CH Activation of Complexed Cycloheptatriene: Synthesis and Structure of Heterobimetallic Hydrido Complexes with a *syn*-Coordinated Cycloheptatrienyl Bridge

Hubert Wadepohl,* Wolfgang Galm, and Hans Pritzkow

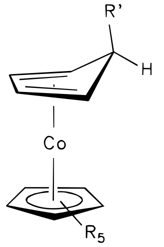
Anorganisch-Chemisches Institut der Ruprecht-Karls-Universität, Im Neuenheimer Feld 270,
D-69120 Heidelberg, Germany

Received July 10, 1995[⊗]

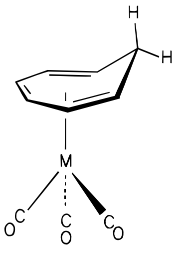
The heterodinuclear complexes [(CO)$_3$M(μ-H)(μ-C$_7$H$_7$)Co(η-C$_5$Me$_5$)] [**7** (M = Cr), **8** (M = Mo), **9** (M = W)] have been prepared from [(CO)$_3$M(η^6-C$_7$H$_8$)] [**2** (M = Cr), **3** (M = Mo), **4** (M = W)] and [(C$_5$Me$_5$)Co(C$_2$H$_4$)$_2$] (**5b**). The X-ray crystal structures of **7** and **8** have been determined. The boat-shaped bridging cycloheptatrienyl ligands adopt the η^4(M):η^3(Co) coordination in the crystalline state. The rather long M−Co vectors were found to be bridged by hydrido ligands, making up 3c−2e MHCo bonds. In solution, hindered rotation of the C$_7$H$_7$ ring was observed, which, in the case of **7**, could be frozen on the NMR time scale at 200 K.

Introduction

Coordination of a transition metal to the (CH)$_n$ π-system of cyclopentadiene (n = 4) and cycloheptatriene (n = 6) has a dramatic effect on the reactivity of the methylene groups of these ligands, even though the former is not directly involved in an interaction with the metal. For example, abstraction of hydride is a common reaction with [CpCo(η^4-C$_5$H$_6$)] (**1**) and [(CO)$_3$M(η^6-C$_7$H$_8$)] [**2** (M = Cr), **3** (M = Mo), **4** (M = W)].[1,2] Some activated alkynes[1d,3] and even styrene[4] stereospecifically insert into a methylene CH bond of **1a** to give *exo*-substituted derivatives. Intra- and interligand hydride shifts have been observed both in η^4-cyclopentadiene[1d] and η^6-cycloheptatriene complexes.[5] It appears that migration of the *endo* methylene hydrogen takes place during these rearrangements.[1d,5a]

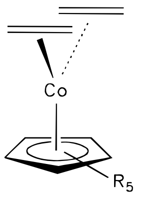


1a, R= R'= H
1b, R= Me, R'= H

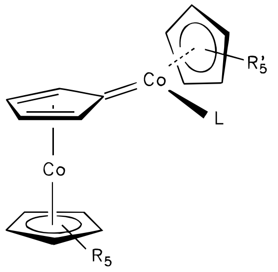


2, M= Cr
3, M= Mo
4, M= W

Some time ago we reported the facile cleavage of both methylene CH bonds of **1** upon reaction with the ethylene complexes [(C$_5$R$_5$)Co(C$_2$H$_4$)$_2$] (**5**) to give a series of unusual dicobalt complexes **6** with a cyclopentadienylidene bridge.[6] Although the CH activating properties of **5** are now well documented,[7,8] the ease of this reaction, which can take place already at room temperature, is quite exceptional for a saturated first-row transition metal complex such as **5**.



5a, R= H
5b, R= Me



6

Here we wish to describe the CH activation of η^6-cycloheptatriene in **2**−**4** with the (pentamethylcyclopentadiene)cobalt complex **5b**. A preliminary note on some of this work has appeared.[9]

Results

Syntheses. When equimolar petroleum ether solutions of **2** and the Jonas reagent **5a** were allowed to

---

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

[1] (a) Fischer, E. O.; Herberich, G. *Chem. Ber.* **1961**, *94*, 1517. (b) Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3753. (c) Pauson, P. L. *J. Organomet. Chem.* **1980**, *200*, 207. (d) Knox, G. R.; Nutley, M.; Pauson, P. L.; Thoma, S.; Watts, P. E.; Elder, P. E.; Griffiths R. *J. Chem. Res. (M)* **1981**, 1901.

[2] Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic Press: London, 1979; Chapters I and II and references cited therein.

[3] Kergoat, R.; Gomes de Lima, L. C.; Jégat, C.; Le Berre, N.; Kubicki, M. M.; Guerchais, J. E.; L'Haridon, P. L. *J. Organomet. Chem.* **1990**, *71*, 389.

[4] Wadepohl, H.; Büchner, K.; Herrmann, M.; Pritzkow, H. *Organometallics* **1991**, *10*, 861.

[5] (a) Roth, W. R.; Grimme, W. *Tetrahedron Lett.* **1966**, *21*, 2347. (b) Foreman, M. I.; Knox, G. R.; Pauson, P. L.; Todd, K. H.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1141. (c) Faller, J. W. *Inorg. Chem.* **1980**, *19*, 2857. (d) Brown, J. M.; Midgley, I.; Albery, W. J. *J. Chem. Soc., Perkin Trans. 2* **1982**, 767. (e) Green, M. L. H.; Newman, P. A.; Bandy, J. A. *J. Chem. Soc., Dalton Trans.* **1989**, 331.

[6] Wadepohl, H.; Pritzkow; H. *Angew. Chem.* **1987**, *99*, 132; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 127.

[7] (a) Wadepohl, H.; Borchert, T.; Büchner, K.; Pritzkow, H. *Chem. Ber.* **1993**, *126*, 1615. (b) Wadepohl, H.; Borchert, T.; Pritzkow, H. *J. Chem. Soc., Chem. Commun.* **1995**, 1447. (c) Wadepohl, H.; Gebert, S. *Coord. Chem. Rev.* **1995**, *143*, 535.

[8] Wadepohl, H. *Comments Inorg. Chem.* **1994**, *15*, 369.

[9] Wadepohl, H.; Galm, W.; Pritzkow, H. *Angew. Chem.* **1989**, *101*, 357; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 345.

