Journal of Organometallic Chemistry, 221 (1981) 183—191
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

METALLOCENIC THIOKETONES AS TWO-ELECTRON LIGANDS

III *. ^{13}C NMR SPECTRA AND STRUCTURE OF A CYMANTRENE DERIVATIVE WITH A CYMANTRENYLPHENYLTHIOKETONE LIGAND

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(Received May 19th, 1981)

Summary

^{13}C NMR spectra of cymantrenylphenylthioketone and a binuclear complex $(\eta^5\text{-}C_5H_5)(CO)_2Mn \leftarrow S{=}C(Ph)C_5H_4Mn(CO)_3$ (I), produced by substitution of the CO ligand in cymantrene by this thioketone, have been studied. A complete X-ray structural investigation of complex I has been performed. It is suggested that in solution both *E* and *Z* isomers of complex I are present.

Introduction

We have shown earlier [1] that metallocenyl thioketones are capable of forming a donor-acceptor bond with a transition metal atom and this ability has been used for the synthesis of binuclear complexes. In the present paper the results of a study of the ^{13}C NMR spectra and an X-ray structural investigation of the binuclear complex $(\eta^5\text{-}C_5H_5)(CO)_2Mn \leftarrow S{=}C(Ph)(C_5H_4Mn(CO)_3$ (I), obtained by substitution of the CO ligand in cymantrene by cymantrenylphenylthioketone (II) via a tetrahydrofuran derivative (Scheme 1), are given.

Results and discussion

The IR spectrum of complex I in the range of carbonyl frequencies reveals 5 absorption bands of different intensities: 1900s, 1942vs, 1960vs, 1955w and 2022s cm^{-1} (in CCl_4), while for the starting thioketone II and cymantrene in the same solvent two absorption bands are recorded for each: 1960vs, 2034s cm^{-1}

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* For part II see ref. 2.

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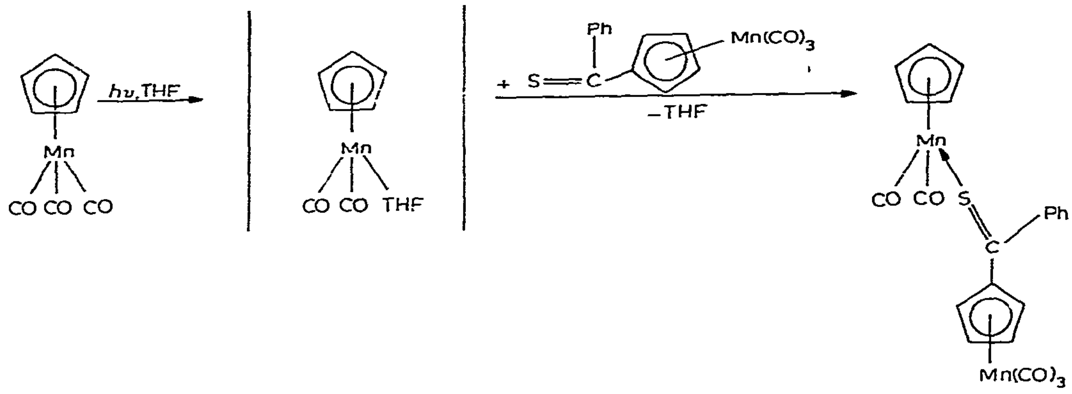


(I)

and 1945vs, 2030s cm^{-1}, respectively. The reduced local symmetry of the $CpMn(CO)_2 \leftarrow S{=}C{-}Ph$ fragment results in splitting of the low-frequency ν(CO) band of the *E* mode in complex I into two components (1960 and 1942 cm^{-1}). It should be noted that the carbonyl frequencies of thioketone II remain substantially unchanged upon coordination to the cymantrenyl moiety.

In the mass spectrum of complex I the peak of the molecular ion (P^+) (m/e = 499.96—500.95) with an intensity of 3.3%, as well as peaks of fragment ions typical for carbonyl-containing π-complexes of transition metals (P^+ — 2 CO, P^+ — 5 CO, etc.) are present. The most intense peak (100%) corresponds to the fragment ion $S{=}C\begin{smallmatrix}\nearrow Ph\\ \searrow (C_5H_4)Mn\end{smallmatrix}$ (m/e = 240). It is significant that the spectrum contains intense peaks of fragment ions wherein the metal atom is directly bonded to the sulphur atom $Mn \leftarrow S{=}C(Ph){-}(C_5H_4)Mn$ (11.2%), $(C_5H_5)MnS$ (40.9%), $MnSCH_3$ (41%), MnSH (10.9%), indicating a fairly stable Mn ← S bond.

