

Redetermination of Bis(η^4 -1,3-cyclohexadiene)monocarbonyliron

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The crystal structure of bis(η^4 -1,3-cyclohexadiene)monocarbonyliron has been redetermined by X-ray data. The compound crystallizes in the enantiomorphous, orthorhombic space group $P2_12_12_1$ with one complete molecule in the asymmetric unit. For concordance to the originally reported structure, which was determined under ambient conditions, the redetermination has been carried out at room temperature and at low temperature ($T = 293$ K: $a = 7.618(2)$, $b = 8.522(2)$, $c = 17.138(4)$ Å, $V = 1112.6(5)$ Å 3 , $R1 = 0.0226$, $wR2 = 0.0539$; $T = 120$ K: $a = 7.509(2)$, $b = 8.417(3)$, $c = 16.778(6)$ Å, $V = 1060.3(6)$ Å 3 , $R1 = 0.0242$, $wR2 = 0.0533$). The redetermination proved this complex to have non-crystallographic C_{2v} point group symmetry. Correlation effects to the atomic coordinates and displacement parameters introduced problems during the structure refinement caused by pseudo-symmetry of the molecule. All bond lengths, angles, and torsion angles appear in this revised crystal structure in the normal range for π -coordinated diene transition metal complexes.

Introduction

Olefin and especially butadiene transition metal complexes have been known for a long time as polymerisation catalysts and are the main subjects of most textbooks on organometallic chemistry [1]. These complexes have been intensively studied by spectroscopic, crystallographic and quantum chemical methods.

π -Coordinated 1,3-cyclohexadienes can be understood as the equivalent of a sterically fixed *s-cis*-1,3-butadiene. According to this relation the coordination modes of 1,3-cyclohexadienes in their transition metal complexes should be very similar to those of the corresponding bis(*s-cis*-1,3-butadiene) transition metal complexes [2, 3]. If substitution effects have only a minor influence on the electronic properties of the conjugated diolefinic π -system, bis(η^4 -1,3-cyclohexadiene)monocarbonyliron complexes should form molecular units of C_{2v} symmetry in solution as well as in the solid state. Krüger and Tsay [4] reported a single crystal structure determination based on X-ray diffraction data of the bis(η^4 -1,3-cyclohexadiene)monocarbonyliron. The analysis of the geometric parameters derived from this diffraction experiment proved the two crystallographically independent

ligands to be significantly different. The findings have been discussed to be the consequence of crystal packing forces or a special mode of coordination. This suspicious structure has been referred to in several monographs and has found access to text books of organometallic chemistry. This report describes the redetermination of the crystal structure of bis(η^4 -1,3-cyclohexadiene)monocarbonyliron and problems that may arise during the refinement of difficult structures [5].

Results and Discussion

Structure redetermination

The redetermination and refinement of the crystal structure of the title compound have shown that the space group assignment as well as the connectivity were derived correctly. Refinements of this compound in the enantiomorphous space group $P2_12_12_1$ are complicated by correlations introduced by pseudo-symmetry effects of the C_{2v} symmetric molecules in general position reducing the stability of the refinement and increase the possibility to end up in a local minimum [5].

Our first refinement attempts on the title structure were based on X-ray diffraction data collected at room temperature using a standard data collection

strategy. These calculations showed serious parameter correlations (positional and displacement parameters) reducing the stability of the refinement. By weighting up weak reflections a plausible structure model with C_{2v} symmetry resulted, with the disadvantage of high R -values. Taking these problems into account it means that the weak reflections have to be collected with a significantly reduced scan speed. As the compound crystallizes in a non-centrosymmetric space group a sufficient set of Friedel-equivalent reflections also has to be collected. Finally, a numerical absorption correction needs to be performed even though the central iron atom is the only heavy atom in this structure. The pseudo symmetry effects in this case are related to pseudo mirror planes. In the early stages of the refinement it is not possible to refine displacement parameters as well as the atomic coordinates. Therefore, successive Fourier syntheses were used to complete the molecule. A convergent refinement of the completed molecule to a plausible structure model depends on some additional conditions. Anisotropic displacement parameters for all non-hydrogen atoms were introduced and all hydrogen atom coordinates and the corresponding isotropic displacement parameters refined freely with the correct absolute structure assignment. To check the absolute structure assignment [6] the enantiomeric structure model was also refined and yielded significantly higher R -values and a Flack-parameter indicating an inverse structure description.

