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THE STRUCTURE OF THE COMPLEXES OF DIMETHYLSULPHONIUM CYCLOPENTADIENYLIDE WITH CHROMIUM AND MOLYBDENUM CARBONYLS. EFFECT OF π -COORDINATION TO THE METAL ON THE PROPERTIES OF THE YLIDE LIGAND

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Summary

An X-ray study of the complex $(C_5H_4SMe_2)Cr(CO)_3$ has shown that the sulphur atom is not coordinated to the metal atom, the non-bonded distance $S \cdots Cr$ being 3.478 Å. Thus the organic ligand is coordinated in its ylide form. The geometries of the ylide ligand in its coordinated and free states are compared with respect to their behaviour in isotopic exchange reactions.

Introduction

Previously we reported that dimethylsulphonium cyclopentadienylide (I) forms complexes with the carbonyls of Group VI metals [1], in which the cyclopentadienyl ring of ylide I manifests the properties of a 6-electron π -ligand. This led to our investigating the effect of coordination to transition metal atoms upon the structure and the reactivity of ylide I.

This paper presents the results of an X-ray diffraction study of dimethylsulphonium cyclopentadienylide chromium tricarbonyl (II) and its molybdenum analogue (III), and these data are compared with the recently obtained data on the structure of ylide I [2].

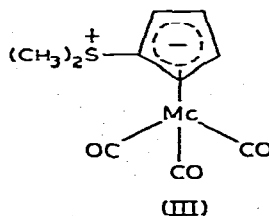
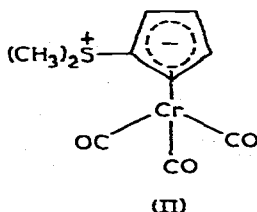
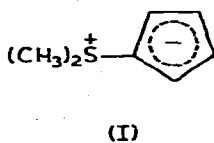


TABLE 1

ATOMIC COORDINATES (FOR Cr X 10⁵, FOR OTHER NONHYDROGEN ATOMS X 10⁴, FOR HYDROGEN ATOMS X 10³) AND THEIR THERMAL FACTORS

Atom	x	y	z	B_{11}^a or B_{44}^a	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	24170(8)	23186(7)	8909(7)	155(4)	212(5)	178(4)	19(4)	-7(4)	13(4)
S	1391(1)	684(1)	2651(1)	178(7)	246(8)	263(9)	-7(7)	42(7)	10(8)
O(1)	3213(5)	3978(4)	-337(4)	577(31)	345(29)	305(27)	-56(24)	52(24)	127(23)
O(2)	1001(4)	1621(4)	-828(4)	426(29)	636(36)	424(32)	124(25)	-266(26)	-201(29)
O(3)	650(4)	3599(4)	1650(4)	325(26)	570(36)	582(34)	253(26)	125(25)	-52(29)
C(1)	2514(5)	1185(4)	2023(4)	140(25)	223(32)	216(29)	-10(25)	17(29)	65(26)
C(2)	3077(6)	847(5)	1130(5)	266(32)	235(38)	219(36)	79(29)	42(28)	12(30)
C(3)	3995(5)	1478(6)	991(6)	149(30)	386(40)	310(40)	60(29)	18(30)	82(36)
C(4)	4003(5)	2182(5)	1774(6)	225(32)	330(42)	320(39)	-29(30)	-86(29)	141(35)
C(5)	3094(6)	2005(5)	2419(6)	268(32)	218(33)	212(23)	-9(27)	-38(30)	28(31)
C(6)	2910(5)	3318(6)	124(5)	224(34)	370(41)	164(34)	60(29)	-10(25)	-9(31)
C(7)	1541(6)	1986(5)	-171(6)	251(35)	237(36)	309(40)	119(28)	43(31)	11(31)
C(8)	1286(6)	3095(5)	1316(5)	240(33)	336(39)	199(35)	-59(31)	-12(29)	21(30)
C(9)	1859(8)	-463(6)	3089(7)	417(49)	270(43)	346(48)	31(37)	-26(44)	89(37)
C(10)	425(7)	314(8)	1628(8)	251(40)	492(57)	442(53)	-123(41)	-162(38)	46(46)
H(2) ^b	284(5)	27(4)	67(4)	2.6(1.6)					
H(3)	468(6)	136(5)	30(5)	6.6(2.0)					
H(4)	477(5)	280(5)	192(4)	5.0(1.7)					
H(5)	288(4)	239(4)	305(4)	1.8(1.4)					
H(9,1)	203(5)	-78(4)	268(5)	3.2(1.7)					
H(9,2)	104(5)	-91(5)	338(5)	7.7(1.6)					
H(9,3)	235(5)	-38(4)	360(4)	3.9(1.7)					
H(10,1)	10(4)	86(4)	136(4)	1.7(1.5)					
H(10,2)	64(6)	-3(6)	103(5)	4.7(2.0)					
H(10,3)	-8(6)	-13(5)	184(5)	5.7(2.4)					

^a Anisotropic thermal factors: $T = \exp[-1/4 \times 10^{-2} (B_{11}h^2 + \dots + 2B_{12}hk + \dots)]$. ^b Numbers of hydrogen atoms are the same as numbers of corresponding heavier atoms.

