Heterobimetallic Sesquifulvalene and Hydrosesquifulvalenyl Manganese(I) Chromium(0) Complexes

Matthias Tamm*[a], Alexander Grzegorzewski[a], and Thomas Steiner[b]

Institut für Anorganische und Analytische Chemie, Freie Universität Berlin[a],
Fabeckstraße 34–36, D-14195 Berlin, Germany

Institut für Kristallographie, Freie Universität Berlin[b],
Takustraße 6, D-14195 Berlin, Germany

Received November 7, 1996

Keywords: Sesquifulvalene / Heterobimetallic complexes / Manganese / Chromium / Stille coupling

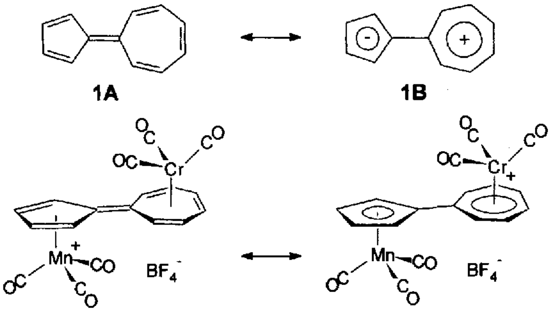
The synthesis of the heterobimetallic sesquifulvalene complex $[(OC)_3Mn(\mu\text{-}\eta^5{:}\eta^7\text{-}C_5H_4\text{-}C_7H_6)Cr(CO)_3]BF_4$ (**2**) is reported. [(2,4,6-Cycloheptatrien-1-yl)-η^5-cyclopentadienyl]tricarbonylmanganese (**3**) reacts with $(CH_3CN)_3Cr(CO)_3$ to give a mixture of *endo*- and *exo*-$[(OC)_3Mn(\mu\text{-}\eta^5{:}\eta^6\text{-}C_5H_4\text{-}C_7H_7)Cr(CO)_3]$ (**4a,b**). Hydride abstraction from this mixture resulted in the formation of **2** in low yield. Alternatively, Stille coupling of 2-trimethylstannyl-1,3,5-cycloheptatriene (**5**) with (iodocyclopentadienyl)tricarbonylmanganese (**6**) gave [(1,3,5-cycloheptatrien-2-yl)-η^5-cyclopentadienyl]tricarbonylmanganese (**7**). After treatment of **7** with $(CH_3CN)_3Cr(CO)_3$, a mixture of two heterobimetallic complexes $[(OC)_3Mn(\mu\text{-}\eta^5{:}\eta^6\text{-}C_5H_4\text{-}C_7H_7)Cr(CO)_3]$ (**8a,b**) was isolated. In **8a**, a bridging (1,3,5-cycloheptatrien-2-yl)cyclopentadienyl ligand was found, while **8b** contains a (1,3,5-cycloheptatrien-1-yl)cyclopentadienyl ligand. The mixture **8a, b** was converted quantitatively into **2** by reaction with triphenylcarbenium tetrafluoroborate. The X-ray crystal structures of **2**, **4a**,**4b** and **8a** are reported.

Introduction

Bimetallic complexes with conjugated π,π-hydrocarbon-bridged transition metal fragments have received considerable attention and have been extensively studied[1], especially with regard to intramolecular electronic interactions between the metal centers which might result in interesting properties (e.g. magnetism, nonlinear optical efficiencies[2]). Whereas compounds incorporating ligand systems with two directly linked aryl units such as $\mu\text{-}\eta^5{:}\eta^5$-fulvalene[3], $\mu\text{-}\eta^6{:}\eta^5$-phenylcyclopentadienyl[4] and $\mu\text{-}\eta^6{:}\eta^6$-biphenyl[5] are relatively well-established, complexes with the cross-conjugated hydrocarbon sesquifulvalene (**1**) are rare (Figure 1)[6,7,8]. Our interest in developing the coordination chemistry of **1** was stimulated by the fact that substantial first molecular hyperpolarizabilities β had been predicted for sesquifulvalene derivatives on the basis of theoretical calculations[9]. Since the instability[10] of **1** prevents its application in optical device technology, we initiated a program to synthesize stable organometallic sesquifulvalene derivatives by complexation of the aromatic cyclopentadienyl and cycloheptatrienyl subunits and have already reported on template syntheses of **1** at $[Mn(CO)_2L]$ metal fragments (L = CO[7a], $P(OMe)_3$, PPh_3[7b]) along with the first molecular hyperpolarizabilities of these complexes[7b]. Independently, Heck et al. have recently published work on iron/chromium sesquifulvalene derivatives exhibiting β values which are among the highest ever measured for organometallic complexes[8].

In continuation of our program, we wish to report on our strategy to build heterobimetallic $\mu\text{-}\eta^5{:}\eta^7$-sesquifulvalene complexes and present herein a detailed physical and structural characterization of the manganese(I) chromium(0) complexes **2**, **4** and **8**.

Figure 1. Canonical presentations for sesquifulvalene (**1**) and the heterobimetallic sesquifulvalene complex **2**



