



Tricarbonyl-6,6'-dimethylfulvene chromium(0) – Structural properties

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ABSTRACT

The crystal structure of tricarbonyl-6,6'-dimethylfulvene chromium(0) was determined using X-ray diffraction at room temperature and at 120 K. The title compound crystallizes in the centrosymmetric, monoclinic space group $P2_1/n$ (no. 14) with one complete molecule in the asymmetric unit. The deviation of the chromium(0) complex from $C_s(m)$ symmetry is negligible in agreement with results derived from density functional calculations using three different methods as well as *ab initio* calculations (MP2). The 6,6'-dimethylfulvene ligand is bent by 30.9° as a result of the $\pi-\eta^2:\pi-\eta^2:\pi-\eta^2$ coordination to the Cr(0) metal. In addition, the chromium(0) complex was studied by IR and Raman spectroscopy and selected vibrational data are compared to values derived from DFT calculations.

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1. Introduction

Transition metal complexes of fulvene ligands that were first described in 1961 [1,2] and as a result of their unique bonding properties and applications resulting thereof, fulvene ligands coordinated to early as well as to late transition metals are still in the focus of current investigations [3]. Fulvene complexes exhibit a wide range of coordination modes of the fulvene ligand to the metal center [3–6] depending on the transition metal, the oxidation state of the metal center, and the substituents of the fulvene ligand, ranging from $\pi-\eta^2:\pi-\eta^2:\pi-\eta^2$ type to a single $\pi-\eta^2$ coordination of the exocyclic C–C double bond [4,7]. For example, for chromium fulvene complexes redox-induced haptotropic rearrangements were described [8]. However, in most cases the pentafulvene ligand acts as a six electron donor to transition metals and the coordination lies in between the two borderline cases $\pi-\eta^2:\pi-\eta^2:\pi-\eta^2$ and $\pi-\eta^5:\sigma-\eta^1$ as depicted in Scheme 1.

Tricarbonyl chromium(0) fulvene complexes are among the first fulvene complexes that were described [2]. A few complexes have been characterized by single-crystal X-ray diffraction [9–13], but high quality crystal structures which enable a detailed discussion of the coordination mode of the fulvene ligand towards the Cr(0) center are rare. In this contribution we report on the crystal structure of tricarbonyl-6,6'-dimethylfulvene chromium(0) determined at 120 K and at room temperature that was a prototype complex used for a molecular orbital analysis of fulvene Cr(CO)₃ complexes [6]. The

discussion of the bonding properties is supported by density functional calculations and *ab initio* calculations (MP2).

2. Experimental

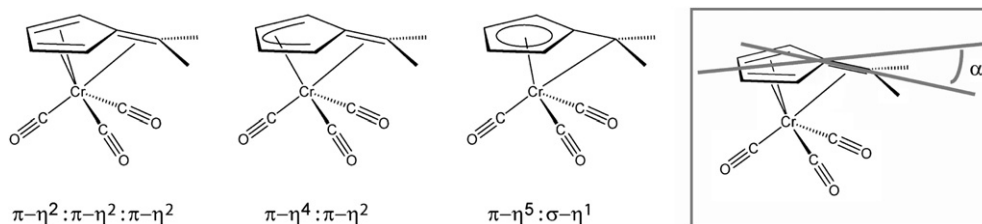
2.1. General

6,6'-dimethylfulvene was obtained from Fluka and tris(acetonitrile)tricarbonyl chromium(0) was purchased from Aldrich. All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried using standard procedures [14] and stored over molecular sieves under a dry nitrogen atmosphere. ¹H and ¹³C NMR spectra were recorded at room temperature in thf-*d*⁸ on a Bruker DRX 500 spectrometer operating at 500.13 and 125.76 MHz for ¹H and ¹³C nuclei, respectively. NMR signals were referenced against TMS as internal standard. Infrared and Raman spectra were recorded at room temperature on an Excalibur FTS 3500 spectrometer (Digilab, Germany) with an apodized resolution of 2 cm⁻¹ (IR) and 4 cm⁻¹ (Raman), respectively. IR spectra were measured in the attenuated total reflection (ATR) mode in the region of 4000–530 cm⁻¹. Raman spectra were measured using the 1064 nm excitation line of a Nd/YAG laser on crystalline samples contained in melting point capillaries in the region of 3500–80 cm⁻¹.