0276-7333/96/2315-0570$12.00/0

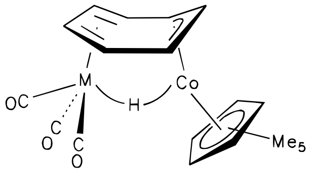
Table 1. ^{1}H NMR Data (200 MHz, δ at Ambient Temperature) for the Complexes [(CO)$_3$M(η-C$_5$Me$_5$)Co(μ-H)(μ-1−4-η^4:5−7-η^3-C$_7$H$_7$)] [7 (M = Cr), 8 (M = Mo), 9 (M = W)]

	7 (M = Cr)[a]	**8** (M = Mo)[b]	**9** (M = W)[b]
C$_5$Me$_5$	1.54 (s, 15H)	1.41 (s, 15H)	1.39 (s, 15H)
C$_7$H$_7$	2.92 (br s, 7H)	3.09 (br s, 7H)	3.00 (br s, 7H)
hydride	−10.18 (s, 1H)	−10.04 (s, 1H)	−10.39 (s, 1H, J(WH) = 35.5 Hz)

[a] In d_8-toluene. [b] In C$_6$D$_6$.

stand at room temperature, or slowly heated to 60 °C, deep brown mixtures were obtained. However, inspection of the IR and ^{1}H NMR spectra indicated a multitude of products, which could not be separated by chromatography or crystallization.

A color change to deep green developed when **2** was refluxed with the pentamethylcyclopentadienyl complex **5b** in petroleum ether for several hours. By repeated recrystallization from toluene the products of this reaction could be separated into the crystalline red-brown heterodinuclear complex **7** (about 20% yield) and a deep green mixture of unreacted **2** (15−20%) and [{Cp*Co(CO)}$_2$] (about 60%). Likewise, the MoCo and WCo complexes **8** and **9** were prepared from **3** and **4**, respectively, with **5b**. The yields of the heterodinuclear products increased on going down group 6 of the periodic table. Thus, 33% and 63% (based on the d^6-metal) of **8** and **9**, respectively, were isolated.



7, M = Cr
8, M = Mo
9, M = W

Because of the low yield of **7** attempts were made to synthesize this complex starting from the (η^4-cycloheptatriene)cobalt complex [Cp*Co(η^4-C$_7$H$_8$)], which was refluxed with [(CO)$_3$Cr(NCMe)$_3$] in thf for several hours. However, the only isolable products in this reaction were **2** and [Cp*Co(CO)$_2$]. Likewise, **2** and [CpCo(CO)$_2$] were obtained from the reaction of [CpCo(η^4- C$_7$H$_8$)] and [(CO)$_3$Cr(NCMe)$_3$] under similar conditions.

When treated with an excess of carbon monoxide at room temperature, **7** quantitatively gave the mononuclear complexes **2** and [Cp*Co(CO)$_2$]. In contrast, the WCo complex **9** did not react with CO or P(OMe)$_3$ (thf solution, room temperature).

Spectroscopic Characterization. Quite simple NMR spectra were obtained for **7**−**9** at room temperature (Tables 1 and 2). Only one broad resonance [δ(^{1}H) ~ 3, δ(^{13}C) = 68 (**7**, **8**), 65 (**9**)] was observed for the C$_7$H$_7$ ligand in the ^{1}H and ^{13}C NMR spectra at ambient temperature. A high-field resonance, integrating to a single hydride ligand, was observed at δ ~ −10. In the case of the tungsten complex **9** this signal was accompanied by satellites due to spin−spin coupling with the ^{183}W nucleus.

Low-temperature NMR spectroscopic data for **7** are summarized in Table 3. When the solution is cooled to 200 K, the C$_7$H$_7$ ^{1}H and ^{13}C resonances split into sets of four multiplets (^{1}H) or singlets (^{13}C). Likewise, the ^{13}C(O) resonance, which was a singlet at room temperature, split into two closely spaced signals at 190 K. No significant changes with temperature were observed for the resonances of the Cp* and hydride ligands.

Table 2. ^{13}C NMR Data (δ) for the Complexes [(CO)$_3$M(η-C$_5$Me$_5$)Co(μ-H)(μ-1−4-η^4:5−7-η^3-C$_7$H$_7$)] [7 (M = Cr), 8 (M = Mo), 9 (M = W)]

	mult[a]	**7** (M = Cr)[b]	**8** (M = Mo)[c]	**9** (M = W)[c]
C$_5$*Me*$_5$	g	8.9	9.9	9.2
C$_7$H$_7$	g	68.2	68.2	64.5
C$_5$Me$_5$	u	93.7	93.9	93.7
CO	u	237.9	227.3	218.7

[a] even (g) or odd (u) as determined by a J-modulated spin echo experiment. [b] In d_8-toluene, 300 K. [c] In C$_6$D$_6$.

Table 3. Low-Temperature NMR Data (δ) for the Complex [(CO)$_3$Cr(η-C$_5$Me$_5$)Co(μ-H)(μ-1−4-η^4:5−7-η^3-C$_7$H$_7$)] (7)

	^{1}H (200 K)	^{13}C (190 K)
C$_7$H$_7$	4.1 (br, 2H)	83.6
C$_7$H$_7$	2.7 (br, 2H)	66.6
C$_7$H$_7$	2.6 (br, 2H)	59.5
C$_7$H$_7$	1.5 (br, 1H)	56.5
C$_5$*Me*$_5$	1.38 (s, 15H)	8.7
C$_5$Me$_5$		93.2
hydride	−10.13 (s, 1H)	
CO		238.4, 238.2

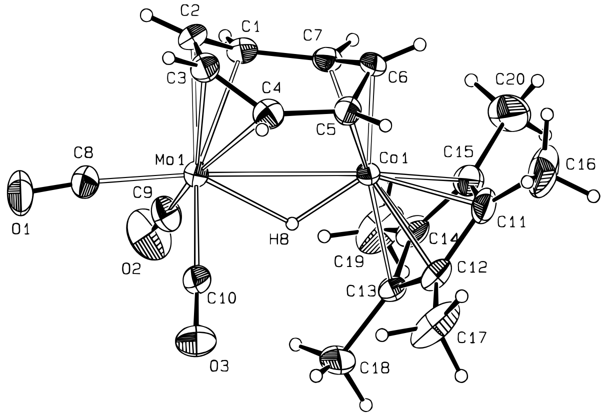


Figure 1. Molecular structure of **8**.

X-ray Crystallography. Single crystals of **7** and **8** were obtained from toluene solutions at −20 °C. Crystal details are given in the Experimental Section. The crystals are isomorphous, with a difference of 2% in the cell volumes. The molecular structure of **8** is shown in Figure 1. Positional and equivalent isotropic displacement parameters are given in Tables 4 and 5; important bond lengths and angles are in Tables 6 and 7.

