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Synthesis, structure, and solid state ^{13}C NMR spectroscopy of a highly substituted tricarbonyl(cyclobutabenzene)chromium(0) derivative *

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Abstract

The synthesis, spectroscopic characterization, and the X-ray crystal structure determination of tricarbonyl-η^6-[1,2-bis(ethylendioxy)cyclobutabenzene]chromium(0) are described. The free enthalpy of activation of the $Cr(CO)_3$ rotation has been determined by variable temperature solid state ^{13}C CP-MAS NMR spectroscopy to be ca. 60 kJ/mol.

Introduction

In connection with our interest in cyclobutabenzene transition metal complexes [1] we wished to prepare more strained derivatives bearing three or four sp^2 carbon atoms in the annulated ring. As the direct complexation of 1,2-dioxocyclobutabenzene to $Cr(CO)_3$ failed, we decided to make use of protecting groups for the keto function. We report here the synthesis and full characterization of tricarbonyl-η^6-[1,2-bis(ethylendioxy)cyclobutabenzene]chromium(0) (**2**), the tricarbonylchromium complex of 1,2-bis(ethylendioxy)cyclobutabenzene (**1**), including an X-ray crystal structure determination. **2** is the first cyclobutabenzene complex with four identical substituents on the annulated ring, and thus is formed as a single diastereomer. The bond C(1)–C(2) keeps the *spiro*-annulated 1,3-dioxolane rings in a nearly perpendicular orientation relative to the arene ring. The tricarbonylchromium(0) group therefore faces two of the four oxygen atoms rigidly held in relatively close proximity, and a steric interaction seemed possible. Because of this the ease of $Cr(CO)_3$ rotation in **2** was of interest, and it was investigated by low temperature NMR in solution as well as by solid state ^{13}C CP-MAS NMR spectroscopy.

Results and discussion

In contrast to the syntheses of most cyclobutabenzene chromium complexes we have prepared [1], no complexation of ligand **1** occurred upon treatment with

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* Dedicated to Professor Erwin Weiss on the occasion of his 65th birthday.

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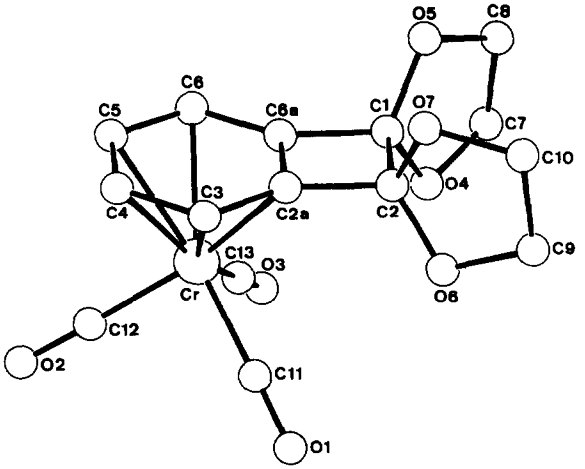
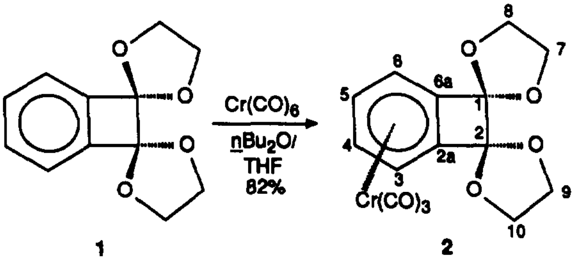


Fig. 1. Crystal structure of **2**.

$Cr(CO)_3(NH_3)_3$. Due to side reactions caused by the more polar work-up conditions neccessary for **2** this reagent was unsuitable. Thus, in spite of the higher reaction temperatures, we resorted to the traditional method involving $Cr(CO)_6$ in di-n-butyl ether/THF [2], and this resulted in a 82% yield of **2**.



Complex **2** has fully been characterized by IR, ^1H, and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. The IR spectrum displays three carbonyl absorptions at 1975, 1912, and 1896 cm^{-1}, indicating local C_s symmetry at the $Cr(CO)_3$ group. In the mass spectrum successive loss of three carbonyl ligands is observed, an intense (45%) peak at $m/z = 128$ suggests a rather stable $C_6H_4Cr^+$ species, possibly a 1,2-dehydrobenzene complex cation. The ^1H and ^{13}C NMR spectra indicate mirror symmetry in solution. Chemical shifts and coupling constants are within the usual range.