2.2. Synthesis of tricarbonyl-6,6'-dimethylfulvene chromium(0)

Tricarbonyl-6,6'-dimethylfulvene chromium(0) was synthesized by a slightly modified literature procedure [11,15]. A solution

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Scheme 1. The coordination modes of the 6,6'-dimethylfulvene to the Cr(CO)₃ fragment (left) and definition of the bending angle α (right).

of 6,6'-dimethylfulvene (1.6 g, 15.4 mmol) in tetrahydrofuran (10 mL) was cannula transferred to a suspension of [Cr(CO)₃(N-CMe)₃] (2.0 g, 7.7 mmol) in THF (50 mL). The reaction mixture was stirred at room temperature for 10 h to result in a dark solution. All volatiles were removed under reduced pressure and the solid residue was extracted with hexane (100 mL). After filtration, the hexane was removed in vacuum to yield brownish, crude tricarbonyl-6,6'-dimethylfulvene chromium(0). Crystallization from diethyl ether afforded yellow crystals. Yield: 0.6 g (2.4 mmol, 31%). ¹H NMR (500 MHz, thf-*d*⁸): δ = 4.69 (s, br, 2H, H2/3), 3.99 (s, br, 2H, H1/4), 1.51 (s, 6H, CH₃) (The expected splitting of the signals of the protons that are bonded to the carbon atoms of the fulvene ring, H2/3 and H1/4, are not observed as a result of line broadening); ¹³C {¹H} NMR (125 MHz, thf-*d*⁸): δ = 238.6 (3C, CO), 122.7 (1C, C6), 106.1 (1C, C5), 94.6 (2C, C2/3), 89.0 (2C, C1/4), 24.8 (2C, CH₃). (The assignment of δ (¹³C) is in agreement with reported data [11].) IR (ATR): ν = 1968 (m, CO, A', ν_s), 1872 (vs, br, CO, A', ν_s), 1844 (s, sh, CO, A'', ν_{as}) cm⁻¹. IR (Nujol, KBr discs): ν = 1987 (vs, CO, A', ν_s), 1919 (vs, sh, CO, A', ν_s), 1906 (s, CO, A'', ν_{as}) cm⁻¹. Raman: ν = 1960 (m, CO, A', ν_s), 1883 (s, CO, A', ν_s), 1878 (m, sh, CO, A'', ν_{as}) cm⁻¹. [B3LYP/6-311++G(d,p)]: ν = 2042 (*I*_{IR} = 1324 km mol⁻¹, *A*_{Ra} = 47 Å⁴ amu⁻¹, CO, A', ν_s), 1993 (*I*_{IR} = 866 km mol⁻¹, *A*_{Ra} = 169 Å⁴ amu⁻¹, CO, A', ν_s), 1983 (*I*_{IR} = 1212 km mol⁻¹, *A*_{Ra} = 109 Å⁴ amu⁻¹, CO, A'', ν_{as}) cm⁻¹.]

2.3. Single-crystal X-ray diffraction

Block shaped yellow crystals of Tricarbonyl-6,6'-dimethylfulvene chromium(0) suitable for X-ray diffraction were obtained from diethyl ether solutions. A crystal (0.40 × 0.35 × 0.30 mm³) was sealed in a thin-walled glass capillary and data were collected at 290 and 120 K. The Cr(0) complex crystallizes in the centrosymmetric monoclinic space group *P*2₁/*n* with *Z* = 4. The crystal was studied using a Siemens-P4 diffractometer and Mo *K* α radiation (λ = 0.71073 Å). The structure was solved by direct methods [16,17], and refinement is based on full-matrix least-squares calculations on *F*² [17,18]. In the latest stages of the refinements the coordinates of all atoms, the anisotropic displacement parameters of all atoms heavier than hydrogen, and the isotropic displacement parameters of the hydrogen atoms of the fulvene ring were refined freely. The hydrogen atoms of the methyl groups were introduced by a riding model with the *U*_{iso} value constrained to one value for each group.

T = 290 K: *a* = 7.2493(10), *b* = 13.3492(13), *c* = 11.3534(14) Å, β = 100.694(9)°, *V* = 1079.6(2) Å³, least-squares refinement of the lattice constants from 40 reflections, *Z* = 4, $\rho_{\text{calc.}}$ = 1.490 Mg m⁻³, μ = 1.041 mm⁻¹, $\omega/2\theta$ -scan, 12836 reflections in the range of 2.38 < θ < 30.00°, 3138 unique intensities, *R*(int) = 3.10%, 2526 intensities with *I* > 2 σ (*I*), minimizing of $\sum w(F_o^2 - F_c^2)$ with *w* = 1/[$\sigma^2(F_o^2) + (0.0482P)^2 + 0.0156P$] where *P* = (*F*_o² + 2*F*_c²)/3, 157 refined parameters, *R*1 (*I* > 2 σ (*I*)) = 3.01%, *wR*2 (all) = 8.58%, *S* = 1.063, -0.32 < $\Delta\rho$ < +0.26e Å⁻³.

