Journal of Organometallic Chemistry, 361 (1989) 173–179
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Bis(trimethylcyclopentadienyldicarbonylchromium), crystal and molecular structure of $[(CH_3)_3C_5H_2Cr(CO)_2]_2$

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(Received May 25th, 1988)

Abstract

The structure of $[Me_3CpCr(CO)_2]_2$ ($Cp = C_5H_2$) has been determined by X-ray diffraction. Structural parameters for monoclinic systems are: $M = 430.3818$; space group $P2_1/n$; unit cell parameters: a 8.0596(6) Å, b 13.4487(7) Å; c 9.6795(8) Å, β 114.277(6) Å, V 956.4(4) Å^3, $Z = 2$, D_x 1.494 g/cm^3, Mo-K_α-radiation (λ 0.71069 Å), μ 0.58 cm^{-1}, $F(000) = 444$, $R = 0.0571$ at room temperature.

Comparison of the structural parameters of the $[Me_3CpCr(CO)_2]_2$ complex with those of the $[Me_nCpM(CO)_2]_2$ ($n = 0$, 5 M = Cr, Mo) complex reveals that the electronic characteristics of the methyl substituent have the most effect on the parameters, despite significant steric limitations.

Introduction

The peculiarities of the crystal structure of the $[CpM(CO)_2]_2$ (M = Cr, Mo) [4,7] dimer complexes are still of interest to researchers. In particular, the views as to the nature of the semibridging CO gruops and the steric and electronic contributions to the structure [7] are divided. The structural features of $[Cp^*Cr(CO)_2]_2$ ($Cp^* = Me_5C_5$) have been interpreted based the basis of steric interactions [4], while a study results on the crystal structure of $[CpCr(CO)_2]_2$ [5] showed electronic interactions to be predominating. Not all the structural details were explicit, thus, although fairly short intramolecular contacts were present, their influence on the structure was usually not clear. Because total Cp ring methylation would have complicated steric interactions in $[Me_5CpCr(CO)_2]_2$, we performed X-ray diffraction studies on the partially substituted analogue, $[Me_3CpCr(CO)_2]_2$ 1,2,4-trimethylcyclopentadienyl homologue.

0022-328X/89/$03.50

Experimental

The compound under study was synthesized by a published procedure [1]. Red prismatic crystals suitable for X-ray diffraction were obtained by recrystallization of the prepared compound from a C_6H_{14}/CH_2Cl_2 solution at $-10\,°C$. The compound crystallizes in the monoclinic system, and a crystal with dimensions $0.3 \times 0.2 \times 0.3$ mm was selected for the X-ray diffraction study.

Unit cell parameters were obtained by a least-squares fit of 15 selected reflections of graphite-monochromatized Mo-K_α-radiation (λ 0.71069 Å). The data, collected on an automated Syntex $P2_1$ diffractometer by θ: 2θ scanning, consist of 1917 reflections with θ_{max} 30° and indices within: $h = 0$–11, $k = 0$–18, $l = -13$–12. No corrections for absorption are applied because of the small linear absorption coefficient. Deviations in the intensities of the three check reflections, (20 – 2), (112), and (31 – 4), were found to be less than 4%. The 1672 unique reflections with $F^2 > 2\sigma\ (F^2)$ were considered observed. The R_{int} value of 0.0422 obtained by merging equivalent reflections indicates that the quality of the crystal is fairly good. The structure was determined by Patterson and heavy atom methods. A three-dimensional Patterson map revealed the positions of the chromium atom. A Fourier map was used to locate ($R = 0.357$) all the non-hydrogen atoms.

Three cycles of least-squares refinement gave an R-value of 0.0954. Four subsequent cycles of anisotropic, full-matrix, least-squares refinement gave a discrepancy factor of 0.0688.

Table 1

Atomic coordinates ($\times 10^4$, for H atoms $\times 10^3$)

Atom type	x	y	z
C	4666(1)	4553(1)	5845(1)
O(1)	1227(5)	4250(4)	3078(4)
O(2)	6516(6)	3021(3)	4712(5)
C(1)	2593(7)	4385(4)	4087(6)
C(2)	5830(7)	3647(4)	5092(6)
C(3)	3419(7)	4918(4)	7428(6)
C(4)	2976(8)	3928(4)	7004(6)
C(5)	4636(9)	3411(4)	7490(6)
C(6)	6097(7)	4082(4)	8213(5)
C(7)	5338(7)	5032(4)	8203(5)
C(8)	1101(11)	3490(8)	6283(10)
C(9)	8081(10)	3817(7)	9015(3)
C(10)	6336(10)	5966(5)	8930(8)
H(81)	64(7)	329(4)	701(7)
H(82)	131(10)	287(6)	590(9)
H(83)	15(8)	375(8)	557(12)
H(91)	835(11)	314(6)	863(9)
H(92)	838(10)	369(5)	1014(9)
H(93)	909(11)	428(6)	903(9)
H(101)	562(10)	654(6)	837(8)
H(102)	758(10)	607(5)	891(8)
H(103)	634(10)	617(6)	984(9)
H(3)	267(7)	553(4)	725(6)
H(5)	491(8)	271(5)	736(6)