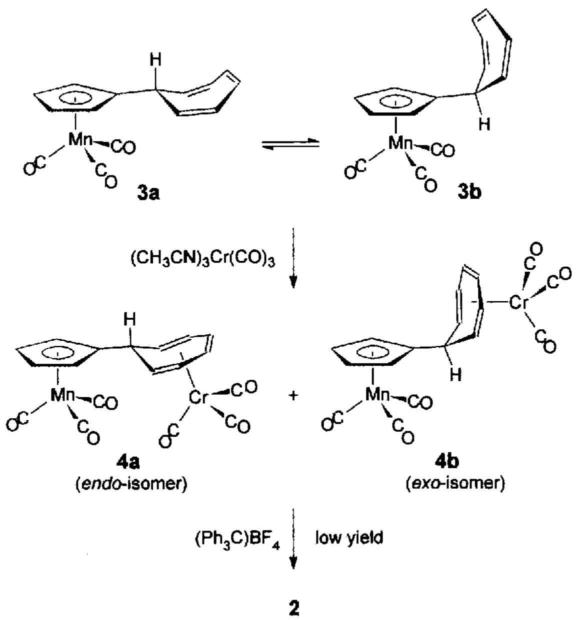
Results and Discussion

In principle, 7-substituted cycloheptatriene complexes of the type $\eta^6\text{-}(C_7H_7R)Cr(CO)_3$ can form two different stereoisomers having eigher *endo* or *exo* configuration. According to Pauson et al., the reaction of 7-substituted cycloheptatrienes with $Cr(CO)_3$-transfer reagents such as $(CH_3CN)_3Cr(CO)_3$ yields stereoselectively the 7-*endo* complexes[11], whereas the addition of nucleophiles to the tropyliumchromiumtricarbonyl cation, $[(C_7H_7)Cr(CO)_3]^+$, occurs from the less sterically hindered *exo*-side giving the 7-*exo* isomers[12]. It has been shown that only the *endo*-substituted complexes are accessible to hydride abstraction with formation of cationic tropylium complexes $[\eta^7\text{-}(C_7H_6R)\text{-}Cr(CO)_3]^+$[12,13]. Consequently, **3**[7a] (Scheme 1) seemed to be a promising starting material for the synthesis of the heterobimetallic complex **2** (Figure 1), and the *endo*-configured complex **4a** could be expected upon addition of the $Cr(CO)_3$-unit to the preferred equatorial conformation **3a**. However, in our

0009–2940/97/0202–0225 $ 15.00+.25/0

hands, treatment of **3** with $(CH_3CN)_3Cr(CO)_3$ in THF at room temperature or under reflux conditions resulted exclusively in the formation of **4a**/**4b** mixtures (ratio approximately 2:1). **4b** can be independently synthesized in pure form by the reaction of $(\eta^5\text{-}C_5H_4Li)Mn(CO)_3$[14] with $[(C_7H_7)Cr(CO)_3]BF_4$, which resembles the method widely used by Beck et al. for the syntheses of various hydrocarbon-bridged bimetallic complexes[15].

Scheme 1



Crystals of **4b** can be grown at −26 °C from a dichloromethane/diethyl ether solution, and their X-ray structure analysis allows the unambiguous verification of the *exo* configuration (Figure 2, bottom). As a result of the complete characterization of **4b**, all NMR resonances of the **4a**/**4b** mixture can be unequivocally assigned. Single crystals of **4a** were obtained from a solution of **4a,b** by fractional crystallization, and the molecular structure of **4a** is depicted in Figure 2 (top). If compared to the molecular structures of the subunits $CpMn(CO)_3$[16] and $(C_7H_8)Cr(CO)_3$[17], all bond lengths and angles in **4a** and **4b** fall in the expected ranges (Table 1).

The sesquifulvalene complex **2** could be isolated in relatively low yield (12−20%) and only in impure form by treating a mixture of **4a** and **4b** with triphenylcarbenium tetrafluoroborate, $(Ph_3C)BF_4$, in dichloromethane. Moreover, we observed that hydride abstraction from **4b** was accompanied by significant decomplexation and formation of the previously published monometallic sesquifulvalene complex $[(C_7H_6\text{-}\eta^5\text{-}C_5H_4)Mn(CO)_3]BF_4$[7a] by loss of the $Cr(CO)_3$ unit.

Figure 2. ORTEP drawings of **4a** (top) and **4b** (bottom)

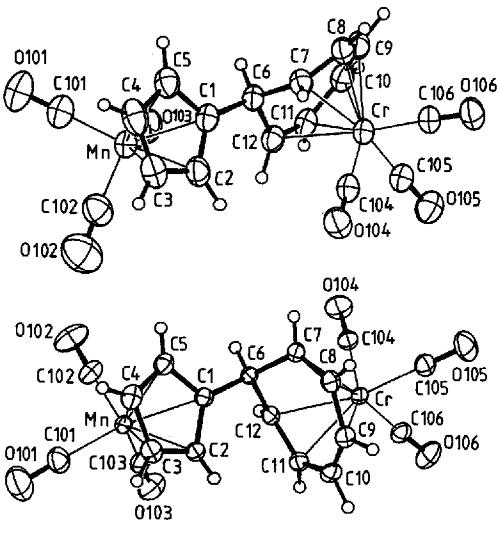
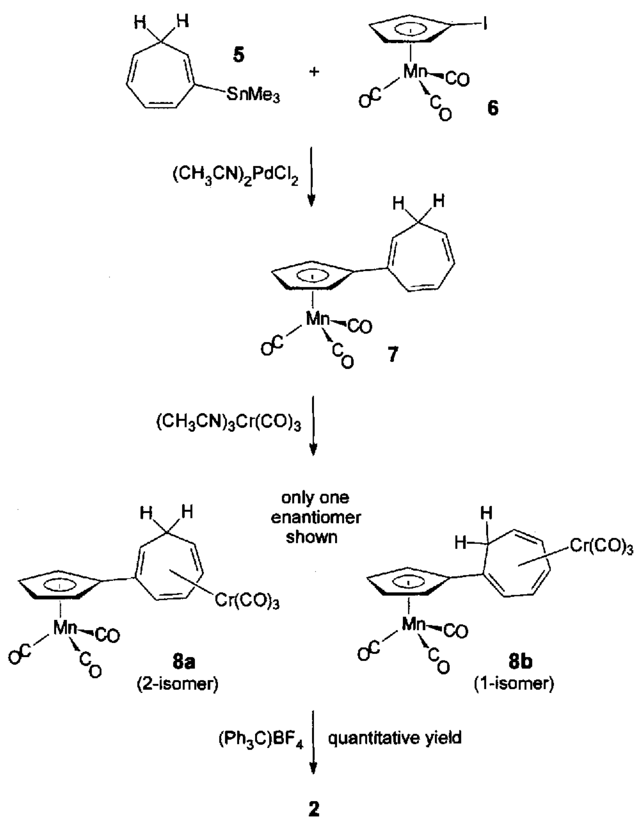