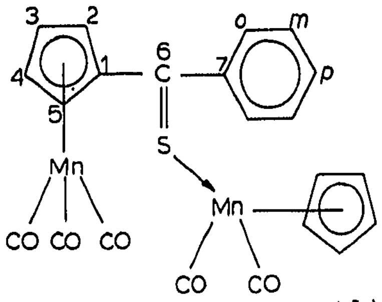
In order to study the structure and the electron density distribution in the binuclear complex I and the metallocenyl thioketone II, the ^{13}C NMR spectra of these compounds have been investigated. The parameters of ^{13}C-{^1H} NMR spectrum of complex I and thioketone II are shown in Table 1. In the spectrum of thioketone $(CO)_3Mn(\eta^5\text{-}C_5H_4C\begin{smallmatrix}\nearrow\!\!\!\nearrow S\\ \searrow Ph\end{smallmatrix})$ recorded at 0°C in CH_2Cl_2 signals of all the non-equivalent carbon nuclei of this system are present (three signals from C(1), C(2,5) and C(3,4) of the Cp fragment, four from C(7), C_o, C_m, C_p of the Ph fragment and one signal from each of the CS and CO groups). The signals of the nuclei C(1) and C(7), just as in the spectrum of ferrocenylphenylthioketone [2], are shifted downfield as compared with the signals of the remaining carbon nuclei of the corresponding fragments. In the downfield region signals of the CO and CS groups are found (δ = 223.22 ppm and 231.73 ppm, respectively). As expected, the acceptor Ph—C=S substituent caused a deshielding of the Cp ring in cymantrene ($\Delta\delta$(C(2,5) —3.8 ppm) and increased shielding of the CO ligands ($\Delta\delta$(CO) = +1.7 ppm).

The ^{13}C-{^1H} NMR spectrum of complex I recorded under the same condi-

(Continued on p. 188)

TABLE 1

CHEMICAL SHIFTS IN ^{13}C-$\{^1H\}$ NMR SPECTRA OF COMPLEX I AND CYMANTRENYLPHENYLTHIOKETONE II IN CH_2Cl_2 (δ in ppm from TMS)



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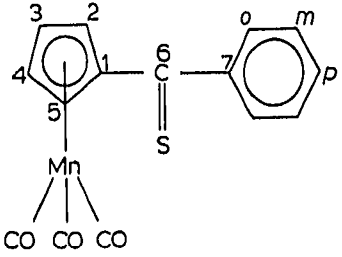

(II)

No.	Compound	Temperature (°C)	Unsubstituted Cp	Substituted Cp				Ph			CS	CO
				C(1)	C(2,5)	C(3,4)	C(7)	C_o	C_m	C_p		
1	Complex I	0	85.53	Not found [a]	82.93 [b]		144.63	128.32 [c]			230.92	224.55 213.20
2		−60	84.85	105.68	82.67	82.97	143.72	127.83 [d] and 128.0 [d]			230.59	224.13 201.55
3		−86	84.69	105.29	82.74 [b]		143.36	127.70 [c]			230.36	224.06 201.13
4	Thioketone II	0	—	101.19	84.69	89.04	147.72	128.09	127.05	131.02	231.73	223.22
5	Cymantrene	—	83.1	—	—	—	—	—	—	—	—	224.90

[a] The absence of this signal is probably due to its broadening caused by accelerated rotation at elevated temperature and the low signal/noise ratio. [b] Signal from C(2)—C(5). [c] Signal from C_o, C_m and C_p. [d] Signals from C_o, C_m and C_p.

TABLE 2

ATOMIC COORDINATES $\times 10^4$ (FOR Mn $\times 10^5$, FOR H $\times 10^3$) AND TEMPERATURE FACTORS (Å^2)^a