Both structures consist of isolated molecules of approximate C_s symmetry. The overall molecular structures of **7** and **8** are very similar. A superposition is shown in Figure 2. Not surprisingly, the largest differences in length between equivalent bonds are found with those involving the d^6-metals M. M−C bonds are about 0.1 Å longer for M = Mo (**8**) than for M = Cr (**7**).

Of the cycloheptatrienyl ring, four carbon atoms are coordinated to M. The other three C$_7$ ring carbons are bonded to the Cp*Co group. The C$_7$H$_7$ rings adopt a boat conformation with fold angles between the metal-coordinated C$_4$ and C$_3$ units to the best plane through C(1), C(7), C(4), C(5) of 26.8(2)° (M = Cr), 26.1(3)° (M = Mo), and 33.8(3)° (M = Cr), 33.0(2)° (M = Mo), respec-

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for [(CO)$_3$Cr(η-C$_5$Me$_5$)Co(μ-H)(μ-1−4-η^4:5−7-η^3-C$_7$H$_7$)] (7)

	x	*y*	*z*	U_{eq}[a]
Cr(1)	790(1)	4140(1)	2895(1)	32(1)
Co(1)	2327(1)	1345(1)	2365(1)	30(1)
C(1)	596(4)	2067(3)	4392(2)	43(1)
C(2)	−875(4)	3194(4)	4178(3)	47(1)
C(3)	−1662(4)	3798(4)	3132(3)	46(1)
C(4)	−1060(3)	3334(4)	2186(3)	41(1)
C(5)	−177(3)	1836(4)	2138(3)	40(1)
C(6)	440(4)	585(3)	3074(3)	43(1)
C(7)	1182(4)	807(3)	3934(3)	41(1)
C(8)	−94(4)	5996(4)	3098(3)	48(1)
O(1)	−604(4)	7205(3)	3166(2)	77(1)
C(10)	1177(4)	5273(3)	1459(3)	40(1)
O(3)	1395(3)	6017(3)	568(2)	64(1)
C(9)	2648(4)	4129(4)	3561(3)	52(1)
O(2)	3767(4)	4144(4)	3987(3)	89(1)
C(13)	4517(3)	1676(3)	1515(3)	39(1)
C(14)	4872(3)	437(4)	2497(3)	46(1)
C(15)	4096(4)	−638(4)	2421(3)	53(1)
C(11)	3259(4)	−71(4)	1390(3)	53(1)
C(12)	3531(3)	1366(4)	816(2)	43(1)
C(18)	5196(4)	3038(4)	1209(4)	66(1)
C(19)	5958(5)	305(6)	3419(3)	83(1)
C(20)	4207(6)	−2160(4)	3261(5)	105(2)
C(16)	2333(6)	−875(6)	936(5)	102(2)
C(17)	2964(5)	2357(6)	−326(3)	84(2)
H(8)	2294(36)	2966(32)	2383(24)	52(9)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for [(CO)$_3$Mo(η-C$_5$Me$_5$)Co(μ-H)(μ-1−4-η^4:5−7-η^3-C$_7$H$_7$)] (8)

	x	*y*	*z*	U_{eq}[a]
Mo(1)	801(1)	4196(1)	2892(1)	35(1)
Co(1)	2332(1)	1349(1)	2367(1)	32(1)
C(1)	552(5)	2045(4)	4407(3)	46(1)
C(2)	−930(5)	3138(4)	4197(3)	49(1)
C(3)	−1728(4)	3750(4)	3147(4)	49(1)
C(4)	−1114(4)	3313(5)	2211(4)	43(1)
C(5)	−189(4)	1865(4)	2145(3)	41(1)
C(6)	451(4)	630(4)	3067(3)	43(1)
C(7)	1186(4)	817(4)	3929(3)	44(1)
C(8)	−188(5)	6133(4)	3104(3)	51(1)
O(1)	−710(5)	7330(4)	3157(3)	83(1)
C(9)	2748(5)	4247(4)	3578(4)	53(1)
O(2)	3853(5)	4259(5)	4003(4)	96(1)
C(10)	1221(4)	5431(4)	1387(3)	43(1)
O(3)	1438(4)	6175(4)	514(2)	68(1)
C(11)	3260(5)	−77(5)	1427(4)	62(1)
C(12)	3518(4)	1341(4)	822(3)	48(1)
C(13)	4509(4)	1643(4)	1506(3)	42(1)
C(14)	4876(4)	449(4)	2494(3)	49(1)
C(15)	4120(5)	−609(4)	2453(4)	60(1)
C(16)	2351(7)	−888(9)	998(7)	117(3)
C(17)	2926(7)	2291(8)	−323(4)	97(2)
C(18)	5172(6)	2996(6)	1161(5)	78(2)
C(19)	5957(6)	349(8)	3402(5)	92(2)
C(20)	4253(8)	−2099(5)	3308(7)	118(3)
H(8)	2544	2889	2276	80(15)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 6. Selected Bond Lengths (Å) for [(CO)$_3$M(η-C$_5$Me$_5$)Co(μ-H)(μ-1−4-η^4:5−7-η^3-C$_7$H$_7$)] [7 (M = Cr), 8 (M = Mo)] with Estimated Standard Deviations in Parentheses

	7 (M = Cr)	**8** (M = Mo)
M−Co(1)	2.899(2)	2.978(2)
M−C(1)	2.307(3)	2.406(4)
M−C(2)	2.168(3)	2.278(3)
M−C(3)	2.165(3)	2.270(3)
M−C(4)	2.298(3)	2.390(4)
M−C(8)	1.826(3)	1.940(4)
M−C(9)	1.859(3)	1.966(4)
M−C(10)	1.843(4)	1.964(4)
M−H(8)	1.67(3)	1.93
C(8)−O(1)	1.154(4)	1.154(5)
C(9)−O(2)	1.145(4)	1.134(5)
C(10)−O(3)	1.152(4)	1.143(4)
Co(1)−C(5)	2.071(3)	2.073(3)
Co(1)−C(6)	1.951(3)	1.935(3)
Co(1)−C(7)	2.077(3)	2.080(3)
Co(1)−C(11)−C(15)	2.058(3)−2.092(3)	2.054(4)−2.095(3)
Co(1)−H(8)	1.57(3)	1.54
C(1)−C(2)	1.394(5)	1.383(6)
C(1)−C(7)	1.449(4)	1.460(5)
C(2)−C(3)	1.420(5)	1.430(6)
C(3)−C(4)	1.395(4)	1.384(6)
C(4)−C(5)	1.449(4)	1.439(5)
C(5)−C(6)	1.418(5)	1.413(5)
C(6)−C(7)	1.410(5)	1.399(5)