The crystal structure of **2** (Fig. 1; final atomic coordinates are given in Table 1) does not show the mirror symmetry of the molecule observed in solution. The distortion may be caused by intermolecular interactions in the crystal arising from the flexibility of the dioxolane rings. There is a rather long bond length C(1)–C(2) [1.609(3) Å], which is possibly due to a repulsive interaction between the four C–O fragments oriented *syn*-periplanar to each other. In contrast to tricarbonyl-η^6-(*exo*-1-methylcyclobutabenzene)chromium(0) [1b] but like the *endo*-1-ethoxy derivative [3], **2** adopts a preferred conformation with no CO ligand located below the annulated ring. Interaction of the tricarbonylchromium(0) group with the *spiro*-an-

Table 1

Fractional atomic coordinates for **2** [a]

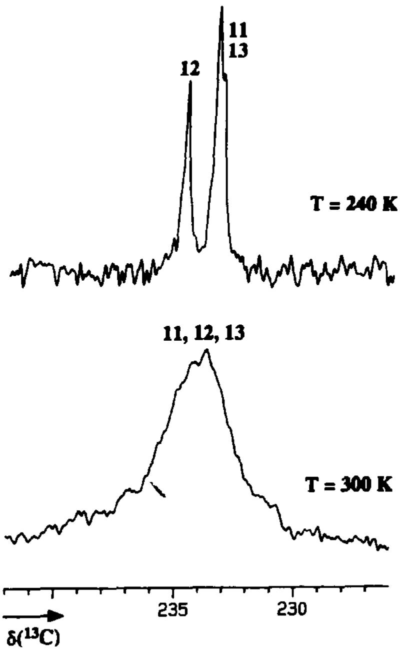
Atom	x	y	z	U_{eq}
Cr	0.0878(1)	0.1937(1)	0.0770(1)	0.031
O(1)	0.0871(2)	0.0706(2)	0.1878(1)	0.081
O(2)	0.2818(2)	0.0393(1)	0.0271(1)	0.071
O(3)	0.3261(2)	0.3105(2)	0.1233(1)	0.065
O(4)	0.0373(2)	0.4231(1)	0.1651(1)	0.050
O(5)	−0.1263(2)	0.5022(1)	0.1120(1)	0.051
O(6)	−0.1527(2)	0.2689(2)	0.1991(1)	0.054
O(7)	−0.3058(2)	0.3393(2)	0.1386(1)	0.053
C(1)	−0.0672(2)	0.4051(2)	0.1253(1)	0.038
C(2)	−0.1694(2)	0.3133(2)	0.1441(1)	0.040
C(2a)	−0.1172(2)	0.2541(2)	0.0918(1)	0.033
C(3)	−0.1293(2)	0.1590(2)	0.0608(1)	0.039
C(4)	−0.0581(2)	0.1541(2)	0.0083(1)	0.038
C(5)	0.0244(2)	0.2376(2)	−0.0113(1)	0.038
C(6)	0.0393(2)	0.3300(2)	0.0209(1)	0.037
C(6a)	−0.0350(2)	0.3365(2)	0.0729(1)	0.034
C(7)	0.0464(4)	0.5312(3)	0.1747(2)	0.064
C(8)	−0.0704(6)	0.5783(3)	0.1492(2)	0.093
C(9)	−0.2537(4)	0.3154(4)	0.2355(1)	0.073
C(10)	−0.3518(4)	0.3650(4)	0.1958(2)	0.079
C(11)	0.0852(3)	0.1180(2)	0.1453(1)	0.049
C(12)	0.2068(2)	0.0987(2)	0.0467(1)	0.043
C(13)	0.2338(2)	0.2671(2)	0.1060(1)	0.039

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^\star a_j^\star (\mathbf{a}_i \cdot \mathbf{a}_j)$