Table 2

Anisotropic thermal factors (for H atoms isotropic)$\times 10^4$ (Å^2)

Atom type	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
C	310(4)	305(4)	246(3)	24(3)	100(3)	−32(4)
O(1)	405(22)	996(37)	402(22)	−33(23)	24(18)	−178(23)
O(2)	681(28)	410(23)	691(28)	−44(20)	340(23)	100(21)
C(1)	361(25)	433(31)	380(26)	7(22)	166(22)	−34(22)
C(2)	421(28)	333(29)	417(28)	27(23)	119(23)	−52(24)
C(3)	415(28)	473(32)	354(26)	13(24)	177(23)	38(25)
C(4)	553(33)	480(33)	348(27)	37(24)	231(25)	−90(27)
C(5)	675(39)	383(32)	345(27)	92(24)	220(27)	−49(28)
C(6)	502(30)	482(33)	255(23)	110(22)	153(22)	87(26)
C(7)	513(30)	410(29)	244(23)	7(21)	183(22)	−46(25)
C(8)	543(43)	1062(70)	670(47)	−28(48)	312(39)	−399(46)
C(9)	555(39)	788(52)	459(36)	177(36)	109(30)	133(38)
C(10)	626(40)	478(38)	473(35)	−145(29)	239(31)	−99(32)
H(81)	502(162)					
H(82)	814(291)					
H(83)	1492(459)					
H(91)	1031(293)					
H(92)	850(234)					
H(93)	950(273)					
H(101)	787(227)					
H(102)	801(217)					
H(103)	920(254)					
H(3)	360(135)					
H(5)	548(198)					

The refinement was followed by a difference Fourier synthesis to locate all the hydrogen atoms. A further three cycles of anisotropic refinement for the non-hydrogen and the H atoms, with anisotropic temperature factors, reduced R to 0.0571. Only unit weighting factors were employed. The maximum shift in atomic coordinates vs. estimated standard deviations did not exceed 0.1. The final difference Fourier synthesis revealed no significant features on the map, with the highest peak, situated 1.03 Å from a Cr atom, being 0.65 Å^{-3}. It is obvious that origin of this peak is associated with the termination of the Fourier series. The atomic scattering factors for all atoms were taken from the International Tables [2].

All the structural computations were performed with SHELX-76 [3] programs. Final atomic coordinates and their anisotropic (in H atoms isotropic) temperature parameters are listed in Tables 1 and 2, respectively.

Results and discussion

Figure 1 shows the crystal structure of $[Me_3CpCr(CO)_2]_2$. Both Fig. 1 and Table 3 shows that $[Me_3CpCr(CO)_2]_2$ in many respects resembles the structures of unsubstituted $[CpCr(CO)_2]_2$ [5] and the completely substituted $[Cp^*Cr(CO)_2]_2$ [4] derivatives. There are no intermolecular contacts that are significantly less than the Van der Waals contacts. $[Me_3CpCr(CO)_2]_2$ is centrosymmetrical with a short Cr–Cr bond (2.267 Å). The Me_3Cp ring connection with Cr atom is not completely

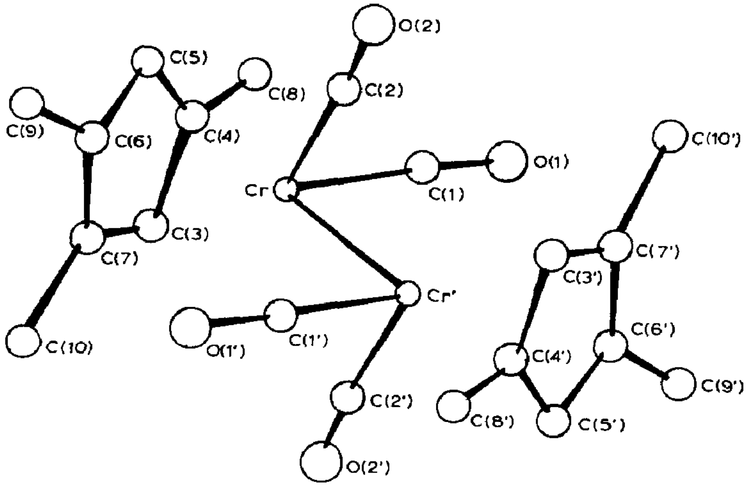

Fig. 1. Molecular structure of $[Me_3CpCr(CO)_2]_2$.