Table 1. Bond lengths (Å) for **4a**. **4b** and **8a**

	4a	**4b**	**8a**
Mn–C1	2.147(5)	2.138(4)	2.152(5)
Mn–C2	2.139(5)	2.131(4)	2.148(6)
Mn–C3	2.138(7)	2.137(4)	2.143(7)
Mn–C4	2.127(6)	2.136(4)	2.128(7)
Mn–C5	2.141(6)	2.138(4)	2.138(6)
Mn–C101	1.782(7)	1.798(5)	1.788(8)
Mn–C102	1.762(7)	1.791(4)	1.784(7)
Mn–C103	1.777(6)	1.789(4)	1.788(8)
Cr–C6			2.241(5)
Cr–C7	2.330(5)	2.307(4)	2.305(5)
Cr–C8	2.190(5)	2.207(4)	
Cr–C9	2.213(5)	2.210(4)	2.332(6)
Cr–C10	2.214(5)	2.201(3)	2.208(6)
Cr–C11	2.205(5)	2.207(4)	2.209(6)
Cr–C12	2.346(5)	2.317(4)	2.229(6)
Cr–C104	1.849(6)	1.865(4)	1.867(7)
Cr–C105	1.822(6)	1.861(4)	1.842(7)
Cr–C106	1.831(5)	1.856(4)	1.836(7)
C1–C2	1.413(8)	1.426(4)	1.424(9)
C1–C5	1.437(8)	1.415(5)	1.437(9)
C1–C6	1.496(7)	1.515(4)	1.483(9)
C2–C3	1.397(8)	1.404(5)	1.402(10)
C3–C4	1.403(11)	1.416(6)	1.407(12)
C4–C5	1.436(9)	1.406(5)	1.403(11)
C6–C7	1.508(7)	1.509(5)	1.383(8)
C6–C12	1.506(7)	1.505(5)	1.427(8)
C7–C8	1.383(7)	1.371(5)	1.491(9)
C8–C9	1.417(8)	1.418(5)	1.503(9)
C9–C10	1.385(8)	1.389(6)	1.361(9)
C10–C11	1.430(8)	1.411(5)	1.428(9)
C11–C12	1.376(7)	1.371(5)	1.383(9)
C101–O101	1.158(7)	1.144(5)	1.151(9)
C102–O102	1.151(8)	1.134(5)	1.154(9)
C103–O103	1.154(6)	1.141(5)	1.151(9)
C104–O104	1.163(6)	1.138(4)	1.147(8)
C105–O105	1.171(6)	1.142(5)	1.154(8)
C106–O106	1.153(6)	1.147(5)	1.164(8)

The problems we encountered in following the route outlined in Scheme 1 encouraged us to develop an alternative strategy for a high-yielding synthesis of **2**. This method was based on the observation that Schlosser et al. have reported selective metallation of 1,3,5-cycloheptatriene in the 2-position on treatment with *n*-butyllithium and sodium *tert*-butoxide in THF. The generated anion could be quenched with Me_3SiCl to form 2-trimethylsilyl-1,3,5-cycloheptatriene[18]. Accordingly, quenching with Me_3SnCl gave the corresponding stannane **5** (b.p. 43 °C/0.1 Torr), which could be used in a Stille coupling reaction[14,19,20] with $(\eta^5\text{-}C_5H_4I)Mn(CO)_3$ (**6**), affording **7** in high yield (Scheme 2). The ^{1}H-NMR spectrum clearly showed the exclusive formation of the 1,3,5-cycloheptatrien-2-yl derivative, exhibiting a triplet for the allylic protons at 2.29 ppm and five resonances for the vinylic protons in a 2:1:1:1:1:1 ratio.

Scheme 2



The reaction of 7 with $(CH_3CN)_3Cr(CO)_3$ in THF under reflux conditions again proved to be more complex than anticipated. After chromatographic workup a mixture of two isomers **8a** ("2-isomer") and **8b** ("1-isomer") was isolated (**8a**:**8b** = 1:10, Scheme 2). In **8a**, the $Cr(CO)_3$ unit is coordinated as expected to a 1,3,5-cycloheptatrien-2-yl ring, whereas **8b** contains a 1,3,5-cycloheptatrien-1-yl ring. **8a,b** cocrystallize and can be separated mechanically. In their ^1H-NMR spectra both isomers exhibit five resonances due to the vinylic protons and two resonances due to the allylic *exo* and *endo* protons. In the spectrum of **8a** the allylic resonances appear as ddd's at $\delta = 1.66$ and 2.94. In **8b** the allylic protons only couple with one neighbouring vinylic proton and dd's are observed at $\delta = 1.69$ and 2.83. As both complexes are racemic mixtures of two enantiomers, four resonances are observed for the diastereotopic cyclopentadienyl protons. The assignment of all cycloheptatrienyl proton resonances in **8a,b** is supported by two-dimensional NMR spectroscopy (COSY experiment). The ^1H-NMR spectrum of **8b** is depicted in Figure 3.

In order to confirm the spectroscopic results, the molecular structure of **8a** was established by X-ray diffraction analysis. Figure 4 shows an ORTEP diagram of **8a**. The bond lengths and angles in **8a** do not differ significantly from those observed in **4a** and **4b** (Table 1).