Table 7. Selected Bond Angles (deg) for [(CO)$_3$M(η-C$_5$Me$_5$)Co(μ-H)(μ-1−4-η^4:5−7-η^3-C$_7$H$_7$)] [7 (M = Cr), 8 (M = Mo)] with Estimated Standard Deviations in Parentheses

	7 (M = Cr)	**8** (M = Mo)
C(8)−M−Co(1)	174.35(10)	175.32(12)
C(9)−M−Co(1)	93.99(10)	96.64(12)
C(10)−M−Co(1)	91.67(11)	93.74(11)
M−C(8)−O(1)	175.8(3)	174.7(4)
M−C(9)−O(2)	178.2(3)	178.0(4)
M−C(10)−O(3)	178.1(3)	178.5(3)
C(2)−C(1)−C(7)	128.0(3)	128.0(4)
C(1)−C(2)−C(3)	124.4(3)	124.6(3)
C(4)−C(3)−C(2)	124.1(3)	124.0(4)
C(3)−C(4)−C(5)	128.2(3)	128.8(4)
C(6)−C(5)−C(4)	125.3(3)	125.0(3)
C(7)−C(6)−C(5)	119.3(3)	120.1(3)
C(6)−C(7)−C(1)	125.6(3)	124.9(4)

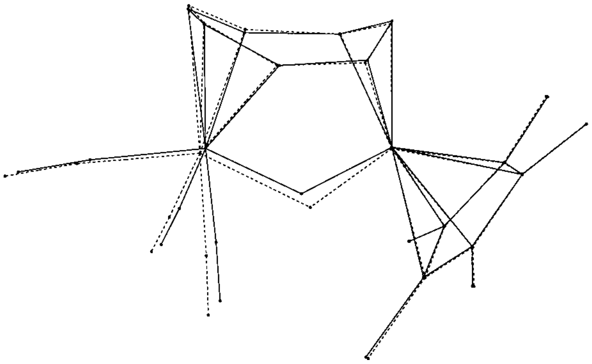


Figure 2. Superposition of the molecular structures of **7** (solid lines) and **8** (dashed lines).

tively. The hydride ligands were located displaced from the M−Co vectors, making up MHCo interactions. The metals M are coordinated in a distorted pseudo-octahedral fashion by the hydride ligand H(8) (or the Co−H(8) bond), the two carbon−carbon "double bonds" of the C$_7$H$_7$ ring, and three CO groups. Of the latter ligands, two are in a *cis* and one is in a *trans* position with respect to Co and thus the MHCo bond.

Discussion

There are close similarities between the η^4-cyclopentadiene and η^6-cycloheptatriene ligands in **1** and **2**−**4**, respectively. Apart from a similar coordination geometry of the ligands—planar (CH)$_n$ π-systems (n = 4, 6),

Table 8. Bond Lengths (Å) and Torsion Angles (deg) within the C_7H_7 Rings in Complexes of the Type $[L_nM(\mu\text{-}\eta^4{:}\eta^3\text{-}C_7H_6R)(L_nM)']$

$L_nM(L_nM)'$	C(1/3)−C(2/4)	C(2)−C(3)	C(1/4)−C(7/5)	C(6)−C(5/7)	M−M′
$(CO)_2Fe(\mu\text{-}CO)Rh(dppe)$[a]	1.42(1), 1.43(2)	1.39(2)	1.44(1), 1.47(2)	1.44(1), 1.42(1)	2.762(2)
$(cod)RhFe(CO)_3$[a]	1.418(14), 1.426(14)	1.387(15)	1.452(13), 1.425(13)	1.389(15), 1.409(14)	2.862(1)
$(CO)_2RhFe(CO)_3$[b]	1.422(7), 1.434(7)	1.379(7)	1.448(7), 1.449(6)	1.398(7), 1.396(6)	2.7638(7)
$Me_3Si(CO)_2RuRu(CO)_3$[c]	1.412(16), 1.412(18)	1.402(18)	1.420(15), 1.427(17)	1.474(16), 1.386(17)	2.937(1)
$(CO)_3Cr(\mu\text{-}H)CoCp^*$ (**7**)[d]	1.394(5), 1.395(4)	1.420(5)	1.449(4), 1.449(5)	1.418(5), 1.410(5)	2.899(2)
$(CO)_3Mo(\mu\text{-}H)CoCp^*$ (**8**)[d]	1.383(6), 1.384(6)	1.430(6)	1.460(5), 1.439(5)	1.413(5), 1.399(5)	2.978(2)

[a] Reference 13e. [b] Reference 13b. [c] Reference 13a. [d] This work.

which are involved in the coordination to the metal, and a methylene group which is bent away from the metal—their chemical reactivity is similar in many respects. For example, hydride ion can be abstracted from the methylene groups of **1** and **2**−**4** to give cationic cyclopentadienyl and cycloheptatrienyl complexes, respectively.[1,2] In **1**, stereospecific abstraction of the *exo* hydrogen is usually observed.[10]

Although the addition of hydride to $[(CO)_3M(\eta^7\text{-}C_7H_7)]^+$ is known to be stereospecific and occurs in the position *exo* to the metal,[2] to our knowledge the stereochemistry of the reverse process has not been established. At elevated temperatures (about 100 °C) the η^4- and η^6-ligands in **1**−**3** undergo hydrogen migrations. It was shown for both types of complexes that only the *endo* hydrogens of the methylene groups are involved in this process.[1d,5a,b]

Nevertheless quite different products (**6** and **7**−**9**, respectively) are obtained when **1** or **2**−**4** are reacted with the Cp*Co complex **5b**. 5-*Exo*-substituted derivatives of **1** ($R' \neq H$) do not react with **5a**.[6] Therefore, the likely site of attack of the cobalt reagent is at the *exo* CH bond of the methylene group. A similar attack at the methylene *exo* CH bond of **2**−**4** would place the cobalt atom in a position on the C_7 ring *anti* to the d^6-metal M. The observed *syn*-arrangement of the metals in the final products **7**−**9** would then require rearrangement of a primary *anti* dinuclear complex. Although such a rearrangement has been observed under special conditions in the somewhat related system $[(CO)_3Cr(\mu\text{-}\eta{:}\eta\text{-indenyl})Rh(nbd)]$,[11] there is no precedence for such a possibility in a C_7H_7-bridged system.[12]

Alternatively, *endo* addition of the Cp*Co reagent could take place. Cleavage of the CH bond could occur at the stage of a dinuclear primary addition product, which has a reduced hapticity of the seven-membered ring with respect to M. Alternatively, the tropylium hydrido complex $[(CO)_3M(H)(\eta^7\text{-}C_7H_7)]$ or more likely $[(CO)_3M(H)(\eta^5\text{-}C_7H_7)]$ could be involved. Such complexes were suggested to be intermediates in the above cited rearrangement of **2** and **3**.[5a,d] The hydrogen shift from the methylene group of cycloheptatriene to the CrHCo bond is reversible, as shown by the quantitative conversion of **7** by excess carbon monoxide into the starting material **2** and $[(Cp^*Co(CO)_2]$.