symmetrical. A similar picture is observed in the complexes $[CpCr(CO)_2]_2$ [5] and $[Cp^*Cr(CO)_2]_2$ [4] studied previously. The structure of $[Cp^*Cr(CO)_2]_2$ is attributed to steric interactions of the C(CO) group and the ring C(Cp). The intramolecular, unbonded contacts C(CO)...C(Cp) that are less than 3.3 Å for $[Me_3CpCr(CO)_2]_2$ listed in Table 4. Similar steric interactions were shown to exist in this molecule. However, these short contacts appear to be unrelated to the dimer peculiarities described since similar contacts are also found in mononuclear $CpMe_nCr(CO)_2NO$

Table 3

Selected bond lengths and angles

Bond	*d* (Å)	Bond angles	(°)
Cr–Cr	2.267(1)	Cr–C1–O(1)	173.6(5)
Cr–C(1)	1.844(5)	Cr–C2–O(2)	173.4(5)
Cr–C(2)	1.860(6)	C'r–Cr–Cp	158.2(2)
Cr–C(3)	2.206(5)	C(1)–Cr–Cr'	78.5(2)
Cr–C(4)	2.253(5)	C(2)–Cr–Cr'	75.9(2)
Cr–C(5)	2.218(5)	C(1)–Cr–Cp	117.2
Cr–C(6)	2.193(5)	C(2)–Cr–Cp	120.0
Cr–C(7)	2.214(5)	C(4)–C(5)–C(6)	109.5(5)
Cr–Cp	1.864	C(5)–C(6)–C(7)	107.6(5)
C(1)–O(1)	1.147(6)	C(6)–C(7)–C(3)	106.2(5)
C(2)–O(2)	1.147(6)	C(7)–C(3)–C(4)	110.4(5)
C(3)–C(4)	1.396(8)	C(3)–C(4)–C(5)	106.3(5)
C(4)–C(5)	1.405(8)		
C(5)–C(6)	1.419(8)		
C(6)–C(7)	1.414(7)		
C(7)–C(3)	1.423(7)		
C(4)–C(8)	1.500(8)		
C(6)–C(9)	1.505(8)		
C(7)–C(10)	1.502(8)		
C(3)–H(3)	0.99(5)		
C(5)–H(5)	0.99(5)		

Table 4

Intramolecular unbonded contacts (in Å) less than 3.4 Å

Cr...O(1)	2.987(4)	C(1)...C(4)	2.780(6)
Cr...O(2)	3.002(4)	C(1)...C(8)	3.085(6)
Cr...C′(1)	2.609(4)	C(1)...C(2′)	2.902(6)
Cr...C′(2)	2.559(5)	C(2)...C(5)	2.872(11)
C(1)...C(2)	2.579(6)	C(2)...C(6)	2.997(11)

($n = 0, 5$) [10,11]. Furthermore in the ($n = 3$) complex, the asymmetrical Cr–C(Cp) bond cannot be attributed only to steric interactions. Thus C_5(Cp) has a short separation from C(CO) (2.872 Å) but it is, nevertheless, shorter than that of C_6 which has a larger separation from C(CO) (2.997 Å, Table 3). The electronic effects by the $Cr(CO)_2L$ ($L = Me_nCpCr(CO)_2$) on the observed asymmetrical Cp–Cr bond are also included. In three of the structures under study $[Me_nCpCr(CO)_2]_2$ ($n = 0, 3, 5$), the C(Cp) ring atoms having shortened contacts to C(CO), form relatively short C–C bonds between themselves and the neighboring C(Cp) atoms (Table 3).

An increase in the Me_nCp ligand steric interaction with the $Cr(CO)_2L$ fragment is reflected in variation of the Cr–C(Cp) separation. Despite the growth in nucleophility in the substituted Cp ring, an increasing Cr–$CpMe_n$ separation is observed with substitution (Table 3). Similar trends have been found elsewhere for M–C(Cp) bond lengths with a rise in n [4–7,10,11].