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn(1)	59203(10)	11573(9)	29819(8)	1.85(4)	1.26(4)	1.94(4)	0.69(3)	0.86(3)	0.38(3)
Mn(2)	92228(10)	69471(9)	11134(8)	1.68(4)	1.45(4)	1.80(4)	0.56(3)	0.86(3)	0.42(3)
S	6540(2)	2703(1)	1772(1)	2.09(6)	1.38(6)	1.83(6)	0.83(5)	0.95(5)	0.37(4)
O(1)	3016(5)	1516(4)	2523(4)	2.3(2)	3.0(2)	3.9(2)	1.5(2)	1.8(2)	1.3(2)
O(2)	7274(5)	2963(4)	5464(4)	3.0(2)	2.2(2)	2.2(2)	0.6(2)	0.8(2)	0.0(2)
O(3)	10864(5)	9124(5)	3438(4)	4.1(2)	2.5(2)	2.3(2)	0.5(2)	1.0(2)	−0.4(2)
O(4)	10943(5)	5124(5)	1933(4)	3.9(2)	1.1(2)	3.1(2)	3.0(2)	1.3(2)	0.6(2)
O(5)	11334(5)	8735(5)	−55(4)	3.8(2)	4.2(2)	3.5(2)	0.8(2)	2.3(2)	1.5(2)
C(1)	4158(7)	1383(6)	2719(5)	2.4(3)	1.5(2)	2.4(3)	0.6(2)	1.5(2)	0.5(2)
C(2)	6785(6)	2331(6)	4460(5)	1.7(2)	1.8(2)	2.4(3)	0.5(2)	1.1(2)	0.9(2)
C(3)	10247(7)	8273(6)	2540(6)	1.8(2)	2.0(3)	2.6(3)	0.4(2)	1.0(2)	0.9(2)
C(4)	10305(7)	5868(7)	1620(5)	1.9(3)	2.8(3)	2.0(3)	0.9(2)	0.8(2)	0.0(2)
C(5)	10528(7)	8041(7)	417(5)	3.0(3)	2.2(3)	2.0(3)	0.8(2)	1.0(2)	0.3(2)
C(6)	5938(8)	−733(6)	3765(6)	3.6(3)	1.6(2)	2.8(3)	1.1(2)	1.6(3)	0.8(2)
C(7)	7326(8)	−59(7)	3512(6)	2.5(3)	2.3(3)	3.3(3)	1.6(2)	1.0(3)	0.8(2)
C(8)	6897(8)	−78(6)	2242(6)	3.9(3)	1.6(3)	3.6(3)	1.8(2)	2.2(3)	0.8(2)
C(9)	5244(8)	−784(6)	1696(6)	4.4(4)	1.6(3)	2.3(3)	1.9(3)	0.4(3)	−0.2(2)
C(10)	4668(8)	−1180(7)	2647(6)	2.6(3)	1.4(3)	3.8(3)	0.7(2)	1.1(3)	0.0(2)
C(11)	7059(6)	5353(6)	1141(5)	0.8(2)	1.3(2)	2.1(2)	0.5(2)	0.3(2)	0.3(2)

C(12)	7213(6)	5023(6)	11(5)	1.8(2)	1.6(2)	2.2(3)	0.9(2)	0.5(2)	−0.0(2)
C(13)	7295(6)	6198(6)	−603(5)	1.8(2)	2.6(3)	1.2(2)	0.8(2)	0.5(2)	0.4(2)
C(14)	7212(7)	7298(6)	127(5)	2.1(3)	1.7(2)	2.6(3)	1.2(2)	0.8(2)	1.1(2)
C(15)	7064(7)	6786(6)	1197(6)	1.8(2)	1.5(2)	2.7(3)	0.5(2)	1.1(2)	0.3(2)
C(16)	6925(6)	4470(6)	2086(5)	1.0(2)	1.8(2)	2.3(2)	0.7(2)	0.7(2)	0.4(2)
C(17)	7256(6)	5241(5)	3330(5)	2.0(2)	0.7(2)	2.2(2)	0.7(2)	1.3(2)	0.8(2)
C(18)	6122(7)	5526(6)	3627(6)	1.8(2)	2.3(3)	2.6(3)	1.0(2)	1.1(2)	0.5(2)
C(19)	6516(8)	6304(7)	4765(6)	3.0(3)	2.3(3)	3.1(3)	1.6(2)	1.9(3)	0.4(2)
C(20)	7999(7)	6811(6)	5635(6)	3.1(3)	1.3(2)	2.3(3)	0.6(2)	1.3(2)	−0.2(2)
C(21)	9117(7)	6541(6)	5352(6)	2.3(3)	2.2(3)	2.7(3)	0.6(2)	1.3(2)	0.3(2)
C(22)	8755(7)	5779(6)	4209(5)	1.7(2)	2.1(3)	2.2(3)	0.7(2)	0.8(2)	0.4(2)

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
H(6)	582(8)	−98(7)	450(7)	4(2)	H(14)	721(5)	817(5)	−7(4)	0.6(9)
H(7)	831(8)	37(7)	412(6)	3(2)	H(15)	707(6)	723(6)	188(5)	2(1)
H(8)	756(8)	32(7)	174(6)	4(2)	H(18)	511(7)	519(6)	299(5)	2(1)
H(9)	479(8)	−92(7)	88(7)	4(2)	H(19)	579(7)	654(7)	492(6)	3(1)
H(10)	360(8)	−180(7)	249(6)	4(2)	H(20)	826(6)	735(6)	637(5)	1(1)
H(12)	723(5)	426(5)	−25(4)	0.0(9)	H(21)	1031(9)	690(8)	598(7)	5(2)
H(13)	735(5)	614(5)	−126(5)	0(1)	H(22)	950(8)	563(7)	406(6)	4(2)