Table 2

Selected bond distances (Å) and bond angles (°) for **2**

Cr–C(2a)	2.203(2)	Cr–C(3)	2.232(2)
Cr–C(4)	2.203(2)	Cr–C(5)	2.200(2)
Cr–C(6)	2.217(2)	Cr–C(6a)	2.193(2)
Cr–C(11)	1.846(3)	Cr–C(12)	1.830(2)
Cr–C(13)	1.850(2)	O(4)–C(1)	1.403(3)
O(4)–C(7)	1.399(4)	O(5)–C(1)	1.405(3)
O(5)–C(8)	1.408(5)	O(6)–C(2)	1.396(3)
O(6)–C(9)	1.436(4)	O(7)–C(2)	1.401(3)
O(7)–C(10)	1.433(4)	C(1)–C(2)	1.609(3)
C(1)–C(6a)	1.523(3)	C(2)–C(2a)	1.512(3)
C(2a)–C(3)	1.413(4)	C(2a)–C(6a)	1.398(3)
C(3)–C(4)	1.403(3)	C(4)–C(5)	1.418(3)
C(5)–C(6)	1.401(3)	C(6)–C(6a)	1.409(3)
C(7)–C(8)	1.433(6)	C(9)–C(10)	1.477(5)
C(6a)–C(1)–C(2)	85.8(2)	C(6a)–C(1)–O(5)	115.0(2)
C(6a)–C(1)–O(4)	117.1(2)	C(2)–C(1)–O(5)	115.9(2)
C(2)–C(1)–O(4)	114.2(2)	O(5)–C(1)–O(4)	107.8(2)
C(2a)–C(2)–C(1)	86.2(2)	C(2a)–C(2)–O(7)	112.2(2)
C(2a)–C(2)–O(6)	118.6(2)	C(1)–C(2)–O(7)	114.4(2)
C(1)–C(2)–O(6)	117.7(2)	O(7)–C(2)–O(6)	107.0(2)
C(6a)–C(2a)–C(2)	94.1(2)	C(2a)–C(6a)–C(1)	93.7(2)



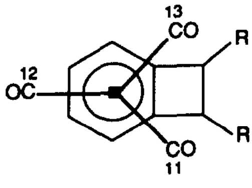


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Fig. 2. Solid state ^{13}C CP-MAS NMR spectra of **2** at 300 and at 240 K. ■ = Cr, R = -OCH$_2$CH$_2$O-.

nulated dioxolane rings can thus be avoided. As an alternative to this steric explanation, the electronic similarity of the substituents in **2** and in the *endo*-ethoxy derivative might account for the conformation preferences observed.

To investigate whether the steric interaction between the tricarbonylchromium group and the dioxolane rings is large enough to be detected, and with some recent literature precedents [4] in mind, we examined the possibility of hindered Cr(CO)$_3$ rotation by low temperature ^{13}C NMR spectroscopy in solution. However, even at 193 K the signal of the carbonyl ligands showed no broadening.

The solid state ^{13}C CP-MAS NMR spectrum recorded at 240 K (Fig. 2) confirms the asymmetry of crystalline **2**, that was revealed by the crystal structure analysis. The twelve carbon atoms of the arene ligand give rise to ten signals between 67.0 and 116.6 ppm (two signals of the cyclobutane ring and two of the 1,3-dioxolane rings are degenerate), demonstrating the absence of a symmetry element. For the carbonyl ligands two signals (integrated ratio 1 : 2) are observed. With the aid of the crystal structure analysis the signal at 234.7 ppm is assigned to the carbonyl ligand located opposite to the cyclobutane ring, and the signal at 233.4 ppm is assigned to the two carbonyl ligands located close to the cyclobutane ring. The splitting of the latter signal appears to be a result of an asymmetric molecular environment causing the asymmetry of the molecule in the solid state.

As the temperature is raised broadening of the carbonyl resonances is observed; the ^{13}C CP-MAS spectrum recorded at 300 K under otherwise identical conditions shows a single broad resonance at 234 ppm and only insignificant changes of the signals assigned to the arene ligand. This is due to a fast exchange of the CO ligands on the NMR time scale. The free enthalpy of activation of the process can be calculated as ca 60 kJ/mol [5]; however, due to the extremely small chemical shift difference between the two signals (<1 ppm) the error in this value may be high [4b].

To our knowledge there is only one literature report of a determination of a free enthalpy of activation of a $Cr(CO)_3$ rotation in an arene complex in the solid state. The value of ca 60 kJ/mol obtained for **2** agrees well (within the experimental error) with that of 65 kJ/mol obtained for (toluene)$Cr(CO)_3$ by Hanson et al. [4c]. The similarity of the values obtained for (toluene)$Cr(CO)_3$ and the sterically more demanding **2** indicates, that any steric interaction between the tricarbonylchromium(0) group and the dioxolane rings in **2** cannot be detected by the method used here. It is more likely that the observed $Cr(CO)_3$ conformation results from electronic effects of the *spiro*-annulated dioxolane rings.