However, variation of the structural parameters of the $Cr_2(CO)_4$ fragment shows a successive rise in nucleophility as the Cp ring becomes more substituted. The Cr≡Cr bond length grows with n owing to an increase in electron density at the antibonding $\pi^\star$, $\sigma^\star$ orbitals of this bond. When n varies from 0 to 5 the Cr≡Cr bond length increment is 0.065 Å [4,5], with a similar change (0.040 Å) [7] being observed in the Mo≡Mo bond length in $[Me_nCpMo(CO)_2]_2$ ($n = 0, 5$) is. The observed difference in M≡M bond length increases probably results solely from electronic factors since every additional Cp ring substitution (even when M≡M bond length is constant from electronic factors) must result in elongation of the intramolecular C(CO)...C′(C′O′) and Cr...C(CO) contacts, and in M≡M bond strain. This should take place because (a) M–C(CO) bond length shortens (Table 3) as n rises, and (b) the C(1)MC(2) angle (vide infra) becomes larger in contrast to the emergence and successive increases (in respect to $n \to 5$) in steric interactions between C(CO) and $C(CH_3)$ [11].

The greater electronic effect by methyl group on the Cr≡Cr bond as compared to Mo≡Mo bond can be also accounted for within the framework of electronic concepts presented in ref. 5. The initial bend of the $[CpCr(CO)_2]_2$ molecule allows the methyl groups to affect the Cr≡Cr bond via both the π- and σ-electron subsystems, whereas the linear structure of $[CpMo(CO)_2]_2$ allows the electronic effect by methyl substituent to act on the Mo≡Mo bond only via the π-system, and so results in reduced Mo≡Mo antibonding.

Variations in the bending of the CO group over the M≡M bond is also determined by changes in the electronic characteristics of the Me_nCp ligand. From a steric viewpoint, a reduction in the inclination angle (C(1,2)CrCr) of CO group over the M≡M bond is to be expected with increased n, because (1) the intramolecular

Cr...C(CO) and C(CO)...C′(C′O′) contacts grow due to the M≡M bond elongation and M–C(CO) bond shortening; and (2) Cp ring methylation provides additional CH_3 group steric hinder towards C(CO) and this tends to press it against the M≡M bond. In reality, no such phenomenon takes place, for CO group bend over M≡M bond tends to decrease as *n* increases (C(1,2)CrCr′ angle grows) (Table 3). In this way if the magnitude of C(1,2)CrCr′ were determined by CO and Cp steric interactions then the C_2O_2 group in $[Me_5CpCr(CO)_2]_2$ should have the larger tilt towards the Cr≡Cr bond because its C(Cp) contact is shorter (2.780 Å) than that of the C(1)O(1) group (2.810 Å). In fact, the C(2)O(2) group bends over the Cr≡Cr bond less (C(2)CrCr′ 79°) than C(1)O(1) (C(1)CrCr′ 73° [4]).

Therefore, variation of CO group bend over M≡M bond with *n* is caused by two factors, (i) elongation of the M≡M bond, leading to M...C′(C′O′) contact increasing, and consecutively to a decrease in the semibridging interaction; (ii) and growth of the C(1,2)CrCr′ and C(1)CrCr′ angles. The latter has been observed both in the $[Me_nCpCr(CO)_2]_2$ ($n = 0$, 3, 5) complexes we have investigated and in other mononuclear complexes such as $Me_nCpM(CO)_2NO$ ($n = 0$, 5; M = Cr, Mo, W) described elsewhere [10,11] and may be attributed to the dative Md → π^* (CO) interaction.

The findings mentioned above relate CO group bending, over the Cr≡Cr bond to the CO group's semibridging interactions with second Cr atom rather than with the molecular steric hindrance [4]. ^{13}C NMR spectra studies on $[Me_nCpM(CO)_2]_2$ ($n = 0$, 1, 3–5; M = Cr, Mo, W) complexes [12,13] also suggest the emergence of an additional interaction (with CO group contributions) which results in considerable shift downfield of the $^{13}C(CO)$ signal from these groups. It is of interest that the deviation of the O(1,2)C(1,2)Cr angle from 180° correlates with the CO angle of incidence relative to the Cr≡Cr bond (and hence with the semibridging C(CO)...Cr interaction value). The nearer C(CO) is to the second Cr atom, the larger the deviation of O(1,2)C(1,2)Cr from 180° (Table 3).

The shortening of the Cr–C(CO) bond and the lengthening of the C(CO)–O bond as *n* increases is also determined by the electron-donor properties of the CH_3 group which induces a successive rise in the Cr$d \to \pi^*$(CO) dative interaction. A decrease in the stretching vibration frequency (ν) of C≡O bond and the stepwise downfield shifts of $^{13}C(CO)$ resonance signal with increase in *n* [12,13] are also indicative of a reverse Cr $d \to \pi^*$ (CO) interaction.

To sum up, the variation of the basic structural parameters in the complexes $[Me_nCpCr(CO)_2]_2$ ($n = 0$, 3, 5) as the number of Cp ring substituents is increased according to [5], indicates that their structural features are due to electronic rather than to steric interactions.

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