4 ^a)	5.03	(H _{ring})		(<i>s</i>)	212.5	(2CO)		(<i>s</i>)
	5.02	(H _{ring})		(<i>s</i>)	103.6, 98.4	(7C _{ring})		(<i>s</i>)
	4.72	(H _{ring})		(<i>s</i>)	94.8, 89.9			
	2.63	(2CH ₃)		(<i>s</i>)	26.1	(2CH ₃)		(<i>s</i>)
	2.28	(2CH ₃)		(<i>s</i>)	23.4	(2CH ₃)		(<i>s</i>)
5 ^a)	4.50	(H _{ring})		(<i>s</i>)	209.2	(2CO)		(<i>s</i>)
	4.99	(H _{ring})		(<i>s</i>)	102.0, 97.7	(7C _{ring})		(<i>s</i>)
	3.86	(H _{ring})		(<i>s</i>)	93.9, 89.4			
	2.66	(2CH ₃)		(<i>s</i>)	26.4	(2CH ₃)		(<i>s</i>)
	2.39	(2CH ₃)		(<i>s</i>)	24.2	(2CH ₃)		(<i>s</i>)
6a ^a)	4.9	(2H _{ring})		(<i>m</i>)	234.5	(CO)	19.5	(<i>d</i>)
	4.58	(H _{ring})		(<i>m</i>)	100.2, 97.3,			
	3.6	(2CH ₃ O)	11	(<i>d</i>)	97.0, 96.8, 92.4			
	2.55	(CH ₃)		(<i>s</i>)	89.6, 86.7	(7C _{ring})		
	2.48	(CH ₃)		(<i>s</i>)	52.5	(3CH ₃ O)	4.5	(<i>d</i>)
	2.26	(CH ₃)		(<i>s</i>)	26.2, 25.1	(2CH ₃)		(<i>s</i>)
	2.24	(CH ₃)		(<i>s</i>)	23.5, 23.3	(2CH ₃)		(<i>s</i>)

Table 1 (cont.)

	¹ H-NMR			¹³ C-NMR			
	δ [ppm] (group)	<i>J</i> [Hz] (multiplicity)		δ [ppm] (group)	<i>J</i> [Hz] (multiplicity)		
6b^a	4.86	(2H _{ring})	(<i>m</i>)	236.8	(CO)	19.5	(<i>d</i>)
	4.68	(3CHO)	(<i>m</i>)	100.3, 98.5,			
	4.51	(H _{ring})	(<i>m</i>)	97.6, 94.9, 91.1,			
	2.5	(CH ₃)	(<i>s</i>)	89.5, 86.9	(7C _{ring})		
	2.49	(CH ₃)	(<i>s</i>)	69.9	(3CHO)	6.6	(<i>d</i>)
	2.23	(CH ₃)	(<i>s</i>)	25.9, 25.1	(2CH ₃)		(<i>s</i>)
	2.21	(CH ₃)	(<i>s</i>)	24.1	(6CH ₃)	6	(<i>d</i>)
6c^a	1.25	(6CH ₃)	13.5, 6.1	(<i>dd</i>)	23.3, 23.1	(2CH ₃)	(<i>s</i>)
	7.5	(C ₆ H ₅)	(<i>m</i>)	238.2	(CO)	11	(<i>d</i>)
	7.3	(C ₆ H ₅)	(<i>m</i>)	136.4, 135.6, 134.7,			
	4.67	(H _{ring})	(<i>m</i>)	134.5, 129.9,	(3C ₆ H ₅)		
	4.61	(H _{ring})	(<i>m</i>)	128.0, 101.6, 100.5,			
	4.44	(H _{ring})	(<i>m</i>)	95.9, 92.4, 91.4,			
	2.32	(CH ₃)	(<i>s</i>)	88.4, 86.7	(7C _{ring})		
	2.27	(CH ₃)	(<i>s</i>)	25.7	(CH ₃)		(<i>s</i>)
	2.17	(CH ₃)	(<i>s</i>)	24.2	(CH ₃)	1.3	(<i>d</i>)
	2.07	(CH ₃)	(<i>s</i>)	23.4	(2CH ₃)	1.5	(<i>d</i>)
	7a^b	4.85	(3H _{ring})	(<i>m</i>)	233.2	(CO)	18
3.38		(3CH ₃ O)	11.3	(<i>d</i>)	97.7, 96.8, 95.3,		
2.55		(CH ₃)	(<i>s</i>)	94.2, 88.0,			
2.52		(CH ₃)	(<i>s</i>)	86.2, 84.8	(7C _{ring})		
2.40		(CH ₃)	(<i>s</i>)	51.7	(3CH ₃ O)		(<i>s</i>)
2.35		(CH ₃)	0.9	(<i>d</i>)	27.6, 27.3	(2CH ₃)	(<i>s</i>)
-4.4		(W,H)	88 <i>J</i> (W, H) 54 <i>J</i> (P, H) 1.3 <i>J</i> (H(ring), H)	(<i>d</i>)	25.9, 25.8	(2CH ₃)	(<i>s</i>)
7b^b		4.9	(2H _{ring})	(<i>m</i>)	235.2	(CO)	
	4.83	(H _{ring})	(<i>m</i>)	95.4, 94.3, 94.0,			
	4.7	(3CHO)	(<i>m</i>)	93.8, 89.3,			
	2.58	(CH ₃)	(<i>s</i>)	87.0, 85.7	(7C _{ring})		
	2.54	(CH ₃)	(<i>s</i>)	68.6	(3CHO)	4	(<i>d</i>)
	2.48	(CH ₃)	(<i>s</i>)	27.4, 27.1	(2CH ₃)		(<i>s</i>)
	2.39	(CH ₃)	(<i>s</i>)	26.0, 25.6	(2CH ₃)		(<i>s</i>)
	1.2	(6CH ₃)	(<i>m</i>)	24.0	(6CH ₃)	3.5	(<i>d</i>)
	-4.23	(W,H)	87 <i>J</i> (W, H) 53 <i>J</i> (P, H) 1 <i>J</i> (H(ring), H)	(<i>d</i>)			
7d^b	4.72	(2H _{ring})	(<i>t</i>) ^d	218	(CO)		(<i>s</i>)
	4.63	(H _{ring})	(<i>q</i>) ^d	99.2, 98.7,			(<i>s</i>)
	2.33	(2CH ₃)	(<i>s</i>)	89.6, 87.4	(7C _{ring})		(<i>s</i>)
	2.13	(2CH ₃)	(<i>s</i>)	27.0	(2CH ₃)		(<i>s</i>)
	-3.99	(W,H)	93 <i>J</i> (W, H) (<i>m</i>) ^d	25.3	(2CH ₃)		(<i>s</i>)