Figure 3. ^1H-NMR spectrum (500 MHz, $CDCl_3$) of **8b**; the resonances for the diastereotopic cyclopentadienyl protons are marked with asterisks

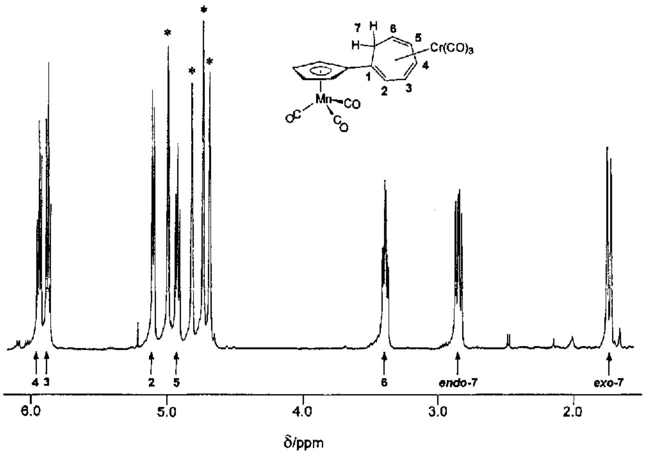
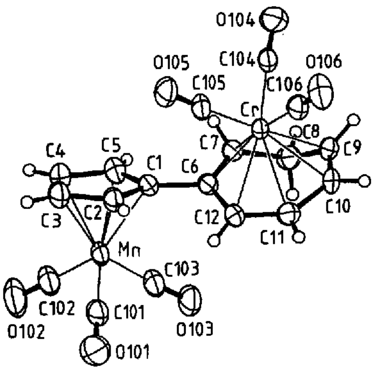


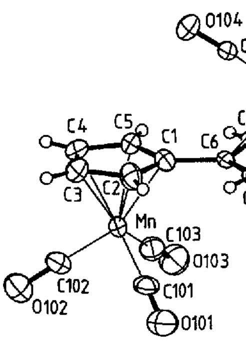
Figure 4. ORTEP drawing of **8a**



Heating 7 in THF under reflux for 18 h did not lead to any detectable amount of the respective 1-isomer. We therefore assume that the formation of the unexpected isomer **8b** could have resulted from a thermally induced 1,2-hydride shift in **8a**. If the $Cr(CO)_3$ transfer is performed with either $(CH_3CN)_3Cr(CO)_3$ or $(CH_3CH_2CN)_3Cr(CO)_3$[8] at room temperature, only **8a** is isolated, albeit in much lower yield (0–15%). From a synthetic point of view, the mixture **8a**/**8b** is equally useful for the synthesis of the sesquifulvalene complex **2**, as in both isomers the *exo*-hydrogen atom is easily accessible for hydride abstraction, and **2** is formed quantitatively upon treatment with $(Ph_3C)BF_4$. The molecular structure of one cation in **2** is shown in Figure 5. The metal fragments coordinate to the coplanar five- and seven-membered rings and adopt an anti-facial arrangement. Unfortunately, due to severe disorder of the tetrafluoroborate anions, the structure could only be refined with reduced accuracy, not allowing a reasonable discussion of the bonding geometry.

2 is an intensely yellow-orange coloured compound. It shows strong solvatochromic behaviour, and in its UV/Vis spectrum the lowest energy band λ_{max} is hypsochromically shifted ($\Delta\tilde{\nu} = -788\ cm^{-1}$) upon changing the solvent from

Figure 5. ORTEP drawing of one cation in **2**; the asymmetric unit contains two symmetry independent molecules of **2**, which differ only in the orientation of the carbonyl ligands



dichloromethane (λ_{max} = 444 nm) to acetonitrile (λ_{max} = 429 nm). As in other sesquifulvalene complexes[7,8], the lowest energy transition can be assigned to the π-π^* charge-transfer excitation[21], which is *approximately* (!) represented by the canonical forms **B** (ground state) and **A** (excited state) shown in Figure 1. Comparison with the monometallic sesquifulvalene complex $[(C_7H_6$-η^5-$C_5H_4)Mn(CO)_3]BF_4$, exhibiting λ_{max} = 536 nm in dichloromethane and λ_{max} = 506 nm in acetonitrile solution ($\Delta\tilde{\nu}$ = -1110 cm^{-1})[7], clearly shows that complexation of the seven-membered ring increases the energy of the respective CT excitation significantly. This is also true for the corresponding ferrocene derivatives[6b,8].

In summary, we have presented a new and efficient method for the preparation of heterobimetallic sesquifulvalene complexes, as well as the characterization of four isomeric hydrosesquifulvalenyl complexes. The development of a general coordination chemistry based on sesquifulvalene (**1**) is of interest especially with regard to the syntheses of other homo- and heterobimetallic complexes containing metal fragments with odd electron numbers. Thus, the extent of electronic and magnetic interaction through the sesquifulvalene ligand could be studied in detail and compared to other π-bridges. Whereas the combination of metal fragments used in this contribution led to a complex with a sesquifulvalene ligand coordinated in a dipolar fashion (Figure 1, **1B**), the use of other metal fragments suitable for the complexation of the five- and seven-membered subunits can also lead to stabilization of sesquifulvalene in its olefinic ground state (Figure 1, **1A**). We will report on these findings in due course.

Note Added in Proof (December 13, 1996): For a recent publication dealing with problems in synthesizing substituted cycloheptatrienyl complexes, see: A. Roberts, M. W. Whiteley, *J. Organomet. Chem.* **1993**, *458*, 131.

This work was financially supported by the Deutsche Forschungsgemeinschaft (Ta 189/1-1,2,3) and the Fonds der Chemischen Industrie. We wish to thank Prof. Dr. J. Kroon (Utrecht University) for providing access to X-ray equipment, and A. M. M. Schreurs (Utrecht University) and I. Brüdgam (FU Berlin) for X-ray data collection on **4a** and **2**, respectively. We are grateful to Prof. Dr. *F. E. Hahn* for is generous support.

Experimental Section

General: All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. NMR spectra were recorded on Bruker AMX 250 (250 MHz), JEOL LA 400 (400 MHz) or Bruker AMX 500 (500 MHz) instruments using TMS as internal reference. Infrared spectra were recorded on a Perkin-Elmer 983 instrument. Elemental analyses (C, H, N) were performed at the Freie Universität Berlin on a Heraeus CHN-Rapid elemental analyzer. Mass spectra were recorded on a Varian MAT 711 instrument and UV/Vis spectra on a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer.