To proof the importance of the appropriate refinement strategy several different strategies were tested and compared. Using the high quality data of this investigation a *brute force* refinement strategy (diffraction data up to $50^\circ(2\theta)$, weighting by a $1/\sigma^2$ scheme, no hydrogen atoms, inverted structure description) converged, but showed a lot of serious parameter correlations even in the last refinement cycles, (e. g. correlations between u_{13} (C_1) and u_{13} (C_7) are introduced by a pseudo mirror plane parallel ac) affecting the results of the structure determination. In this case the C-C distance for C_8-C_9 is *artefactic* shortened ($1.366(9)$ Å) and that of C_3-C_4 elongated ($1.447(9)$ Å) although the final $R1$ value for this refinement is in the typical range of crystallographic routine work ($R1 = 4.66\%$).

Summarizing the experiences from the comparative refinements of the structure of the title compound it was difficult to reach the global minimum

Table 1. Selected distances [Å] and bond angles [°] with s_u 's in parentheses of bis(η^4 -1,3-cyclohexadiene)-monocarbonyliron.

$T = 294\text{ K}:$			
Fe1-C1	2.1292(13)	Fe1-C2	2.0498(14)
Fe1-C3	2.0512(15)	Fe1-C4	2.1308(17)
Fe1-C7	2.1260(13)	Fe1-C8	2.0506(14)
Fe1-C9	2.0489(16)	Fe1-C10	2.1252(17)
C1-C2	1.410(2)	C2-C3	1.419(3)
C3-C4	1.416(3)	C7-C8	1.409(3)
C8-C9	1.415(3)	C9-C10	1.413(3)
C1-C2-C3	115.62(13)	C2-C3-C4	115.07(14)
C3-C4-C5	119.35(15)	C2-C1-C6	119.86(16)
C7-C8-C9	115.82(14)	C8-C9-C10	115.19(15)
C9-C10-C11	119.86(16)	C8-C7-C12	119.48(17)
C1-C2-C3-C4	-0.2(2)	C7-C8-C9-C10	-0.5(2)
Root mean squares planes. a) Deviations: $p_1(C_1, C_2, C_3, C_4) = 0.001$, $p_2(C_4, C_5, C_6, C_1) = 0.005$, $p_3(C_7, C_8, C_9, C_{10}) = 0.002$, $p_4(C_{10}, C_{11}, C_{12}, C_7) = 0.002$; b) $\angle(p_1, p_2) = 39.60(11)^\circ$, $\angle(p_3, p_4) = 39.34(10)^\circ$.			
$T = 120\text{ K}:$			
Fe1-C1	2.1229(18)	Fe1-C2	2.0460(14)
Fe1-C3	2.0421(12)	Fe1-C4	2.1262(12)
Fe1-C7	2.1200(18)	Fe1-C8	2.0463(15)
Fe1-C9	2.0409(12)	Fe1-C10	2.1154(13)
C1-C2	1.4103(18)	C2-C3	1.421(2)
C3-C4	1.4137(18)	C7-C8	1.4098(19)
C8-C9	1.418(2)	C9-C10	1.4149(19)
C1-C2-C3	115.58(10)	C2-C1-C6	119.72(11)
C2-C3-C4	115.17(11)	C3-C4-C5	119.57(11)
C7-C8-C9	115.63(11)	C8-C9-C10	115.39(11)
C8-C7-C12	119.49(11)	C9-C10-C11	119.64(12)
C1-C2-C3-C4	-0.81(16)	C7-C8-C9-C10	-0.36(16)
Root mean squares planes. a) Deviations: $p_1(C_1, C_2, C_3, C_4) = 0.003$, $p_2(C_4, C_5, C_6, C_1) = 0.004$, $p_3(C_7, C_8, C_9, C_{10}) = 0.001$, $p_4(C_{10}, C_{11}, C_{12}, C_7) = 0.000$; b) $\angle(p_1, p_2) = 39.62(9)^\circ$, $\angle(p_3, p_4) = 39.52(9)^\circ$.			

based on standard diffraction data. For refinements based on the high quality data it is more easier to refine the structure model towards the global minimum.