In the order from Cr to W, the increase in the yield of the heterobimetallic complexes **7**−**9** reflects the increasing stability of the mononuclear starting materials **2**−**4**.[2] The preferred side reaction is abstraction of CO to give $[(Cp^*Co(CO)]_2$. This compound is the main product (60%) in the reaction with **2**; it is still formed from **3** (15%) but not from the tungsten complex **4**, where consequently the highest yield of the μ-cycloheptatrienyl product is obtained. The preference of (C_5R_5)-Co to scavenge carbon monoxide rather than cycloheptatriene is also shown in the reactions of $[(C_5R_5)Co(\eta^4\text{-}C_7H_8)]$ with $[(CO)_3Cr(NCMe)_3]$, where $[(C_5R_5)Co(CO)_2]$ is formed. The failure of the WCo derivative **9** to react with CO or trimethyl phosphite is also consistent with a higher stability of the W−C(O) and W−H bonds.

Compared to the large number of mononuclear complexes with the cycloheptatrienyl ligand,[2] relatively few dinuclear complexes with a C_7H_7 bridge are known. The hapticity of the latter is governed by the electronic requirements of the metal fragments, which tend to complete their valence electron count to 18. In almost all the cases with two metals in a *syn* arrangement with respect to the C_7H_7 bridge, the $\eta^4{:}\eta^3$ coordination is adopted in the ground state.[13,14] However, these complexes are highly dynamic in solution and undergo C_7 ring whizzing with very low energy barriers. In the crystals, **7** and **8** clearly show the *syn* η^4(M):η^3(Co) coordination geometry of the cycloheptatrienyl ligand. Carbon−carbon bond lengths for several dinuclear complexes with $\mu\text{-}\eta^4{:}\eta^3$ coordinated C_7H_7 ligands are compiled in Table 8. Due to relatively large standard deviations, not all of the values lend themselves to a meaningful comparison. Nevertheless the general pattern of η^4-diene and η^3-enyl units, separated by some-

---

(10) Abstraction of the *endo* hydrogen has been observed in some *exo*-substituted derivatives of **1**: El Murr, N. *J. Organomet. Chem.* **1981**, *208*, C9.

(11) Bonifaci, C.; Ceccon, A.; Gambaro, A.; Ganis, P.; Santi, S.; Venzo, A. *Organometallics* **1995**, *14*, 2430.

(12) It was pointed out to us by one of the reviewers that isomerization of *anti*-$[(CO)_3Os(\mu\text{-}\eta^4{:}\eta^3\text{-}C_7H_7)Rh(cod)]$ to give the *syn*-($\mu\text{-}\eta^3{:}\eta^4$) isomer has actually been observed: Astley, S. T. Ph.D. Thesis, University of Alberta, 1990. In the present case, the apparently obvious experiment to test for *exo vs endo* attack, namely reaction of *exo*-D-substituted **2**−**4** with **5b**, cannot resolve the question. At the temperature needed for this reaction, there is already substantial isomerization (*endo*-H shifts) of **2**−**4**.

(13) (a) Howard, J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 59. (b) Bennett, M. J.; Pratt, J. L.; Simpson, K. A.; LiShingMan, L. K. K.; Takats, J. *J. Am. Chem. Soc.* **1976**, *98*, 4810. (c) Salzer, A.; Egolf, T.; v. Philipsborn, W. *Helv. Chim. Acta* **1982**, *65*, 1145. (d) Lin, G.-Y.; Takats, J. *J. Organomet. Chem.* **1984**, *269*, C4. (e) Ball, R. G.; Edelmann, F.; Kiel, G.-Y.; Takats, J. *Organometallics* **1986**, *5*, 829. (f) Edelmann, F.; Kiel, G.-Y.; Vasudemamurthy, A.; Yeung, M.-Y. *J. Chem. Soc., Chem. Commun.* **1988**, 296. (g) Astley, S. T.; Takats, J. *J. Organomet. Chem.* **1989**, *363*, 167.

(14) To our knowledge, there are only very few well-characterized exceptions. In $[(CO)_3Fe(\mu\text{-}C_7H_7)ML]$ (M = Pd, L = η-Cp,[15a] $\eta\text{-}C_3H_5$;[15b] M = Pt, L = $\eta^2,\sigma^1\text{-}C_8H_{12}\text{-}Cp$[15c]) the η^3(Fe):η^2(M) coordination is attained. A distorted $\eta^3{:}\eta^3$ coordination with some additional interaction of both metals with the "unique" ring carbon was found in the crystalline states for $[\{(CO)_2Ru\}_2(\mu\text{-}I)(\mu\text{-}C_7H_6Ph)]$ (Howard, J. A. K.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 366) and $[\{(CO)_2Fe\}_2(\mu\text{-}CO)(\mu\text{-}C_7H_7)]^-$.[16] For the latter complex this was explained by a fluxional behavior.[16] C_7 ring whizzing in the solid is however excluded by the presence of the phenyl substituent in the Ru_2 complex. Thus the experimental structures may well approximate the ground states of both the Ru_2 and Fe_2 complexes.

(15) (a) Airoldi, M.; Deganello, G.; Gennaro, G.; Moret, M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1992**, 850; *Organometallics* **1993**, *12*, 3964. (b) Fu, W.; McDonald, R.; Takats, J.; Bond, A. H.; Rogers, R. D. *Inorg. Chim. Acta* **1995**, *229*, 307. (c) Airoldi, M.; Beringhelli, T.; Deganello, G.; Gennaro, G.; Moret, M.; Saiano, F.; Sironi, A. *Inorg. Chim. Acta* **1995**, *229*, 461.