3[7a], **6**[14], $(CH_3CN)_3Cr(CO)_3$[22], $[(C_7H_7)Cr(CO)_3]BF_4$[22] and tropylium tetrafluoroborate[23] were prepared by literature methods.

exo-$[(OC)_3Mn(\mu$-η^5:η^6-C_5H_4-1-$C_7H_7)Cr(CO)_3]$ (**4b**): To a solution of $CpMn(CO)_3$ (1.3 g, 6.4 mmol) in 40 ml of THF, *tert*-butyllithium (3.9 ml of a 1.7 M solution in cyclohexane, 6.6 mmol) was added dropwise at −78 °C. After stirring for 45 min, solid $[(C_7H_7)Cr(CO)_3]BF_4$ (2.05 g, 6.5 mmol) was added to the orange solution. The mixture was allowed to warm to room temperature, stirred for 1 h, and then refluxed for a further 1 h. After removal of the solvent in vacuo, the crude product was purified chromatographically on silica with dichloromethane/petroleum ether (1:1). Evaporation of the solvent afforded **4b** as a red crystalline solid, 1.47 g (54%), m.p. 135–138 °C. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2021, 1981, 1930, 1888 cm^{-1} (CO). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.88 (m, 3H, C_7 ring: 2,7-H + 1-*endo*-H), 4.18 (m, 2H, C_5 ring: CH), 4.46 (m, 2H, C_5 ring: CH), 4.90 (m, 2H, C_7 ring: 3,6-H), 6.04 (m, 2H, C_7 ring: 4,5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 35.6 (C_7 ring: C-1), 67.8 (C_7 ring: CH), 81.2, 82.4 (C_5 ring: CH), 97.4, 99.7 (C_7 ring: CH), 107.9 (C_5 ring: C-1), 224.6 (Mn–CO), 231.1 (Cr–CO). – MS (70 eV); *m/z* (%): 430 (20) [M$^+$], 262 (100) [M$^+$ – 6 CO]. – $C_{18}H_{11}CrMnO_6$ (430.21): calcd. C 50.25, H 2.58; found C 50.33, H 2.77.

Mixture of endo- (**4a**) *and exo-*$[(OC)_3Mn(\mu$-η^5:η^6-C_5H_4-1-$C_7H_7)Cr(CO)_3]$ (**4b**): To a solution of **3** (1.47 g, 5 mmol) in 20 ml of THF, was added solid $(CH_3CN)_3Cr(CO)_3$ (1.3 g, 5 mmol), and the mixture was stirred for 15 h at room temperature. After removal of the solvent in vacuo, the crude product was purified chromatographically on silica with dichloromethane/petroleum ether (2:1). Evaporation of the solvent afforded **4a/4b** (2:1) as a red solid, 1.03 g (48%). – $C_{18}H_{11}CrMnO_6$ (430.21): calcd. C 50.25, H 2.58; found C 50.18, H 2.79. – **4a**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.22 (t, 1H, 1-*exo*-H), 3.08 (dm, 2H, C_7 ring: 2,7-H), 4.72 (m, 2H, C_5 ring: CH), 4.84 (m, 2H, C_5 ring: CH), 4.90 (m, 2H, C_7 ring: 3,6-H), 5.96 (m, 2H, C_7 ring: 4,5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 33.9 (C_7 ring: C-1), 58.8 (C_7 ring: CH), 81.5, 82.4 (C_5 ring: CH), 97.7, 98.2 (C_7 ring: CH), 106.8 (C_5 ring: C-1), 224.3 (Mn–CO), 230.8 (Cr–CO). – MS (70 eV); *m/z* (%): 430 (20) [M$^+$], 262 (100) [M$^+$ – 6 CO].

2-Trimethylstannyl-1,3,5-cycloheptatriene (**5**): The 1,3,5-cycloheptatrien-2-yl anion, generated by the method of Schlosser et al.[18] from cycloheptatriene (5.03 g, 55 mmol), butyllithium (22 ml of a 2.5 M solution in hexane, 55 mmol), and sodium *tert*-butoxide (5.30 g, 55 mmol) in 50 ml of THF, was treated with Me_3SnCl (10 g, 50 mmol) at −50 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 30 min. The solvent was then removed in vacuo and the residue was redissolved by adding diethyl ether and water. The organic phase was separated and dried over Na_2SO_4. After evaporation of the solvent, the crude orange oil was distilled and **5** was obtained as a yellowish oil, 3.4 g (27%), b.p. 50 °C (3 Torr). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 9H, Sn–CH_3), 2.27 (t, *J* = 7 Hz, 2H, 7-CH_2), 5.35 (m, 2H, 1-H + 6-H), 6.22 (dd, *J* = 9, 5.5 Hz, 1H, 5-H), 6.53 (dd, *J* =

11, 5.5 Hz, 1 H, 4-H), 6.74 (d, J = 11 Hz, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = −9.3 (Sn−CH_3), 30.8 (CH_2), 119.6, 125.7, 126.2, 128.1, 136.5 (CH), 138.6 (C−$SnMe_3$). – MS (70 eV); *m/z* (%): 256 (7.8) [M^+], 165 (57.2) [$SnMe_3^+$], 91 (100) [$C_7H_7^+$]. – $C_{10}H_{16}Sn$ (254.93): calcd. C 47.12, H 6.33; found C 45.92, H 6.22.