T = 120 K: *a* = 7.217(1), *b* = 13.263(3), *c* = 11.083(2) Å, β = 100.56(3)°, *V* = 1042.9(3) Å³, least-squares refinement of the lattice

constants from 30 reflections, *Z* = 4, $\rho_{\text{calc.}}$ = 1.543 Mg m⁻³, μ = 1.078 mm⁻¹, $\omega/2\theta$ -scan, 7428 reflections in the range of 2.42 < θ < 29.99°, 3019 unique intensities, *R*(int) = 5.08%, 2740 intensities with *I* > 2 σ (*I*), minimizing of $\sum w(F_o^2 - F_c^2)$ with *w* = 1/[$\sigma^2(F_o^2) + (0.015P)^2 + 0.5P$] where *P* = (*F*_o² + 2*F*_c²)/3, 157 parameters, *R*1 (*I* > 2 σ (*I*)) = 2.69%, *wR*2 (all) = 6.82%, *S* = 1.033, -0.57 < $\Delta\rho$ < +0.43e Å⁻³.

The molecular structure diagrams were drawn with the program Diamond 3.2d [19]. CCDC-767309 (*T* = 290 K) and CCDC-767310 (*T* = 120 K) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

2.4. Quantum chemical calculations

Density functional calculations (DFT) [20] were carried out using Becke's three-parameter hybrid functional and the Lee–Yang–Parr correlation functional (B3LYP) [21–23] and the GGA functional BP86 [21,24,25] as well as *ab initio* calculations employing second-order Møller–Plesset (MP2) perturbation theory [26] and the 6-311++G(d,p) or the 6-311++G(3df,3pd) basis sets. Except for the optimized geometry obtained from the MP2/6-311++G(d,p) calculation, for all other structures vibrational analysis was performed at the same level of theory in order to verify that they represent minima on the respective hypersurface. All calculations were carried out using the Gaussian03 program suite [27].

3. Results and discussion

Tricarbonyl-6,6'-dimethylfulvene chromium(0) crystallizes in the centrosymmetric monoclinic space group *P*2₁/*n* with the whole molecule in the asymmetric unit. In Table 1 selected bond lengths and angles for the title complex derived from X-ray diffraction at 120 and 290 K are listed and compared to values derived from density functional (DFT) calculations at three different levels of theory as well as an *ab initio* calculation at the MP2/6-311++G(d,p) level of theory. The quality of the data of the low temperature experiment is slightly improved due to the smaller effect of vibrational motion.

The theoretical bond parameters of the DFT and *ab initio* calculations are in very good agreement with the geometric parameters derived from the X-ray diffraction experiments. The structure obtained from the B3LYP/6-311++G(d,p) calculation fits best with the geometric parameters of the X-ray diffraction model for the coordinated fulvene but slightly underestimates the interaction of the fulvene with the chromium metal. *Vice versa* the calculation at the MP2/6-311++G(d,p) overestimates the chromium ligand interaction.

In the structure of the title compound the chromium metal is coordinated by three carbonyl groups and by a 6,6'-dimethylfulvene ligand. The coordination of the chromium atom is best described as a distorted octahedron with respect to the carbon atoms of the three

Table 1Selected experimental (120 K) and calculated^a bond parameters of ($\eta^2:\eta^2:\eta^2$ -6,6'-dimethylfulvene)Cr(CO)₃ and 6,6'-dimethylfulvene.

	$(\eta^2:\eta^2:\eta^2$ -6,6'-dimethylfulvene)Cr(CO) ₃				6,6'-dimethylfulvene				
	X-ray 120 K	X-ray 290 K	B3LYP 6-311++ G(3df,3pd)	B3LYP 6-311++ G(d,p)	BP86 6-311++ G(d,p)	MP2 6-311++ G(d,p)	X-ray ^b 120 K	GED ^c 273 K	B3LYP 6-311++ G(d,p)
Bond lengths [Å]									
C1–C5/C4–C5	1.461(2)/1.459(2)	1.456(2)/1.451(2)	1.458	1.461	1.466	1.462	1.439	1.476	1.472
C1–C2/C3–C4	1.395(2)/1.395(2)	1.390(3)/1.394(2)	1.394	1.398	1.411	1.408	1.346	1.340	1.356
C2–C3	1.434(2)	1.422(3)	1.433	1.436	1.442	1.443	1.435	1.462	1.464
C5–C6	1.404(2)	1.398(2)	1.397	1.402	1.418	1.417	1.343	1.347	1.358
C6–C7/C6–C8	1.502(2)/1.499(2)	1.505(3)/1.499(3)	1.503	1.506	1.509	1.504	1.520	1.510	1.503
Cr–C5	2.070(1)	2.071(2)	2.110	2.109	2.097	2.044			
Cr–C1/Cr–C4	2.167(1)/2.148(1)	2.164(2)/2.149(2)	2.187	2.187	2.171	2.115			
Cr–C2/Cr–C3	2.239(1)/2.233(2)	2.234(2)/2.228(2)	2.264	2.264	2.244	2.183			
Cr–C6	2.495(1)	2.515(2)	2.610	2.606	2.576	2.436			
Cr–CO	1.846(1)/1.856(1)/1.860(1)	1.845(2)/1.851(2)/1.868(2)	1.863	1.864	1.849	1.755			
C–O	1.146(2)/1.149(2)/1.150(2)	1.139(2)/1.147(2)/1.145(2)	1.150	1.153	1.168	1.192			
Cr–M(C5–C6)	2.182(1)	2.114(1)	2.268	2.265	2.239	2.134			
Cr–M(C1–C2)/Cr–M(C3–C4)	2.077(1)/2.090(1)	2.086(2)/2.075(2)	2.114	2.113	2.092	2.060			
Bond angles [°]									
C1–C5–C4	105.7(1)	106.0(2)	105.8	105.8	106.1	106.1	106.2	106	105.6
C5–C1–C2/C3–C4–C5	108.3(1)/108.5(1)	108.1(2)/108.1(2)	108.4	108.4	108.3	108.4	107.9	108	108.3
C1–C2–C3/C2–C3–C4	108.8(1)/108.5(1)	108.9(2)/108.9(2)	108.7	108.7	108.6	108.5	108.9	109	108.9
Dihedral angles [°]									
α	30.9	29.8	26.3	26.7	28.8	34.8	0	0	0

