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ansa-METALLOCENE DERIVATIVES

VI *. SYNTHESIS AND MOLECULAR STRUCTURE OF A STABLE TETRAMETHYLETHYLENE-BRIDGED CHROMOCENE CARBONYL COMPLEX, $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$

HEINZ SCHWEMLEIN, LASZLO ZSOLNAI, GOTTFRIED HUTTNER and
HANS H. BRINTZINGER **
Fakultät für Chemie, Universität Konstanz, Postfach 5560, 7750 Konstanz (F.R.G.)

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Summary

The tetramethylethylene-bridged chromocene carbonyl complex $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ is obtained by reaction of the Grignard compound $(CH_3)_4C_2(C_5H_4MgCl)_2 \cdot 4THF$ with $CrCl_2 \cdot THF$ under CO. The diamagnetic carbonyl complex is the first thermally stable chromocene ligand adduct; its structure is that of a normal wedge-shaped metallocene derivative whose ring ligands span a centroid–chromium–centroid angle of 143°; the molecule closely approximates to C_2 symmetry with respect to the Cr–C≡O axis.

Introduction

While molybdocene and tungstenocene form a great variety of ligand derivatives, coordinative adducts of chromocene are rare, and none of those reported are thermally stable. Wilkinson, Cotton and Birmingham observed the formation of NH_3 adducts of $(C_5H_5)_2Cr$ in liquid ammonia [2]; at ambient temperatures $(C_5H_5)_2Cr$ is regenerated from these complexes [3]. Later, we found that $(C_5H_5)_2Cr$ is quantitatively converted to the diamagnetic adduct $(C_5H_5)_2Cr(CO)$ by reaction with CO in pentane at −78°C [4]; at room temperature, however, the CO dissociation pressure rises above 100 mbar. Finally, Chisholm et al. reported that $F_3CC{\equiv}CCF_3$ to form a diamagnetic $(C_5H_5)_2Cr$ adduct at temperatures below −30°C; at room temperature, this complex is converted into an incompletely characterized paramagnetic material [5]. We now report the synthesis and molecular structure of a

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* For Part V see ref. 1.

** To whom correspondence should be addressed.

surprisingly stable carbonyl derivative of an *ansa*-chromocene containing an interannular tetramethylethylene bridge.

Results and discussion

When the Grignard compound $(CH_3)_4C_2(C_5H_4MgCl)_2 \cdot 4THF$, obtained by reductive coupling of 6,6-dimethyl fulvene with Mg/CCl_4 [1] was treated with an equimolar quantity of $CrCl_2 \cdot THF$ in THF in an attempt to obtain the tetramethylethylene-bridged chromocene $(CH_3)_4C_2(C_5H_4)_2Cr$, only an insoluble, very air-sensitive, red product, probably of polymeric nature was obtained. However, when the reaction is carried out under an atmosphere of CO, a dark red solution is formed, from which, by evaporation of solvent, extraction with pentane and subsequent recrystallization, dark red needles of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ are obtained in ca. 50% yield. This product can be further purified by sublimation in vacuo, which is, however, accompanied by loss of material due to partial decomposition to an unsublimable residue.

The product is characterized by an IR spectrum with a strong $\nu(CO)$ absorption at 1905 cm^{-1} (pentane solution). In the reversibly formed unbridged CO adduct $(C_5H_5)_2Cr(CO)$ the $\nu(CO)$ absorption appears at 1900 cm^{-1} [4]. This close spectral coincidence indicates a very similar degree of back donation in the two CO adducts; the increased stability of the bridged derivative would thus have to be ascribed primarily to steric reasons, i.e. to the fixation of a deformed ligand framework by the interannular bridge.

In its ^1H NMR spectrum, the ring protons of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ give rise to the AA'XX' pair of triplets normally observed in *ansa*-metallocenes. The chemical shifts for these resonances, at 3.60 and 4.38 ppm, are rather similar to those, viz. 3.89 and 4.63 ppm, observed for tetramethylethylene-bridged ferrocene in $CDCl_3$ [6]; the ^1H NMR spectrum confirms the diamagnetism of the *ansa*-chromocene carbonyl adduct.