Structure description

Within the experimental standard uncertainties the molecular geometry shows the highest possible point symmetry C_{2v} . This means both crystallographically independent cyclohexadiene ligands have the same geometry and the same coordination mode. The η^4 -coordinated conjugated diene fragments ($C_1-C_2-C_3-C_4$ and $C_7-C_8-C_9-C_{10}$) are planar (Table 1) in both independent 1,3-cyclohexadiene ligands. The respective C-C bond lengths in

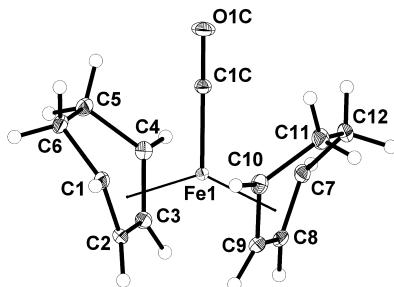


Fig. 1. The molecular structure of bis(η^4 -1,3-cyclohexadiene)monocarbonyliron at 120 K (displacement ellipsoids are drawn at the 50% probability level; H atoms are drawn with a radius of arbitrary size).

the olefinic region of both crystallographically independent molecules are equal within their experimental standard uncertainties (Table 1). This fact can be understood as a consequence of the bonding back bonding mechanism for transition metal coordinated diolefinc systems [3]. The aliphatic parts (C4-C5-C6-C1 and C10-C11-C12-C7) are also planar and enclose an angle of approximately 39.5° with the plane of the olefinic part of the corresponding ligand. All bond lengths, bond angles, and torsion angles are in the typical range of η^4 -coordinated 1,3-cyclohexadiene transition metal complexes [7].

Experimental

General procedures

The reaction and all manipulations were performed under a nitrogen atmosphere by using standard Schlenk techniques. The solvent was purified, dried, and kept under nitrogen prior to use. According to procedures known from the literature [8], metal carbonyl compounds react readily with olefins under photochemical conditions to give the corresponding substitution products.

Synthesis

Bis(η^4 -1,3-cyclohexdiene)monocarbonyliron was synthesized by photochemical reaction of diironnonacarbonyl (1.0 g, 2.75 mmol) with an excess of 1,3-cyclohexadiene (2.0 ml, 21.5 mmol) in *n*-pentane solution (200 ml) at 260 K. The use of diironnonacarbonyl instead of iron-pentacarbonyl, as described in the literature [9], had no negative effect on yield or reaction time. During the irradiation – three hours are sufficient as monitored by the decrease of the carbonyl bands of diironnonacarbonyl – nitrogen was bubbled through the solution to remove carbon monoxide. Isometric yellow-orange crystals of the

title compound can be grown at -34 °C from *n*-pentane solution within a few days.

Single crystal structure determination

$T = 293$: An isometric single crystal was sealed into a thin-walled glass capillary under a nitrogen atmosphere and mounted on a four-circle diffractometer (Siemens P4, Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$, controlled by the program XSCANS 2.10b [10]. A numerical absorption correction has been applied to the intensity data by the use of optically determined crystal faces (min./max. transmission: 0.4821 / 0.7653) [11].

$C_{13}H_{16}OFe$, $M = 244.11$, orthorhombic, space group $P2_12_12_1$, $a = 7.618(2)$, $b = 8.522(2)$, $c = 17.138(4) \text{ \AA}$, $V = 1112.6(5) \text{ \AA}^3$, (43 centred reflections, $15.08 < 2\theta < 24.85^\circ$), $Z = 4$, crystal size $0.80 \times 0.55 \times 0.45 \text{ mm}$.