TABLE 2
BOND LENGTHS d (Å) AND BOND ANGLES ω (°)

Bond	d	Bond	d	Angle	ω	Angle	ω
Cr-C(1)	2.172(6)	C(1)-C(2)	1.438(9)	C(6)-Cr-C(7)	90.5(3)	C(1)-S-C(9)	104.5(4)
Cr-C(2)	2.215(7)	C(2)-C(3)	1.423(10)	C(6)-Cr-C(8)	88.0(3)	C(1)-S-C(10)	106.2(4)
Cr-C(3)	2.235(7)	C(3)-C(4)	1.421(11)	C(7)-Cr-C(8)	89.2(3)	C(9)-S-C(10)	100.7(4)
Cr-C(4)	2.46(7)	C(4)-C(5)	1.418(10)	Av. C-Cr-C	89.2(3)	Av. C-S-C	103.8(4)
Cr-C(5)	2.211(7)	C(5)-C(1)	1.430(9)	Cr-C(6)-O(1)	177.6(6)	S-C(1)-C(2)	129.0(5)
Av. Cr-C	2.216(7)	Av. C-C	1.426(10)	Cr-C(7)-O(2)	179.0(6)	S-C(1)-C(5)	121.5(2)
Cr-C(6)	1.820(7)	S-C(1)	1.743(6)	Cr-C(8)-O(3)	178.1(6)		
Cr-C(7)	1.848(7)	S-C(9)	1.795(9)	Av. Cr-C-O	178.2(6)		
Cr-C(8)	1.847(7)	S-C(10)	1.796(10)	C(5)-C(1)-C(2)	109.3(6)		
Av. Cr-C	1.838(7)			C(1)-C(2)-C(3)	105.8(6)		
C(6)-O(1)	1.160(9)			C(2)-C(3)-C(4)	105.7(6)		
C(7)-O(2)	1.150(9)			C(3)-C(4)-C(5)	108.1(6)		
C(8)	1.148(9)			C(4)-C(5)-C(1)	107.2(6)		
Av. C-O	1.153(9)			Av. C-C-C	108.0(6)		

bond lengths are practically the same (1.861(3) in IV and 1.848(15) Å in V).

It should be noted that the cyclopentadienyl ring in structure I is also planar, however, in contrast to II, the S atom is coplanar with the ring, and the C—C bond lengths are somewhat more spread (1.353–1.394 Å) and their average value (1.375 Å) is smaller by ca. 0.05 Å than in II.

It is also to be noted that the carbon atoms of the methyl groups in I are located at almost the same distance from the cyclopentadienyl ring plane on each side of it (1.41(2) and 1.39(3) Å), i.e., molecule I has C_s symmetry (with the exception of the hydrogen atoms of the methyl groups), whereas in II this symmetry of the ligand is no longer observed (the corresponding deviations of the carbon atoms of the methyl groups are 1.73(1) and 0.96(1) Å). The deviation of the ligand from C_s symmetry in II may be due to the short intermolecular contacts O(2)···H(92) (2.0 Å) between the O atoms of the CO groups and the Me groups.

The sulphonium atom, $-\overset{\ominus}{S}<$, in II has a pyramidal configuration: the bond angles C(1)—S—C(9), C(1)—S—C(10) and C(9)—S—C(10) are equal to 104.5(4), 106.2(4) and 100.7(4)°, respectively, the S—C(1) bond in the cyclopentadienyl ring (1.743(6) Å) being appreciably shorter than the other two bonds, S—C(9) and S—C(10), in the methyl groups (1.795(9) and 1.796(10) Å, respectively). In the known sulphonium salts 1-acetyl-1-thionia-5-thiacyclooctane perchlorate [7], phenylsulphonium iodide [8] and 2,3-dimethyl-2-butenyl-1,1,2-trimethylmethylsulphonium 2,4,6-trinitrobenzenesulphonate [9], the limits of the S—C bond variations are rather wide (1.78–1.88 Å), and the bond angles at the S atom are within 100–108°, the values of individual angles, as in II, differing appreciably from the average. The analysis of the geometry of the sulphur coordination environment in complex II and in sulphur ylides I [2] and 2-dimethylsulphuranilidenemalonitrile $(CH_3)_2\overset{\ominus}{S}\overset{\ominus}{C}(CN)_2$ [10] shows that the $\overset{\ominus}{S}-(C_5H_4)^-$ and $\overset{\ominus}{S}-\overset{\ominus}{C}(CN)_2$ bond lengths are shorter, as compared with the $\overset{\ominus}{S}-Me$ bonds, by 0.05, 0.07 and 0.09 Å, respectively; at the same time, the S—C(C_5H_4) bond in II proves to be 0.031 Å longer than in I, which seems to be the result of the coordination of the ylide ligand with the metal atoms.