(16) Moll, M.; Behrens, H.; Popp, W.; Liehr, G.; Fehlhammer, W. P. *Z. Naturforsch.* **1983**, *38b*, 1446.

Table 9. Geometrical Parameters (deg) Describing the Conformation of the μ-C_7H_7 Ligands in Complexes of the Type $[L_nM(\mu\text{-}\eta^4{:}\eta^3\text{-}C_7H_6R)(L_nM)']$

$L_nM(L_nM)'$	torsion angles[a]	fold angle[b]
$(CO)_2Fe(\mu\text{-}CO)Rh(dppe)$[c]	27.0, −12.9	53
$(cod)RhFe(CO)_3$[c]	25.2, −21.4	62
$(CO)_2RhFe(CO)_3$[d]	21.9, −23.5	56
$Me_3Si(CO)_2RuRu(CO)_3$[e]	25.4, −17.6	57
$(CO)_3Cr(\mu\text{-}H)CoCp^*$ (**7**)[f]	7.8, −9.2	60
$(CO)_3Mo(\mu\text{-}H)CoCp^*$ (**8**)[f]	7.2, −8.4	60

[a] C(2)−C(1)−C(7)−C(6), C(3)−C(4)−C(5)−C(6). [b] Angle between normals to the planes through C(1), C(2), C(3), C(4) (η^4-diene) and C(5), C(6), C(7) (η^3-enyl). [c] Reference 13e. [d] Reference 13b. [e] Reference 13a. [f] This work.

what longer bonds (C(1/4)−C(7/5)) emerges. The bond length pattern short−long−short in the η^4-diene unit in **7** and **8** is the reverse of what is observed in the other examples in Table 8, indicative of a weaker bonding of the d^6-metals to the π-system.

Some geometrical parameters which relate to the folding of the μ-$\eta^4{:}\eta^3$-C_7H_7 ligand can be found in Table 9. Obviously, the deviation from planarity is similar in most of the complexes with known structures. There does not seem to be correlation between the amount of folding and the metal−metal distance.

An 18 valence electron configuration is attained on both metals by the formation of a three-center MHCo bond. Although the MCo bonds are comparatively long, the observed distances of 2.899(2) Å (**7**) and 2.978(2) Å (**8**) can still be considered as metal−metal bonding.[17] Thus the three-center MHCo interaction is of the "closed" type.[19] The donor effect to Cr and Mo, respectively, is reflected in the shorter bond to the CO ligand *trans* to the cobalt atom, caused by an increased metal-to-ligand back-donation in this direction. A similar bonding situation, but without the bridging hydride, was observed in $[(CO)_3Mo(\mu\text{-}\eta^4{:}\eta^4\text{-}C_8H_8)Co(Cp)]$.[18] Despite the rather long Mo−Co distances (2.969(1) and 2.998(2) Å for the two independent molecules) a dative bond Mo←Co is required by electron bookkeeping in this molecule.

As indicated by the ^1H and ^{13}C NMR spectra, the seven CH groups of the bridging cycloheptatrienyl ligands in **7**−**9** are equivalent at high temperature. However, C_7H_7 ring whizzing is already slowed down on the NMR time scale at room temperature, causing a considerable broadening of the ^1H resonance. The observation of four resonances for the bridging ligand in the ^1H and ^{13}C NMR spectra of **7** at 200 K is consistent with a static η^4(Cr):η^3(Co) coordination at that temperature. Tripodal rotation of the $Cr(CO)_3$ group is also frozen at 190 K, and the two resonances due to the CO ligands in the positions *cis* and *trans* to the CrHCo bond are resolved in the ^{13}C spectrum.

Compared to dinuclear complexes with an *anti* coordination of the bridging cycloheptatrienyl ligand,[20] the corresponding *syn* complexes are much more fluxional.[13] Indeed, attempts to reach the slow-exchange limiting NMR spectra of the cycloheptatrienyl unit have failed in most cases. The only exceptions reported in the literature are the complexes $[(CO)_3Ru\{\mu\text{-}\eta^3(Ru){:}\eta^4(Ir)\text{-}C_7H_7\}IrL_2]$ [**10a** (L_2 = cod), **10b** (L = CO)][13h] and $[(CO)_3Fe\{\mu\text{-}\eta^3(Fe){:}\eta^2(Pd)\text{-}C_7H_7\}Pd(\eta\text{-}Cp)]$.[15a] In the latter case, the relatively high barrier of the fluxional process was first attributed to the presence of a noncoordinated double bond in the cycloheptatrienyl ring.[15a] However, the C_7H_7 ligand in the structurally very similar $[(CO)_3Fe\{\mu\text{-}\eta^3(Fe){:}\eta^2(Pd)\text{-}C_7H_7\}ML)]$ [ML = $Pd(\eta\text{-}C_3H_5)$, $Pt\{\eta^2,\sigma^1\text{-}(C_8H_{12}\text{-}Cp)\}$] was recently shown to be very fluxional.[15b,c] In these molecules, ring whizzing is possibly assisted by a transient conversion of M from a 16 to a 18 valence electron species.[15b] The somewhat reduced fluxionality of the RuIr complex (limiting spectra are approached at 170 K) may be due to the increased metal−ligand bond strength associated with the heavier transition metals. Interestingly, the ^1H resonance (δ = 1.5) of the central proton (H-6) of the η^3-enyl unit of the cycloheptatrienyl ligand in **7** is shifted upfield of the outer protons H-5 and H-7. In mononuclear η^3-allyl complexes the reverse order is observed.[21] In our earlier communication[9] we mentioned the possible influence of the boat conformation of the C_7H_7 ring on the relative positions of the allyl resonances. High-field shifts of the central proton of the η^3-enyl unit in $[Cp(CO)_2Mo(\eta^3\text{-}C_7H_7)]$ and $[(CO)_3Co(\eta^3\text{-}C_7H_7)]$ have been explained in this way.[22] In **10a**, the H-6 resonance (δ = 3.54) is also at higher field than the outer H-5/7 signals (δ = 3.76), and in **10b** all three signals are accidentally at the same position (δ = 4.0).[13h] However, the chemical shifts and relative positions of the C_7H_7 ^1H resonances are variable and metal dependent (note shift of H-6 and H-5/7 to much lower field in **10**), and therefore such an explanation appears not justified.[23]

The large difference in activation energy of C_7 ring-whizzing in *syn*- and *anti*- $M(\mu\text{-}1{-}4\text{-}\eta{:}5{-}7\text{-}\eta\text{-}C_7H_7)M'$ complexes has been explained by the different degree of electronic localisation of η^4-diene and η^3-enyl ring fragments.[13b] The interaction between these fragments depends on the overlap between the p_π orbitals on the carbon atoms at the termini of the C_4 and C_3 fragments. p_π−p_π overlap should be a function of both the distance and the angle φ between the respective orbitals.