^a) Solvent: CDCl₃. ^b) Solvent: C₆D₆. ^c) Solvent: (D₆) acetone. ^d) *J* < 1 Hz.

contrast to **2d** and **7d**, a relatively strong $J(\text{H}(\text{metal}), \text{H}(\text{ring}))$ of > 1 Hz was noticeable in the spectra of **2a–c** and **7a,b**. This could be caused by either a normal 3J coupling, by a 2J coupling with direct contact of $\text{H}(\text{metal})$ to the ring, or a fast exchange equilibrium involving a species of type **2** or **7** and a short-lived triene-type 16-electron intermediate. Although there is not sufficient evidence for the preference of any of these cases at the moment, we would like to suggest that the latter mechanism is at work. First, there is precedence for the metal-to-ring migration of H-atoms and related one-electron residues in (cyclopentadienyl)metal chemistry [9], and secondly, we would expect that a chemical variation in the series of compounds **2** should show a noticeable NMR effect concomitant with the latter two coupling mechanisms. In fact **2d** does exhibit a very small $J(\text{H}(\text{metal}), \text{H}(\text{ring}))$ and a larger W,H coupling compared to **2c**.

X-Ray Crystal Structure of 2a and 7b. – Contributing to the search for unique structural features in organometallic compounds, we thought the (cycloheptatrienyl)-hydrido compounds **2** and **7** might be good examples of second-order *Jahn-Teller* distortion because of their green color and their obviously small HOMO/LUMO gap. We,