A crystal of approximate dimensions $0.2 \times 0.2 \times 0.9$ mm, sealed in a glass capillary under argon, was used for X-ray measurements. Space group, cell parameters and X-ray diffraction intensities were determined on a Syntex-P3 four-circle diffractometer at 233 K (Mo-K_α, λ 71.069 pm), graphite monochromator, ω-scan with $1.4 \le \dot{\omega} \le 29.3°$ min^{-1} and $1 < 2\theta < 44°$. The crystals are monoclinic, space group $P2_1/c$; a 1036(1), b 725.2(7), c 1859(4) pm; β 97.05(0.15)°; 4 crystallographically equivalent molecules per unit cell; V 1387×10^6 pm^3; d_{calc} 1.25 g/m^3; absorption coefficient μ 8.2 cm^{-1}.

Of 1658 reflexes measured, 1320 with $I \ge 2\sigma$ were used for solving and refining the structure. The structure was solved by direct methods (SHELXTL program [7]) and refined with a partially anisotropic model (H atom positions were taken from the Fourier difference map, but not refined). The refinement converged at $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.076$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2]^{1/2}/[\Sigma w|F_o|^2]^{1/2} = 0.087$. Structural data are listed in Tab. 1; bond lengths and bong angles are listed in Table 2; the molecular structure obtained is represented in Fig. 1.

The Cr–C(ring) distances are identical within standard deviations; their mean value of 216 ± 1 pm is in close agreement with a value of 216.9(0.4) pm observed for $(C_5H_5)_2Cr$ by gas phase electron diffraction [8]. The centroid–metal–centroid angle is 143.3°, substantially larger than the angles of 128 and 130° observed in ethylene-

TABLE 1

STRUCTURAL PARAMETERS FOR $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$

Fractional coordinates (with e.s.d.'s) and isotropic temperature factors [a]

Atom	x/a	y/b	z/c	U
Cr	0.7610(1)	0.3858(2)	0.5108(1)	
C(1)	0.8123(9)	0.135(1)	0.4579(5)	0.029(2)
C(2)	0.8580(8)	0.126(1)	0.5316(5)	0.029(2)
C(3)	0.7461(8)	0.137(1)	0.5714(5)	0.025(2)
C(4)	0.6345(8)	0.155(1)	0.5188(5)	0.026(2)
C(5)	0.6738(9)	0.152(1)	0.4496(5)	0.031(2)
C(6)	0.7366(8)	0.475(1)	0.6178(5)	0.025(2)
C(7)	0.8652(9)	0.524(1)	0.6032(5)	0.032(2)
C(8)	0.8557(9)	0.644(1)	0.5454(5)	0.034(2)
C(9)	0.7208(9)	0.672(1)	0.5228(5)	0.033(2)
C(10)	0.6467(9)	0.570(1)	0.5665(5)	0.032(5)
C(11)	0.7005(8)	0.339(1)	0.6751(5)	0.025(2)
C(12)	0.7496(8)	0.141(1)	0.6529(5)	0.029(2)
C(13)	0.554(1)	0.345(2)	0.6768(6)	0.045(3)
C(14)	0.763(1)	0.402(2)	0.7490(6)	0.047(3)
C(15)	0.891(1)	0.100(2)	0.6890(6)	0.045(3)
C(16)	0.663(1)	−0.017(2)	0.6766(6)	0.043(3)
C(17)	0.7821(9)	0.479(1)	0.4207(5)	0.032(2)
O	0.7982(8)	0.540(1)	0.3648(4)	
H(1)	0.852	0.146	0.418	
H(2)	0.947	0.103	0.560	
H(4)	0.548	0.165	0.524	
H(5)	0.611	0.149	0.403	
H(7)	0.928	0.487	0.633	
H(8)	0.930	0.705	0.519	
H(9)	0.676	0.715	0.484	
H(10)	0.558	0.558	0.561	
H(13A)	0.512	0.310	0.636	
H(13B)	0.511	0.258	0.709	
H(13C)	0.523	0.456	0.691	
H(14A)	0.842	0.396	0.753	
H(14B)	0.710	0.495	0.768	
H(14C)	0.755	0.336	0.797	
H(15A)	0.803	0.116	0.699	
H(15B)	0.908	0.012	0.666	
H(15C)	0.927	0.156	0.679	
H(16A)	0.586	−0.006	0.658	
H(16B)	0.724	−0.077	0.674	
H(16C)	0.673	−0.005	0.730	

Anisotropic temperature factors [b]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr	0.0256(8)	0.0156(8)	0.0256(8)	−0.0004(7)	0.0047(6)	−0.0006(7)
O(1)	0.076(6)	0.050(5)	0.032(4)	0.010(4)	0.014(4)	0.000(4)

[a] The designations HxA, HxB, HxC refer to the methyl hydrogen atoms bonded to Cx. Other hydrogens: Hx bonded to Cx. [b] The anisotropic factors U_{ij} refer to: $T=\exp(-2\pi^2[U_{11}h^2a^{\star}+\ldots 2hka^{\star}b^{\star}U_{12}+\ldots])$; U_{ij} in 10^4 pm^2.