(η^5-C_5H_4-2-C_7H_7)Mn(CO)$_3$ (**7**): To a solution of **6** (2.5 g, 7.6 mmol) and **5** (1.93 g, 7.6 mmol) in 150 ml of DMF, was added a catalytic amount of $(CH_3CN)_2PdCl_2$ (100 mg, 5 mol-%) in 20 ml of DMF. The solution turned brown and was stirred for 6 h at room temperature, whereupon TLC control showed the reaction to be complete. After addition of 150 ml of diethyl ether followed by 50 g of KF dissolved in 50 ml of water, the mixture was stirred for one hour while argon was bubbled through the solution. The organic phase was then separated and washed three times with 100 ml of water. The combined aqueous phases were extracted twice with 50 ml of diethyl ether and the ethereal extracts were dried over Na_2SO_4. After removal of the solvent in vacuo, the crude product was purified chromatographically on silica with petroleum ether. Evaporation of the solvent afforded **7** as a yellow solid, 850 mg (38%), m.p. 26−28 °C. – IR (CH_2Cl_2): ṽ = 2020, 1933 cm^{-1} (CO). – ^{1}H NMR (400 MHz, $CDCl_3$)[24]: δ = 2.29 (t, 2 H, J = 7 Hz, 7-CH_2), 4.68 (s, 2 H, C_5 ring: CH), 4.85 (s, 2 H, C_5 ring: CH), 5.51 (td, J ≈ 7 Hz, 1 H, C_7 ring: 6-H), 5.62 (t, J = 7 Hz, 1 H, C_7 ring: 1-H), 6.19 (dd br, 1 H, C_7 ring: 5-H), 6.66 (m br, 2 H, C_7 ring: 3-H + 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 27.4 (CH_2), 81.1, 82.1 (C_5 ring: CH), 104.5 (C_5 ring: C-1), 117.9, 122.9, 126.9, 129.6 (C_7 ring: CH), 130.1 (C_7 ring: C-2), 132.5 (C_7 ring: CH), 224.9 (Mn−CO). – MS (70 eV); *m/z* (%): 294 (40) [M^+], 210 (100) [M^+ − 3 CO]. – $C_{15}H_{11}MnO_3$ (294.19): calcd.C 61.24, H 3.77; found C 60.17, H 3.98.

(OC)$_3$Mn(μ-η^5:η^6-C_5H_4-2-C_7H_7)Cr(CO)$_3$ (**8a**) *and (OC)$_3$Mn(μ-η^5:η^6-C_5H_4-1-C_7H_7)Cr(CO)$_3$* (**8b**): To a solution of **7** (275 mg, 0.9 mmol) in 10 ml of THF was added solid $(CH_3CN)_3Cr(CO)_3$ (240 mg, 0.9 mmol), and the mixture was refluxed for 3 h. After removal of the solvent in vacuo, the crude product was purified chromatographically on silica with dichloromethane/petroleum ether (3:5). Evaporation of the solvent afforded **8a,b** as a red crystalline solid, 290 mg (73%). – **8a**: M.p. 139 °C (dec.). – ^{1}H NMR (500 MHz, $CDCl_3$)[24]: δ = 1.66 (ddd, J = 14.0, 3.3, 2.3 Hz, 1 H, 7-*exo*-H), 2.94 (ddd, J = 14.0, 8.6, 7.9 Hz, 1 H, 7-*endo*-H), 3.45 (dm, J = 7.9, 2.3 Hz, 1 H, C_7 ring: 1-H), 3.49 (td, J ≈ 8.6, 3.3 Hz, 1 H, C_7 ring: 6-H), 4.70 (m, 2 H, C_5 ring: CH), 4.78 (t, J ≈ 7.6 Hz, 1 H, C_7 ring: 5-H), 4.84 (m, 1 H, C_5 ring: CH), 5.12 (m, 1 H, C_5 ring: CH), 6.07 (t, J ≈ 7.9 Hz, 1 H, C_7 ring: 4-H), 6.14 (t, J = 8.8 Hz, 1 H, C_7 ring: 3-H). – **8b**: M.p. 155 °C. – IR (CH_2Cl_2): ṽ = 2021, 1975, 1935, 1885 cm^{-1} (CO). – ^{1}H NMR (500 MHz, $CDCl_3$)[24]: δ = 1.69 (dd, J = 14.0, 3.8 Hz, 1 H, 7-*exo*-H), 2.83 (dd, J = 14.0, 9.5 Hz, 1 H, 7-*endo*-H), 3.38 (td, J ≈ 8.9, 3.8 Hz, 1 H, C_7 ring: 6-H), 4.70 (m, 1 H, C_5 ring: CH), 4.75 (m, 1 H, C_5 ring: CH), 4.83 (m, 1 H, C_5 ring: CH), 4.94 (t, J ≈ 7.6 Hz, 1 H, C_7 ring: 5-H), 5.01 (m, 1 H, C_5 ring: CH), 5.12 (d, J = 7.1 Hz, 1 H, C_7 ring: 2-H), 5.93 (t, J ≈ 7.9 Hz, 1 H, C_7 ring: 3-H), 5.98 (t, J ≈ 7.6 Hz, 1h,

Table 2. Crystallographic data for **2**, **4a**, **4b**, **8a**

	2	**4a**	**4b**	**8a**
crystal size, mm	0.40 x 0.10 x 0.08	0.40 x 0.35 x 0.07	0.40 x 0.20 x 0.20	0.45 x 0.20 x 0.03
formula	$C_{18}H_{10}BCrF_4MnO_6$	$C_{18}H_{11}CrMnO_6$	$C_{18}H_{11}CrMnO_6$	$C_{18}H_{11}CrMnO_6$
formula weight	516.01	430.21	430.21	430.21
wavelength, Å	0.71073	1.54176	0.71073	1.54176
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	P 2_1 (No. 4)	P$\bar{1}$ (No. 2)	P$\bar{1}$ (No. 2)	P$\bar{1}$ (No. 2)
a, Å	10.5129(13)	6.7598(5)	8.2148(11)	6.8750(10)
b, Å	18.534(4)	10.756(2)	9.490(8)	11.343(3)
c, Å	10.6176(10)	12.367(2)	11.821(13)	12.240(3)
α, deg		74.38(2)	101.31(11)	115.02(2)
β, deg	109.694(8)	87.21(2)	101.71(7)	97.48(3)
γ, deg		89.04(3)	97.64(4)	95.81(3)
V, Å^3	1947.8(5)	864.9(2)	870.4(12)	844.5(3)
Z	4	2	2	2
ρ_{calc}, g/cm^3	1.760	1.652	1.641	1.692
μ, mm^{-1}	1.278	11.411	1.381	11.687
θ range, deg	$2.04 \le \theta \le 24.96$	$3.71 \le \theta \le 59.95$	$1.81 \le \theta \le 30.03$	$4.06 \le \theta \le 59.94$
index ranges	$0 \le h \le 12$ $-22 \le k \le 0$ $-12 \le l \le 11$	$-7 \le h \le 0$ $-11 \le k \le 12$ $-13 \le l \le 13$	$-11 \le h \le 10$ $-13 \le k \le 9$ $-14 \le l \le 16$	$-7 \le h \le 0$ $-12 \le k \le 12$ $-13 \le l \le 13$
rflns collected	3990	2792	7094	2727
independent rflns	3538 [R(int) = 0.0589]	2563 [R(int) = 0.0495]	4981 [R(int) = 0.0647]	2511 [R(int) = 0.0328]
observed rflns [I > 2σ(I)]	2194	2159	3729	2228
no. of params	525	247	280	235
R [I > 2σ(I)]	0.0589	0.0634	0.0500	0.0827
wR2 (all data)	0.1749	0.1891	0.1393	0.2405