Table 2. *Crystal, Structure-Solution, and Refinement Data of 2a and 7b*

	2a	7b
Empirical formula	C ₁₁ H ₁₇ O ₄ PW	C ₂₁ H ₃₆ O ₄ PW
Color; habit	green cube	dark green prism
Crystal size	0.12 × 0.1 × 0.08 mm	0.15 × 0.20 × 0.50 mm
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i>	6.653(2) Å	17.402(9) Å
<i>b</i>	8.868(3) Å	8.283(4) Å
<i>c</i>	12.108(3) Å	17.676(9) Å
α	97.88(2)°	
β	104.08(2)°	109.32(4)°
γ	103.81(3)°	
Volume	658.2(3) Å ³	2404(2) Å ³
<i>Z</i>	2	4
Formula weight	428.1	567.3
Density (calc.)	2.160 Mg/m ³	1.567 Mg/m ³
Absorption coefficient	9.083 mm ⁻¹	4.993 mm ⁻¹
<i>F</i> (000)	408	1132
Solution	direct methods (<i>Siemens</i> SHELXTL PLUS; <i>Micro</i> VAX II)	
Diffractionmeter	<i>Siemens</i> <i>R₃m/V</i>	
Radiation	MoK α ($\lambda = 0.71073$ Å)	
Temperature	216 K	235 K
Monochromator	highly oriented graphite crystal	
2θ Range	3.0–58.0°	6.0–58.0°
Scan type	ω	ω
Scan speed	variable; 1.50–15.00°/min in ω	variable; 2.50–15.00°/min in ω
Scan range (ω)	1.60°	1.80°
Independent reflections	3003 ($R_{\text{int}} = 1.50\%$)	5507 ($R_{\text{int}} = 1.55\%$)
Observed reflections	2804 ($F > 6.0\sigma(F)$)	4634 ($F > 6.0\sigma(F)$)
Absorption correction	semi-empirical	
Min./max. transmission	0.0564/0.1372	0.0379/0.0733
<i>R_F</i>	4.15	2.84
<i>R_F2</i>	5.00	2.83

therefore, carried out X-ray structure analyses on **2a** and **7b**. Crystals suitable for this purpose were obtained by slowly cooling hexane solutions of these complexes to -80° (for crystals, structure-solution, and refinement data of **2a** and **7b**, see *Table 2*). Complexes **2a** and **7b** show a three-legged piano-stool structure, in both cases with a nearly planar C_7 ring. Because of the large ring system, the normal from the tungsten center to the ring plane is quite short which causes steric contacts between the ring atoms and the sterically demanding ligand groups of the ML_3 unit (see the *Fig.*). As a consequence of that situa-

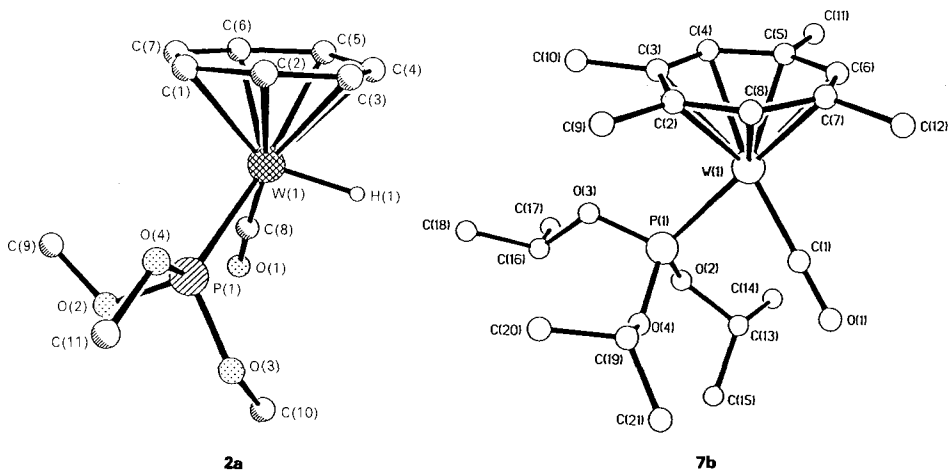


Figure. Structure models of the compounds **2a** and **7b**

tion, in **2a** and **7b** a quite narrow stool-leg angle between the CO and the P-ligand and consequently a wide angle between the normal to the ring and these ligands result. This observation agrees well with comparable parameters of the structures of $[MoBr(C_7H_7)(CO)_2]$ [10] and $[MoSn(C_7H_7)Cl_3]$ [11]. The metal-bound H-atom in **2a**, although not located reliably, is found almost eclipsed underneath a C(ring) atom. Trusting the H-position in **2a**, we even find it disposed towards the C_7 ring.

We thank the *Swiss National Science Foundation* for financial support.