TABLE 2

INTERATOMIC DISTANCES (pm) AND BOND ANGLES (°) (Cp(1) = centroid of ring 1, plane 1 = mean plane of ring 1)

Cr–C(1)	217(1)	Cr–C(6)	214(1)
Cr–C(2)	216(1)	Cr–C(7)	217(1)
Cr–C(3)	214(1)	Cr–C(8)	218(1)
Cr–C(4)	216(1)	Cr–C(9)	213(1)
Cr–C(5)	218(1)	Cr–C(10)	215(1)
Cr–Cp(1)	178(1)	Cr–Cp(2)	178(1)
Cr–C(17)	185(1)	C(17)–O	116(1)
C–C(ring 1)	144 ± 3	C–C(ring 2)	143 ± 3
C(6)–C(11)	153(1)	C(3)–C(12)	151(1)
C(11)–C(12)	160(1)		
Cr–C(17)–O	178.4(9)	Cp(1)–Cr–Cp(2)	143.3(5)
C(6)–C(11)–C(12)	106.1(7)	C(3)–C(12)–C(11)	107.9(7)
Angles between ring planes (°)			
Plane 1–Plane 2	38.5(5)		

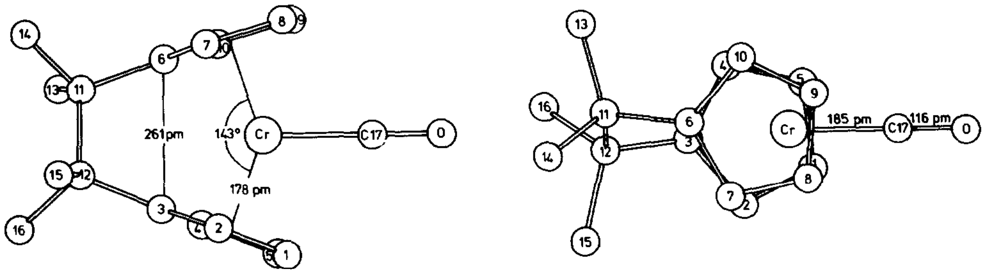

Fig. 1. Molecular structure of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$. Mutually perpendicular projections on to plane containing the two ring centroids and the Cr–C≡O axis (left) and on to the bisector plane between the two ring mean planes (right). Atomic positions designated by numbers only refer to carbon atoms of the ligand framework.

bridged [9] and in unbridged titanocene dichloride [10], but quite close to a centroid–metal–centroid angle of 145.8° observed for $(C_5H_5)_2MoH_2$ [11]. Although not fixed by crystallographic site symmetry, the structure depicted in Fig. 1 maintains, without major deviations, the C_2 symmetry along the Cr–C≡O axis expected for a monoligated metallocene derivative with low-spin d^4 electron configuration [12].

Experimental

All operations were carried out with exclusion of air and moisture, using Schlenk and vacuum line techniques. Anhydrous $CrCl_2 \cdot THF$ was obtained from Cr metal and HCl/THF [13]; the Grignard compound $(CH_3)_4C_2(C_5H_4MgCl)_2 \cdot 4THF$ was prepared as described in ref. 1.

$(CH_3)_4C_2(C_5H_4)_2Cr(CO)$

In a 250 ml side-arm flask, 80 ml THF are condensed at −78°C on to 0.72 g (3.7 mmol) $CrCl_2 \cdot THF$ and 2.34 g (3.7 mmol) $(CH_3)_4C_2(C_5H_4MgCl)_2 \cdot 4THF$. After introduction of an atmosphere of CO, the mixture is stirred and allowed to warm during 12 h to room temperature, at which it is stirred for another day. The solvent is then removed in vacuo. The residue is dried without further warming and taken up in ca. 100 ml of pentane, filtered off and washed twice with pentane. The combined pentane extracts are concentrated to 10 ml and kept at −40°C to give 570 mg (1.94 mmol, 52% theoretical yield) of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ as red-brown crystals. The material can be further purified by sublimation at 40–45°C on to a cold finger or at 60–70°C in a sublimation tube; it is very air-sensitive.

^1H NMR in benzene-d_6 at 25°C: 0.91 ppm (s, 12H), 3.60 ppm (t, 4H, J 2.14 Hz), 4.38 ppm (t, 4H, J 2.14 Hz).

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