The above data allow us to conclude that the structure of complex II is described with sufficient accuracy by the structural formula given above. Comparison of complex II with its Mo-analogue (III) (cell parameters: $a = 13.538(6)$, $b = 12.167(5)$, $c = 14.175(6)$ Å, $V = 2335(2)$ Å³, Mol. wt. 306.2, $D_m = 1.79$, $D_c = 1.742$ g/cm³ for $Z = 8$, space group $Pbca$), and results of a preliminary X-ray study (Mo···S distance 3.67 Å) are indicative of the isostructurality and the similar electronic structure of these complexes.

Thus the results of the X-ray study make it possible to conclude that the coordination of dimethylsulphonium cyclopentadienylide to the $Cr(CO)_3$ group is not accompanied by a sharp change in the structure of this ylide but results in increasing the contribution of the ylide structure in the π -bonded ligand, as compared with the non-coordinated ylide.

It was considered essential to compare the conclusions drawn from the X-ray study of I, II and III with the results of studying these systems by other methods. The previous study by ¹³C NMR spectra of cyclopentadienylides and their π -complexes with the carbonyls of Group VI metals showed coordination to the metal to result in a noticeable equalization of electron density in the π -cyclopen-

TABLE 3

ACCUMULATION OF DEUTERIUM IN THE α - AND β -POSITIONS OF Cp RINGS I AND III IN THE PROCESS OF IEH^a

		Deuterium content in the Cp ring (atomic %)	
		Calculated for isotopic equilibrium	Found ^b in the process of IEH for the protons with chem. shift δ
			$\delta = 5.89 \text{ ppm}$ $\delta = 6.23 \text{ ppm}$
I	83.9	22.0	35.0
	83.9	16.0	27.5
	83.9	26.0	39.5
		$\delta = 5.47 \text{ ppm}$	$\delta = 6.09 \text{ ppm}$
III ^c	94.9	23.4	24.6
	94.9	30.1	30.1
	94.9	19.7	19.8
	91.3	23.2	23.2

^a IEH is conducted in C₂H₂OD/acetone mixture, molar ratio of substance: C₂H₅OD: acetone = 1 : 200 : 600, at 30° for I, at 50°C for III. ^b Determined by PMR from the integral intensity of the signals of corresponding protons. ^c [12].

tadienyl groups of coordinated ylides, concurrent with an overall increase in the screening of the carbon nuclei in this group [11].

It was also very important to ascertain the changes in the reactivity of an ylide as a result of coordination to transition metals. It has been recently established that hydrogen atoms of the cyclopentadienyl ring in ylide I and in its complexes II and III are capable of entering the IEH reaction with deuterioethanol in neutral media [12]. On the basis of this reaction and PMR data, according to which the hydrogen atoms in the α - and β -positions of the cyclopentadienyl ring differ appreciably in their chemical shifts, we could determine the deuterium content in the α - and β -positions of the compounds studied at different stages of deuterium enrichment.

As a result, it was found that in the ylide I two protons of the cyclopentadienyl ring with the chemical shift $\delta = 6.23 \text{ ppm}$ enter the IEH reaction with a rate which is ~ 1.6 times higher than that of the two protons with the chemical shift $\delta = 5.92 \text{ ppm}$, whereas in the case of complex III the hydrogen exchange in the α - and β -positions of the cyclopentadienyl ligand proceeds at the same rate (Table 3).

The results obtained show that, when ylide I is coordinated to a transition metal, the differences in the reactivity of nonequivalent positions in the π -cyclopentadienyl group are completely levelled off, although, even in the initial ylide, these differences are only slight.

The overall data obtained by X-ray diffraction analysis, ¹³C NMR spectra and investigation of the IEH reaction, show that, when ylide I is coordinated to a transition metal, the degree of equalization of the C—C bonds and electron density in the π -cyclopentadienyl ring is increased and the differences in the reactivity of its α - and β -positions are levelled off.

Experimental

Cyclopentadienylide I, and complexes II and III were obtained by literature methods [13, 1b and 1a, respectively].

The X-ray study of II was carried out with the "Syntex-P2₁" automatic diffractometer (λ Mo-K α , graphite monochromator $\theta/2\theta$ scan, 1172 reflections). The structure was solved by the heavy atom method and refined by the least squares method in full-matrix anisotropic (isotropic for H) approximation, $R = 0.046$.

Experiments on IEH of I and III were conducted in a deuterioethanol/acetone mixture under argon. After the experiment, I was purified by crystallization from benzene, and II by chromatography on aluminium oxide. The deuterium content of I and II was determined from the excess density of the incineration water using the droplet method and the deuterium distribution from the integral intensity of the signals of the α - and β -protons of the cyclopentadienyl ring in the PMR spectra. The PMR spectra were taken on Perkin-Elmer apparatus, $R = 20$ (60 MHz), solvent (CD₃)₂SO.

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