Experimental Part

General. All reactions were carried out under dry N_2 . Et_2O , toluene, and THF were distilled from Na/benzophenone, CH_2Cl_2 was distilled from CaH_2 and acetone from P_2O_5 . Chromatography: silica gel 60 (*Merck*). $[W(CO)_3(EtCN)_3]$ [8], $[Fe(Cp)_2]BF_4$ [12], $[W(C_7H_7)(CO)_2]$ [6], $[WBr(C_7H_7)(CO)_2]$ [13], and $[W(C_7H_7)(CO)(PPh_3)]$ [7] were prepared as described in the literature. IR spectra (cm^{-1}): *Biorad FTS 45*. 1H and ^{13}C -NMR spectra: *Varian Gemini-200*. MS: *Finnigan MAT 8240*.

1,2,4,6-Tetramethylcycloheptatrienyl Hexafluorophosphate. A soln. of 1,3,5-trimethyl-6-methylidenetricyclo-[3.2.1.0^{2,7}]oct-3-en-8-one [14] (17.3 g, 0.1 mol) in 30 ml of hexane was dropped slowly into 50 ml of boiling CF_3COOH . The soln. was refluxed for 15 min and then poured into a soln. of $(NH_4)PF_6$ (20 g, 0.12 mol) in 400 ml of ice-water. The mixture was stirred very rapidly (\rightarrow brown precipitate). The precipitate was filtered off and

washed with H₂O to neutrality (pH ca. 7) and then with Et₂O to remove the brown impurities: 16.9 g (58%) of colorless powder.

Tricarbonyl(1,2,4,6-tetramethylcycloheptatrienyl)tungsten Hexafluorophosphate (3). A soln. of [W(CO)₃(EtCN)₃] (4.3 g, 10 mmol), 1,2,4,6-tetramethylcycloheptatrienyl hexafluorophosphate (2.92 g, 10 mmol), and [Fe(Cp)₂]BF₄ (0.27 g, 1 mmol) in 100 ml of THF was stirred at r.t. for 2 h. The product precipitated as a fine orange powder. This was filtered off and recrystallized from CH₂Cl₂ at –30° to give 4.3 g (77%) of **3** as orange crystals. IR (CH₂Cl₂): 2055, 1998 (CO). FAB-MS: 414 (100, [M – PF₆]⁺), 386 (11), 358 (5), 330 (4).

Dicarbonylhalogeno(1,2,4,6-tetramethylcycloheptatrienyl)tungsten Complexes 4 and 5. To an orange soln. of **3** (2 g, 3.6 mmol) in 30 ml of acetone was added at 0° 3.6 mmol of tetrabutylammomium halogenide. The mixture was slowly warmed up to r.t. and stirred, until the evolution of CO was finished. After evaporation of the solvent, the product was separated from the tetrabutylammomium salts by chromatography (silica gel column, toluene). The green product fraction was evaporated and the residue recrystallized from Et₂O/hexane at –30°: pure product as green crystals.

Bromodicarbonyl(1,2,4,6-tetramethylcycloheptatrienyl)tungsten (4): Yield 0.8 g (48%). IR (CH₂Cl₂): 1985, 1926 (CO). MS: 468 (10, M⁺), 440 (22), 412 (84), 410 (100), 146 (63), 133 (70).

Dicarbonyliodo(1,2,4,6-tetramethylcycloheptatrienyl)tungsten (5): Yield 0.7 g (38%). IR (CH₂Cl₂): 1984, 1927 (CO). MS: 515 (12, M⁺), 487 (29), 459 (71), 457 (87), 146 (94), 131 (91).

Preparation of 1a,b and 6a–c. The complexes [W(C₇H₇(CO)₂)] or [WBr(C₁₁H₁₃(CO)₂)] (**4**; 10 mmol) were dissolved in MeCN and 11 mmol of phosphite or phosphane were added at r.t. After stirring for 1 h, the color of the soln. changed from green to dark red. To the stirred soln. was added Me₃NO (1.33 g, 12 mmol) at r.t. After the evolution of CO₂ had stopped and only one CO band was detected in the IR, the mixture was filtered through *Celite* and evaporated. The green-brown residue was chromatographed at –20° over a 200-ml column (silica gel, CH₂Cl₂/hexane 2:1). The green (**1a,b**, **6a,b**) or brown (**6c**) product fraction was evaporated.

Carbonyl(cycloheptatrienyl)iido(trimethyl phosphite)tungsten (1a): Green crystals. Yield: 3.5 g (64%). IR (CH₂Cl₂): 1923 (CO). MS: 554 (18, M⁺), 526 (82), 402 (100), 376 (48), 291 (70), 124 (16).