Experimental

All operations were performed under argon in flame dried vessels. Pentane, di-n-butyl ether, and THF were dried over $LiAlH_4$ and distilled from Na/K-alloy/benzophenone under argon. Instruments used were: IR, Nicolet 7199 FT-IR; ^1H NMR Bruker AM 200 (200.1 MHz); ^{13}C CP-MAS NMR, Bruker MSL 300 (chemical shifts (± 0.1 ppm) are relative to that of the methylene carbon signal of adamantane [$\delta_{TMS}(CH_2)$] = 38.4; preparation time 4 s, contact time 3 ms); ^{13}C NMR (solution), Bruker WM 300 (75.5 MHz) (signal multiplicities and coupling constants were determined by inspection of gated spectra); chemical shifts are quoted to $\delta_{TMS} = 0.00$ but determined relative to the chemical shifts for THF-d_7; MS, Varian 311 A. Elemental analyses were performed by Mikroanalytisches Laboratorium Dornis and Kolbe, Mülheim a.d. Ruhr.

Tricarbonyl-η^6-[1,2-bis(ethylendioxy)cyclobutabenzene]chromium(0) (2). A mixture of 5.0 g (22.7 mmol) of 1,2-bis(ethylendioxy)cyclobutabenzene [6] (**1**), 5.5 g (25.0 mmol) of $Cr(CO)_6$, 200 mL of di-n-butyl ether, and 25 mL of THF was heated under reflux for 48 h. The solvents were then evaporated *in vacuo* and the residue dissolved in a few mL of THF. The solution was filtered through a P4 glass frit and a threefold volume of pentane added to the filtrate, causing immediate precipitation of crystals. The crystallization was completed by cooling the mixture to −30 °C, the solvent was filtered off, and the residue purified twice by dissolution in THF and subsequent reprecipitation by addition of pentane. The residue was washed three times with 20 mL of pentane and then dried at 0.001 mbar for 2 h. Yield 6.63 g (82%) of yellow crystals, m.p. 226 °C. IR (THF): $\nu = 1975$ cm^{-1} (s, C=O), 1912 (s, C=O), 1896 (s, C=O). ^1H NMR (200 MHz, THF-d_8): $\delta = 3.93$ (m, 4H, α-CH_2 or β-CH_2); 4.08 (m, 4H, α-CH_2 or β-CH_2); 5.27 + 5.66 (2m, 2 × 2H, 3(6)-H, 4(5)-H). ^{13}C NMR (75.5 MHz, THF-d_8, −80 °C): $\delta = 66.4$ (t, α-CH_2 or β-CH_2, ^1J(C,H) = 150 Hz); 67.0 (t, α-CH_2 or β-CH_2, ^1J(C,H) = 152 Hz); 88.0 (d, C-3(6), ^1J(C,H) = 180 Hz); 94.2 (d, C-4(5), ^1J(C,H) = 175 Hz); 114.2 (s, C-2a(6a)); 115.8 (s, C-1(2)); 233.1 (s, C-11). MS (70 eV): m/z (%) = 356 (16) [M^+], 328 (4) [$M^+ - CO$], 300 (14) [$M^+ - 2CO$], 272 (25) [$M - 3CO$], 216 (13), 200 (7), 186 (12), 172 (15), 158 (8), 157 (8), 128 (45) [$C_6H_4Cr^+$], 52 (100) [Cr^+]. Anal. Found: C, 50.62; H, 3.46; Cr, 14.58. $C_{15}H_{12}CrO_7$ (356.25) calcd.: C, 50.57; H, 3.40; Cr, 14.60%.

*Crystal structure determination [7 *]*

2: $C_{15}H_{12}CrO_7$, crystal size 0.36 × 0.50 × 0.22 mm, colour yellow $a = 9.929(1)$, $b = 12.754(1)$, $c = 23.003(3)$ Å, $V = 2913.0$ Å^3, $d_{calc} = 1.62$ g · cm^{-3}, $\mu = 7.98$ cm^{-1}, Mo-K_α-radiation, $\lambda = 0.71069$ Å, $F(000) = 1456$ e, crystal system orthorhombic, space group $Pbca$, $Z = 8$, Enraf–Nonius CAD4 diffractometer, scan mode ω–2θ, $[(\sin\theta)/\lambda]_{max} = 0.65$, 3763 measured reflections $(+h, +k, +l)$, 3316 independent reflections, 2614 observed reflections $[I > 2\sigma(I)]$ for 256 refined parameters, structure solved by heavy atom method, H-atom positions located and refined isotropically, $R = 0.036$, $R_w = 0.041$ $[w = 1/\sigma^2(F_o)]$, EOF = 1.92, residual electron density 0.27 e Å^{-3}.

Acknowledgements

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7 Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55248, the names of the authors, and the journal citation.

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* Reference number with an asterisk indicates a note in the list of references.