C_7 ring: 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 26.9 (CH_2), 55.2 (C_7 ring: CH), 61.4 (C_7 ring: C-1), 79.5, 80.8, 82.0, 84.9 (C_5 ring: CH), 96.3, 96.5, 98.1, 100.7 (C_7 ring: CH), 104.2 (C_5 ring: C-1), 224.4 (Mn–CO), 231.1 (Cr–CO). – MS (70 eV); *m/z* (%): 430 (18) [M^+], 262 (100) [M^+ – 6 CO]. – $C_{18}H_{11}CrMnO_6$ (430.21): calcd. C 50.25, H 2.58; found C 49.51, H 2.89.

[(OC)$_3$Mn(μ-η^5:η^7-C$_5$H$_4$-C$_7$H$_6$)Cr(CO)$_3$]BF$_4$ (**2**): A solution of triphenylcarbenium tetrafluoroborate (460 mg, 1.4 mmol) in 10 ml of CH_2Cl_2 was slowly added to a solution of **8** (600 mg, 1.4 mmol) in 15 ml of CH_2Cl_2 at −78 °C. The mixture was allowed to warm to room temperature whereupon a red precipiate formed. The precipitate was filtered off and washed with diethyl ether. Crystallization from acetonitrile/dichloromethane afforded **2** as red crystals, 670 mg (93%), m.p. 150 °C (dec.). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2068, 2032, 1960 cm^{-1} (CO). – ^{1}H NMR (250 MHz, CD_3CN): δ = 5.22 (t, 2H, C_5 ring: CH), 5.80 (t, 2H, C_5 ring: CH), 6.50 (m, 4H, C_7 ring: CH), 6.69 (m, 2H, C_7 ring: CH). ^{13}C NMR (62.9 MHz, CD_3CN): δ = 86.8, 87.3 (C_5 ring: CH), 95.9 (C_5 ring: C-1), 101.1, 105.6, 106.0 (C_7 ring: CH), 153.2 (C_7 ring: C-1), 222.5 (Mn–CO), 223.2 (Cr–CO). – MS (FAB): *m/z* (%): 429 (35) [M^+], 373 (20) [M^+ – 2 CO], 345 (26) [M^+ – 3 CO], 154 (100) [C_5H_4–$C_7H_6^+$]. – $C_{18}H_{10}BCrF_4MnO_6$ (516.01): calcd. C 41.90, H 1.95; found C 40.50, H 2.39. – UV (CH_2Cl_2): λ (lg ε) = 279 nm (3.96), 312 (3.89), 444 (3.57). – UV (CH_3CN): λ (lg ε) = 277 nm (3.79), 317 (3.78), 429 (3.49).

X-ray Structural Determination of **2**, **4a**, **4b** *and* **8a**[27]: Single crystals were stable under ambient conditions and were mounted on glass pins for data collection (room temperature). **2**: Enraf-Nonius CAD4 single crystal diffractometer, Mo-K_α radiation, ω-2Θ-scan mode; **4a**, **8a**: Enraf-Nonius Turbo-CAD4 single crystal diffractometer, rotating anode, Cu-K_α radiation, ω-scan mode; **4b**: Enraf-Nnonius FAST area detector, Mo-K_α radiation. Unit cell dimensions were determined from the angular setting of 25 reflections. Crystal data are given in Table 2. Semiempirical absorption correction (ψ-scan) was applied for **2** and **8a**. Structures were solved with direct methods (SHELXS 86)[25] and refined with standard methods (refinement against F^2 of all reflections with SHELXL 93)[26]. For **4b**, hydrogen atoms were refined isotropically. In **2**, **4a** and **8a** all hydrogen atoms were refined in the riding model.

Initial attempts to solve the structure of **2** in a centrosymmetric space group with one molecule per asymmetric unit were unsuccessful. Instead, the structure solution was only possible in the unexpected space group $P2_1$ with two molecules per asymmetric unit. Due to the different orientation of the carbonyl ligands, these two molecules are not related by pseudo-symmetry. The fluorine atoms of the tetrafluoroborate anions in **2** exhibit very high displacement parameters indicating disorder, which could not be resolved. Probably as a result of this disorder, crystals of **2** showed reduced diffraction power compared to the other compounds, so that constraints on the covalent geometry had to be used in the refinement (cyclopentadienyl units treated as ideal pentagons, bond lengths of the seven-membered rings restrained to 1.38(2) Å, tetrahedral geometry for the BF_4^- anions).

---

[1] W. Beck, B. Niemer, M. Wieser, *Angew. Chem.* **1993**, *105*, 969; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 923.

[2] N. J. Long, *Angew. Chem.* **1995**, *107*, 37; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 6.

[3] For recent publications see: [3a] P. A. McGovern, K. P. C. Vollhardt, *J. Chem. Soc., Chem. Comun.* **1996**, 1593. – [3b] I. Kovács, M. C. Baird, *Organometallics* **1996**, *15*, 3588. – [3c] D. S. Brown, M. H. Delville, K. P. C. Vollhardt, D. Astruc, *Organometallics* **1996**, *15*, 2360.– [3d] T. T. Chin, W. E. Geiger, *Organometallics* **1995**, *14*, 1316. – [3e] M. Tilset, K. P. C. Vollhardt, R. Boese, *Organometallics* **1994**, 3146.