By assuming that the p_π orbital is perpendicular to the plane defined by the atom at the junction of the two bonding units and its two neighboring carbon atoms, φ is equivalent to the torsion angles C(2)−C(1)−C(7)−C(6) and C(3)−C(4)−C(5)−C(6). With the distances C(1/4)−C(7/5) being roughly comparable to those of the other examples in Tables 8 and 9 a higher degree of delocalization is expected for **7** and **8** on the basis of the much smaller values of φ. However, judging from the variation of the bond lengths within the C_7 rings, this

---

(17) The structure of only one dinuclear complex with a Co−Cr bond has been reported, viz. $[(PMe_3)(CO)_3(\mu\text{-}P^tBu_2)(\mu\text{-}CO)Co(CO)(PMe_3)]$, *d*(Co−Cr) = 2.505(1) Å (Chandler, D. J.; Jones, R. A.; Stuart, A. L.; Wright, T. C. *Organometallics* **1984**, *3*, 1830). In oligonuclear cluster complexes, Cr−Co bonds have been assigned to distances up to 2.959 Å (Eremenko, I. L.; Pasynskii, A. A.; Gasanov, G. Sh.; Orazsakhatov, B.; Struchkov, Yu. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *275*, 71). Reported Mo−Co bond lengths in dinuclear complexes range from 2.676 Å (Yanez, R.; Lugan, N.; Mathieu, R. *Organometallics* **1990**, *9*, 2998) to 2.998 Å.[18]

(18) Salzer, A.; Egolf, T.; Linowsky, L.; Petter, W. *J. Organomet. Chem.* **1981**, *221*, 339.

(19) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

(20) Cotton, F. A.; Reich, C. R. *J. Am. Chem. Soc.* **1969**, *91*, 847.

(21) Green, M. L. H.; Nagy, P. L. I. *Adv. Organomet. Chem.* **1964**, *2*, 325.

(22) (a) Faller, J. W. *Inorg. Chem.* **1969**, *8*, 767. (b) Bennett, M. A.; Bramley, R.; Watt, R. *J. Am. Chem. Soc.* **1969**, *91*, 3089.

(23) Additional data illustrating this point were made available to us by one reviewer for $[(CO)_3Os\{\mu\text{-}\eta^3(Os){:}\eta^4(M)\text{-}C_7H_7\}M(cod)]$: M = Rh, δ(H-6) = 4.10, δ(H-5/7) = 3.46; M = Ir, δ(H-6) = 3.07, δ(H-5/7) = 3.30.

statement does not appear to be justified. In any case, the simple π overlap argument based on the solid-state geometry cannot be correlated with the molecular dynamics in solution without further evidence.

Experimental Section

General Procedures. All operations were carried out under an atmosphere of purified nitrogen or argon (BASF R3-11 catalyst) using Schlenk techniques. Solvents were dried by conventional methods. Petroleum ether refers to the fraction with bp 40−70 °C. The compounds $[(CO)_3M(C_7H_8)]$ [**2** (M = Cr),[24] **3** (M = Mo),[25] **4** (M = W)][26] and $[(C_5Me_5)Co(C_2H_4)_2]$ (**5b**)[27] were prepared as described in the literature. NMR spectra were obtained on a Bruker AC 200 instrument (200.1 MHz for ^{1}H, 50.3 MHz for ^{13}C). ^{1}H and ^{13}C chemical shifts are reported vs $SiMe_4$ and were determined by reference to internal $SiMe_4$ or residual solvent peaks. The multiplicities of the ^{13}C resonances were determined using the DEPT or the *J*-modulated spin echo (JMOD) techniques; multiplicities determined by the latter method are indicated as odd (u) or even (g). Infrared spectra were recorded in the ν(CO) region in CaF_2 cells on a Perkin-Elmer 983 grating IR spectrometer. Mass spectra were measured in the electron impact ionization mode (EI) at 70 eV on Finnegan MAT 8230 and MAT CH7 spectrometers. Elemental analyses were performed locally by the microanalytical laboratory of the Organisch-chemisches Institut der Universität Heidelberg and by Mikroanalytisches Labor Beller, Göttingen, Germany.

Synthesis of $[(CO)_3M(\mu\text{-H})(\mu\text{-}C_7H_7)Co(Cp^*)]$ [7 (M = Cr), 8 (M = Mo), 9 (M = W)]. General Procedure. The educts were heated in 40−70 mL of petroleum ether at 60−80 °C for 6 h. After the solution was cooled to room temperature, the solvent was removed under reduced pressure. The dark residue was redissolved in a minimum amount of toluene. Fractional crystallization at −25 °C gave microcrystals of the crude heterobimetallic complexes, which were recrystallized several times from toluene. By further solvent concentration and cooling (−25 °C), unreacted $[(CO)_3M(C_7H_8)]$ and $[Cp^*Co(CO)]_2$[28] could be isolated.

$[(CO)_3Cr(\mu\text{-H})(\mu\text{-}C_7H_7)Co(Cp^*)]$ (7). A 100 mg (19% based on Cr) amount of **7** was obtained from 280 mg (1.22 mmol) of **2** and 320 mg (1.28 mmol) of **5b**. Red brown crystals, mp 180 °C (dec), formed. IR: ν(CO) 1959.5, 1881 cm^{-1}. MS [*m*/*z* (relative intensity)]: 422 (9, M$^+$), 394 (5, M$^+$ − CO), 366 (6, M$^+$ − 2CO), 336 (92, M$^+$ − 3CO − 2H), 250 (27, $[Cp^*Co(CO)_2]^+$), 222 (18, $[Cp^*Co(CO)]^+$), 194 (100, $[Cp^*Co]^+$), 192 (60), 133 (36), 92 (35, $[C_7H_8]^+$), 91 (80, $[C_7H_7]^+$), 59 (16, Co$^+$), 52 (38, Cr$^+$).

Anal. Calcd for $C_{20}H_{23}CoCrO_3$: C, 56.87; H, 5.45. Found: C, 56.70; H, 5.50.