^a C_s symmetry.^b Ref. [31].^c Ref. [32].

carbonyl ligands and the centers of the formal double bonds of the fulvene ligand as shown in Fig. 1.

A comparison of the bond lengths of the five-membered ring and the exocyclic C5–C6 bond in the Cr(CO)₃ complex to those of the uncoordinated 6,6'-dimethylfulvene molecule reveals nearly unchanged C–C single bonds (C5–C1, C4–C5, C2–C3) and only slightly elongated C–C double bonds (C1–C2, C3–C4, C5–C6); the latter is typical for the π -coordination of double bonds to Cr(0) (Fig. 1, Table 1). Hence, the coordination of 6,6'-dimethylfulvene in the title compound is best described as a [2 + 2 + 2] mode. This observation is furthermore supported by the high quality DFT as well as *ab initio* calculations (Table 1).

A related bonding situation is found for some of the few structurally characterized fulvene Cr(0) complexes [9–13] and in the related *s-cis*-1,3-butadiene complex ($\eta^2:\eta^2$ -*s-cis*-1,3-butadiene)tricarbonyltriethylphosphanechromium(0) [28] but the differences in bond lengths reported are in most cases not significant. This coordination behavior of *cis*-1,3-butadiene fragments to Cr(0) centers contrasts the coordination modes found for some other related complexes with different metals, which exhibit a ligand with a *cis*-1,3-butadiene fragment with nearly equilibrated C–C bonds, for example in bis(η^4 -*s-cis*-1,3-butadiene)monocarbonylmanganese(0) [29] and bis(η^4 -1,3-cyclohexadiene)monocarbonyliron(0) [30].

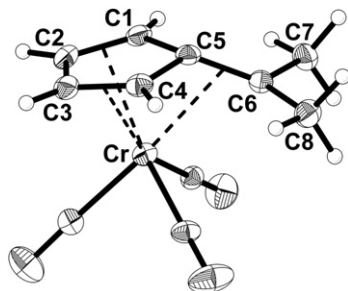


Fig. 1. Molecular structure of the title compound at 120 K (displacement ellipsoids are at the 50% probability level, hydrogen atoms with arbitrary radii).

As a result of the coordination of the exocyclic C–C double bond (C5–C6) the fulvene ligand is bent towards the chromium center by 30.9°. This bending angle is in good agreement to the angles derived from theoretical calculations (Table 1).

In the experimental section the band positions for $\nu(\text{CO})$ derived from ATR-IR (neat sample) as well as Raman experiments on tricarbonyl-6,6'-dimethylfulvene chromium(0) are presented and compared to values calculated at the B3LYP/6-311++G(d,p) level of theory. The IR spectroscopic data agree well with values reported earlier on samples measured either in KBr [15] or in CH₂Cl₂ solution [11]. To the best of our knowledge, no Raman spectroscopic data have been reported for this chromium(0) complex, so far.

4. Conclusions

The coordination mode of the 6,6'-dimethylfulvene ligand in its Cr(CO)₃ complex is best described as π - $\eta^2:\pi$ - $\eta^2:\pi$ - η^2 (Scheme 1). The contribution of the two other coordination modes depicted in Scheme 1, which have been observed for some early (π - $\eta^5:\sigma$ - η^1) or late (π - $\eta^4:\pi$ - η^2) transition metal complexes, is rather small.

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