[4] Y. K. Kang, Y. K. Chung, S. W. Lee, *Organometallics* **1995**, *14*, 4905 and references cited therein.

[5] [5a] S. S. Lee, T.-Y. Lee, J. E. Lee, I. S. Lee, Y. K. Chung, M. S. Lah, *Organometallics* **1996**, *15*, 3664. – [5b] D. T. Pierce, W. E. Geiger, *Inorg. Chem.* **1994**, *33*, 373. – [5c] W. E. Geiger, N. Van Order Jr., D. T. Pierce, T. E. Bitterwolf, A. L. Rheingold, N. D. Chasteen, *Organometallics* **1991**, *10*, 2403. – [5d] T. E. Bitterwolf, K. S. Raghuveer, *Inorg. Chim. Acta* **1990**, *172*, 59. – [5e] K.-D. Plitzko, G. Wehrle, B. Gollas, B. Rapko, J. Dannheim, V. Boekelheide, *J. Am. Chem. Soc.* **1990**, *112*, 6556. – [5f] C. Elschenbroich, J. Heck, W. Massa, M. Birkhahn, *Chem. Ber.* **1990**, *123*, 2321. – [5g] N. Van Order Jr., W. E. Geiger, T. E. Bitterwolf, A. R. Rheingold, *J. Am Chem. Soc.* **1987**, *109*, 5680. – [5h] T. E. Bitterwolf, *J. Organomet. Chem.* **1980**, *252*, 305. – [5i] C. Elschenbroich, J. Heck, *J. Am. Chem. Soc.* **1979**, *101*, 6773.

[6] [6a] M. Cais, A. Eisenstadt, *J. Am. Chem. Soc.* **1967**, *89*, 5468. – [6b] S. K. Brownstein, E. J. Gabe, R. C. Hynes, *Can. J. Chem.* **1992**, *70*, 1011.

[7] [7a] M. Tamm, A. Grzegorzewski, I. Brüdgam, *J. Organomet. Chem.* **1996**, *519*, 217. – [7b] M. Tamm, A. Grzegorzewski, T. Steiner, T. Jentzsch, W. Werncke, *Organometallics* **1996**, in press.

[8] U. Behrens, H. Brussard, U. Hagenau, J. Heck, E. Hendrickx, J. Körnich, J. G. M. van der Linden, A. Persoons, A. L. Spek, N. Veldman, B. Voss, H. Wong, *Chem. Eur. J.* **1996**, *2*, 98.

[9] J. O. Morley, *J. Am. Chem. Soc.* **1988**, *110*, 7660.

[10] [10a] H. Bingmann, A. Beck, H. Fritz, H. Prinzbach, *Chem. Ber.* **1981**, *114*, 1679. – [10b] W. K. Schenk, R. Kyburz, M. Neuenschwander, *Helv. Chim. Acta* **1975**, *58*, 1099.

[11] P. L. Pauson, G. H. Smith, J. H. Valentine, *J. Chem. Soc. C* **1967**, 1061.

[12] P. L. Pauson, G. H. Smith, J. H. Valentine, *J. Chem. Soc. C* **1967**, 1057.

[13] P. L. Pauson, K. H. Todd, *J. Chem. Soc. C* **1967**, 2315 and 2636.

[14] [14a] C. L. Sterzo, M. M. Miller, J. K. Stille, *Organometallics* **1989**, *8*, 2331. – [14b] C. L. Sterzo, J. K. Stille, *Organometallics* **1990**, *9*, 687.

[15] [15a] M. Wieser, K. Sünkel, C. Robl, W. Beck, *Chem. Ber.* **1992**, *125*, 1369. – [15b] J. Breimair, M. Wieser, W. Beck, *J. Organomet. Chem.* **1992**, *441*, 429. – [15c] M. Moll, P. Würstl, H. Behrens, P. Merbach, *Z. Naturforsch.* **1978**, *33b*, 1304.

[16] [16a] J. Cowie, E. J. M. Hamilton, J. C. V. Laurie, A. J. Welch, *J. Organomet. Chem.* **1990**, *394*, 1. – [16b] P. J. Fitzpatrick, Y. Le Page, J. Sedman, I. S. Butler, *Inorg. Chem.* **1981**, *20*, 2852.

[17] F. J. Hadley, T. M. Gilbert, R. D. Rogers, *J. Organomet. Chem.* **1993**, *455*, 107.

[18] M. Stähle, R. Lehmann, J. Kramar, M. Schlosser, *Chimia* **1989**, *39*, 229.

[19] J. K. Stille, *Angew. Chem.* **1986**, *98*, 504; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508.

[20] For recent examples see: [20a] R. Boese, G. Bräunlich, J.-P. Gotteland, J.-T. Hwang, C. Troll, K. P. C. Vollhardt, *Angew. Chem.* **1996**, *108*, 1100; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 995. – [20b] U. H. F. Bunz, J. E. C. Wiegelmann-Kreiter, *Chem. Ber.* **1996**, *129*, 785.

[21] [21a] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319. – [21b] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 1988.

[22] W. P. Fehlhammer, W. A. Herrmann, K. Öfele in *Handbuch der Präparativen Anorganischen Chemie* (Ed.: G. Brauer), Ferdinand Enke Verlag, Stuttgart, **1981**, vol. 3, p. 1866 and p. 2020.

[23] T. Asano, M. Oda in *Methoden der Organischen Chemie (Houben-Weyl) 4th ed.* **1985**, vol. V/2c, p. 49.

[24] Note that some resonances appear as triplets which are virtually doublets of doublets with very similar coupling constants. Here, averaged *J* values are given.

[25] G. M. Sheldrick, *SHELXS 86, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1986.

[26] G. M. Sheldrick, *SHELXL 93, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1993.

[27] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystalligraphic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Boad, Cambridge CB2 1EZ, UK (fax: int. code +(1223) 336-033, e-mail: deposit@chemcrys.cam.ac.uk), on quoting the deposition number CCDC-100050.

[96234]