$[(CO)_3Mo(\mu\text{-H})(\mu\text{-}C_7H_7)Co(Cp^*)]$ (8). A 700 mg (33% based on Mo) amount of **8** was obtained from 1.24 g (4.56 mmol) of **3** and 1.14 g (4.56 mmol) of **5b**. Dark brown crystals, mp 178 °C (dec), formed. IR: ν(CO) 1964, 1885 cm^{-1}. MS [*m*/*z* (relative intensity)]: 468 (18, M$^+$), 440 (3, M$^+$ − CO), 412 (9, M$^+$ − 2CO), 382 (100, M$^+$ − 3CO − 2H), 321 (54), 194 (63, $[Cp^*Co]^+$), 133 (36), 91 (42, $[C_7H_7]^+$), 59 (16, Co$^+$). The peak envelope of the molecular ion agrees well with that calculated from the natural isotope distribution.

Anal. Calcd for $C_{20}H_{23}CoMoO_3$: C, 51.50; H, 4.93. Found: C, 51.44; H, 4.94.

$[(CO)_3W(\mu\text{-H})(\mu\text{-}C_7H_7)Co(Cp^*)]$ (9). A 860 mg (63% based on W) amount of **9** was obtained from 890 mg (2.47 mmol) of **4** and 620 mg (2.48 mmol) of **5b**. The product crystallizes from the reaction mixture with no formation of $[Cp^*Co(CO)]_2$. Dark brown crystals, mp 209 °C, formed. IR: ν(CO) 1963, 1875 cm^{-1}. MS [*m*/*z* (relative intensity)]: 554 (18, M$^+$), 526 (8, M$^+$ − CO), 498 (4, M$^+$ − 2CO), 468 (100, M$^+$ − 3CO − 2H), 409 (20), 274 (14), 194 (4, $[Cp^*Co]^+$), 149 (30), 91 (42, $[C_7H_7]^+$). The peak envelope of the molecular ion agrees well with that calculated from the natural isotope distribution.

Table 10. Details of the Crystal Structure Determinations of $[(CO)_3M(\eta\text{-}C_5Me_5)Co\{\mu\text{-H}\}\{\mu\text{-}1{-}4\text{-}\eta^4{:}5{-}7\text{-}\eta^3\text{-}C_7H_7)\}]$ [7 (M = Cr), 8 (M = Mo)]

	7	**8**
formula	$C_{20}H_{23}CoCrO_3$	$C_{20}H_{23}CoMoO_3$
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.463(4)	8.450(4)
b (Å)	9.656(5)	9.841(5)
c (Å)	12.586(6)	12.659(6)
α (deg)	71.67(3)	71.48(3)
β (deg)	83.53(3)	83.51(3)
γ (deg)	73.84(3)	73.29(3)
V (Å^3)	937.4(8)	955.7(8)
Z	2	2
M_r	422.31	466.25
d_c (g·cm^{-1})	1.496	1.620
F_{000}	436	472
μ(Mo Kα) (mm^{-1})	1.479	1.538
X-radiation, λ (Å)	Mo Kα, graphite monochromated, 0.71069	
data collect temp	ambient	
2θ range (deg)	3−55	3−60
hkl range	−10/10, −11/12, 0/16	0/11, −12/13, −17/17
reflcns measd		
total	4335	4097
unique	4335	4097
obsd [$I \geq 2\sigma(I)$]	3088	4097
abs corr	empirical	empirical
params refined	270	261
GooF	1.035	1.051
R (obsd reflcns only)	0.036	0.035
w*R2* (all reflcns) ($w = 1/[\sigma^2(F) + (AP)^2 + BP]$	0.092	0.087
A, *B*	0.0422, 0.28	0.0440, 0.83
P	$\max(F_o^2,0) + 2F_c^2)/3$	

Anal. Calcd for $C_{20}H_{23}CoO_3W$: C, 43.33; H, 4.15. Found: C, 43.61; H, 4.31.

Crystal Structure Determination of $[(CO)_3Cr(\mu\text{-H})(\mu\text{-}C_7H_7)Co(Cp^*)]$ (7) and $[(CO)_3Mo(\mu\text{-H})(\mu\text{-}C_7H_7)Co(Cp^*)]$ (8). Single crystals were grown from toluene solutions and mounted in Lindemann capillary tubes. Intensity data were collected on Siemens STOE (**7**) or Syntex R3 (**8**) four-circle diffractometers at ambient temperature and corrected for Lorentz, polarization, and absorption effects (Table 10). The structures were solved by the heavy atom method and refined by full-matrix least squares based on F^2 using all measured unique reflections. All non-hydrogen atoms were given anisotropic displacement parameters.

All hydrogens except those of the methyl groups were located in difference Fourier syntheses and refined with isotropic displacement parameters. Refinement of the hydride H(8) in **8** was not stable; therefore, this hydrogen was fixed at the position taken from the difference Fourier map. Methyl hydrogen atoms were input in calculated positions. The calculations were performed using the programs SHELXS-86,[29] SHELXL-93,[30] and IDEAL.[31] Graphical representations were drawn with the ORTEP-II program.[32]

Note Added in Proof. Since the present paper was submitted, we have prepared $[(CO)_3W(\mu\text{-H})(\mu\text{-}C_7H_7)Co(\eta\text{-}$

---

(24) Pauson, P. L.; Todd, K. H. *J. Chem. Soc. C* **1970**, 2315.

(25) Eisch, J. J.; King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. 1, p 125.

(26) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1873.

(27) Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1985**, *23*, 15.

(28) Bailey, W. I., Jr.; Collins, D. M.; Cotton, F. A.; Baldwin, J. C.; Kaska, W. C. *J. Organomet. Chem.* **1979**, *165*, 373.

(29) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(30) Sheldrick, G. M. Universität Göttingen, 1993.

(31) Gould, R. University of Edinburgh, 1988.

(32) Johnson, C. K. *Report ORNL-5138*; Oak Ridge National Laboratory: Oak Ridge, TN.

C_5H_5)], the cyclopentadienyl derivative of **9**, from **4** and **5a**. Preliminary ^1H NMR spectroscopic data for this complex indicate a structure similar to **9** but a lower barrier for C_7H_7 ring whizzing.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft under the auspices of the Sonderforschungsbereich 247 ("Organization and Reorganization of π-Systems with Metals") and the Fonds der Chemischen Industrie. H.W. gratefully acknowledges the award of a Heisenberg Fellowship.

Supporting Information Available: Tables listing X-ray parameters, anisotropic atomic displacement parameters, hydrogen atom coordinates and *U* values, and complete bond distances and angles for **7** and **8** (14 pages). Ordering information is given on any current masthead page.

OM9505266