Carbonyl(cycloheptatrienyl)iido(triisopropyl phosphite)tungsten (1b): Yellow-green crystals. Yield 4.3 g (67%). IR (CH₂Cl₂): 1920 (CO). MS: 638 (31, M⁺), 610 (96), 402 (52), 291 (100).

Bromocarbonyl(1,2,4,6-tetramethylcycloheptatrienyl)(trimethyl phosphite)tungsten (6a): Green crystals. Yield 3.3 g (59%). IR (CH₂Cl₂): 1893 (CO). MS: 564 (20, M⁺), 536 (82), 412 (94), 347 (32), 147 (30).

Bromocarbonyl(1,2,4,6-tetramethylcycloheptatrienyl)(triisopropyl phosphite)tungsten (6b): Green crystals. Yield 3.6 g (56%). IR (CH₂Cl₂): 1881 (CO). MS: 648 (19, M⁺), 620 (79), 618 (100), 410 (48), 347 (96).

Bromocarbonyl(1,2,4,6-tetramethylcycloheptatrienyl)(triphenylphosphane)tungsten (6c): Brown crystals. Yield 3.3 g (47%). IR (CH₂Cl₂): 1884 (CO). MS: 702 (11, M⁺), 700 (24), 674 (44), 672 (95), 491 (21), 409 (100), 347 (48).

Hydrido Complexes 2a–c and 7a,b. To a green-brown soln. of 2 mmol of the halogeno complex **1a–c** or **6a,b** in 100 ml of toluene was added at 0° 4.5 ml of 0.5M sodiumdihydridobis(2-methoxyethoxy)aluminium (*RedAl*) in toluene. The soln. was slowly warmed up to r.t. and stirred until no more starting material was detected in the IR (0.5–3 h). The bright green soln. was again cooled to 0°, and some ice was added to destroy the rest of the *RedAl*. The soln. was filtered through *Celite*, evaporated, and chromatographed at –20° (silica-gel column, CH₂Cl₂/hexane). The bright-green product fraction was concentrated and the product crystallized at –30° after addition of some hexane.

Carbonyl(cycloheptatrienyl)hydrido(trimethyl phosphite)tungsten (2a): Green crystals. Yield 0.56 g (65%). IR (hexane): 1904 (CO). MS: 428 (31, M⁺), 398 (38), 305 (20), 291 (100).

Carbonyl(cycloheptatrienyl)hydrido(triisopropyl phosphite)tungsten (2b): Green crystals. Yield 0.7 g (68%). IR (hexane): 1893 (CO). MS: 512 (22, M⁺), 511 (12), 334 (42), 291 (100), 208 (8), 91 (18).

Carbonyl(cycloheptatrienyl)hydrido(triphenylphosphane)tungsten (2c): Green crystals. Yield 0.94 g (83%). IR (hexane): 1876 (CO). MS: 566 (4, M⁺), 536 (36), 262 (100), 183 (89).

Carbonylhydrido(1,2,4,6-tetramethylcycloheptatrienyl)(trimethyl phosphite)tungsten (7a). Green crystals. Yield 0.68 g (79%). IR (hexane): 1888 (CO). MS: 428 (31, M⁺), 398 (38), 305 (20), 291 (100).

Carbonylhydrido(1,2,4,6-tetramethylcycloheptatrienyl)(triisopropyl phosphite)tungsten (7b): Green crystals. Yield 0.97 g (85%). IR (hexane): 1877 (CO). MS: 567 (38, [M – H]⁺), 509 (4), 390 (44), 347 (100).

Dicarbonylhydrido(1,2,4,6-tetramethylcycloheptatrienyl)tungsten (7d) was prepared from **4** in the same way as the hydrido complexes described above, with the exception that the entire reaction was carried out at 0°: 0.47 g (60%) of brown crystals. IR (hexane): 1976, 1915 (CO). MS: 388 (28, M⁺), 360 (20), 358 (20), 330 (100), 147 (74).

¹H-NMR Experiment for the Preparation of Dicarbonyl(cycloheptatrienyl)hydridotungsten (**2d**). One drop of 0.5M *RedAl* in toluene was layered over a soln. of [WBr(C₇H₇(CO)₂)] in C₆D₆ in a NMR tube. The solns. were mixed just before the measurement: **2d** was stable for ca. 15 min.

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