Data collection using profile fitted omega scans with a variable intensity dependent scan speed (1 - 5°/min), scan range: $2.38 < \theta < 32.50^\circ$ ($-11 < h < 11$, $-12 < k < 12$, $-25 < l < 25$), 16018 reflections collected, all 4016 symmetry-independent reflections ($R_{\text{int}} = 0.0465$) used for refinement, 3656 reflections with $F_o^2 > 2\sigma(F_o^2)$, 201 refined parameters on F_o^2 without restraints, $w = 1/[\sigma^2(F_o^2) + (0.0213P)^2 + 0.0764P]$ where $P = (F_o^2 + 2F_c^2)/3$, extinction coefficient: $\kappa = 0.061(3)$ ($F_c^2 = kF_c [1 + 0.001 \kappa F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$), Flack-parameter: $-0.004(12)$, shift/su_{max} = 0.002, wR2(all) = 0.0539, R1($F_o^2 > 2\sigma(F_o^2)$) = 0.0226, GooF = 1.042, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min.}} = 0.289 / -0.348 \text{ e}/\text{\AA}^3$. For the enantiomeric structure: Flack-parameter: 1.01(2), wR2(all) = 0.0912, R1($F_o^2 > 2\sigma(F_o^2)$) = 0.0346 [12].

$T = 120 \text{ K}$: An isometric single crystal was sealed into a thin-walled glass capillary and mounted on a four-circle diffractometer (Stoe-AED2, equipped with a low temperature device, Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$) controlled by the program STADI-4 [13]). A numerical absorption correction was applied to the intensity data by use of optically determined crystal faces (min./max. transmission: 0.5453, 0.814 [11]). Space group $P2_12_12_1$, $a = 7.509(2)$, $b = 16.778(6)$, $c = 8.417(3) \text{ \AA}$, $V = 1060.3(6) \text{ \AA}^3$, (30 centred reflections, $35.51 < 2\theta < 39.34^\circ$), $Z = 4$, crystal size $0.6 \times 0.5 \times 0.4 \text{ mm}^3$. Data collection using an omega/2 theta scan with a variable, intensity dependent scan speed between 0.45 - 3.60°/min, range: $2.71 < \theta < 37.49^\circ$ ($-12 < h < 0$, $-14 < k < 14$, $0 < l < 28$), 6044 reflections collected, all 5599 symmetry-independent reflections ($R_{\text{int}} = 0.0326$) used for refinement, 5442 reflections with $F_o^2 > 2\sigma(F_o^2)$, 201 refined parameters on F_o^2 without restraints, $w = 1/[\sigma^2(F_o^2) + 0.8P]$ where $P = (F_o^2 + 2F_c^2)/3$, extinction coefficient: $\kappa = 0.0105(4)$ ($F_c^2 = kF_c [1 + 0.001 \kappa F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$), Flack-parameter: $-0.005(10)$, shift/su_{max} = 0.001, wR2(all) = 0.0533, R1($F_o^2 > 2\sigma(F_o^2)$) = 0.0242, GooF = 1.021, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min.}} =$

0.78 / -084 e/ \AA^3 . For the enantiomeric structure: Flack-parameter: 1.01(2), $wR2(\text{all}) = 0.0895$, $R1(F_o^2 > 2\sigma(F_o^2)) = 0.0420$.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 177906 (293 K) and CCDC 177907 (120 K)). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)

Powder diffraction

Grinding a few big crystals of the title compound yielded a highly electrostatic powder sample. The powder diffractogram was measured in transmission geometry on a Stoe STADI P diffractometer ($\text{Cu-K}_{\alpha 1}$, $\lambda = 1.540598 \text{ \AA}$, $T = 294 \text{ K}$) [14]. A Rietveld refinement [15] based on the structure model derived from the single crystal data converged and verified systematic absences for the space

group assignment as well as the lattice constants derived from single crystal diffraction experiment.

Conclusion

The unusual deviations [4] from highest possible molecular symmetry C_{2v} reported for the title compound can be explained by the insufficient quality of the diffraction data and a refinement strategy that did not take correlation effects into account. No unusual bond lengths appear in the redetermined crystal structure of the title compound. The alternative photochemical synthesis described here give ready access to the title compound.

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