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[a] The anisotropic temperature factors are in the form $T = \exp[-1/4(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*)]$.

tions as the spectrum of thioketone II reveals not eleven signals as it would be expected, but only seven signals. It was found that the signals of C_o, C_m and C_p of complex I are seen as one broad singlet with a chemical shift of 128.32 ppm, coinciding in fact with the average chemical shift of the same nuclei in uncoordinated II ($\bar{\delta}(C_o, C_m, C_p) = 128.26$ ppm). Instead of two signals from the Cp-ring carbon nuclei C(2,5) and C(3,4) observed in the spectrum of II, only one signal ($\delta = 82.93$ ppm) shifted upfield by 3.94 ppm is seen, as compared to the average value of chemical shift for the same nuclei in II ($\bar{\delta}(C(2,5)(C(3,4)) =$ 86.87 ppm), while the signal of C(1) is not detected at all. Furthermore, in the coordinated thioketone II insignificant increase in the shielding of the CS group carbon nuclei ($\Delta\delta(CS) \cong 0.7$ ppm) and deshielding for CO ligands ($\Delta\delta(CO) =$ -1.3 ppm) are observed. In contrast, in the case of substitution of the CO ligand in cymantrene by the thioketone ligand II a strong increase in shielding of the remaining CO groups ($\Delta\delta(CO) = +11.7$ ppm) and deshielding of the carbon nuclei of the π-Cp ring ($\Delta\delta(Cp) = -2.5$ ppm) are found, thus demonstrating the acceptor character of the phenylcymantrenylthioketone ligand. From the ^{13}C NMR data it follows that substitution of the CO ligand in cymantrene by thioketone II is accompanied by a redistribution of the electron density in this binuclear system between cyclopentadienyl and carbonyl ligands, whereas the phenyl fragment is not involved in this process.

Interesting changes in the ^{13}C NMR spectrum of complex I are observed with decreasing temperature. Thus, in the spectrum recorded at −60°C, in addition to a slight increase in shielding of all carbon nuclei (both in the thioketone ligand and in the cymantrenyl moiety), a signal from C(1) appears, which is absent at 0°C, and also two signals from the cyclopentadienyl C(2,5) and C(3,4) ($\delta = 82.76$ ppm and 82.97 ppm), instead of one ($\delta = 82.93$ ppm) at 0°C and two signals from C_o, C_m, C_p ($\delta = 127.03$ ppm and 128.00 ppm), instead of one ($\delta = 128.32$ ppm) at 0°C, are recorded. It was found that the carbon nuclei of CO ligands of two types with chemical shifts of 224.5 ppm and 213.2 ppm are shielded differently with decreasing temperature. Thus, on lowering the temperature form 0 to −60° C, the signal at $\delta = 224.55$ ppm is shifted upfield by only 0.42 ppm while the less intense signal at $\delta = 213.2$ ppm is shifted further upfield ($\Delta\delta(CO) = 11.65$ ppm).

These changes in the ^{13}C NMR spectrum of complex I are completely reversible with changing temperature. This fact suggests that the binuclear complex I can exist in solution in two isomeric forms.

A complete X-ray structural investigation of the binuclear complex I has been carried out to establish its structure objectively and to determine all the geometrical parameters of the molecule.

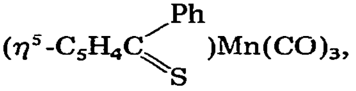
Crystals of I are triclinic, at −120°C $a = 10.007(3)$, $b = 10.009(3)$, $c = 11.729(3)$ Å, $\alpha = 92.26(3)$, $\beta = 109.19(3)$, $\gamma = 112.56(3)°$, $V = 1006(1)$ Å^3; $d_{calc.} = 1.65$ g/cm^3 for $Z = 2$, space group $P\bar{1}$. Atomic coordinates and temperature factors are given in Table 2 and bond angles in Table 3. The molecular geometry with bond lengths is shown in Fig. 1.

The molecule contains two coordination centres, viz. the Mn(1) and Mn(2) atoms linked by the bridging thiobenzoylcyclopentadienyl ligand. The Mn(2) atom interacts with the π-system of cyclopentadienyl ring and the sulphur atom participates in the donor-acceptor bond to another metal atom Mn(1) with its

TABLE 3

BOND ANGLES ω (degrees)

Angle	ω	Angle	ω	Angle	ω
SMn(1)C(1)	90.6(2)	C(7)C(6)C(10)	107.7(6)	SC(16)C(11)	119.2(4)
SMn(1)C(2)	103.1(2)	C(6)C(7)C(8)	108.4(6)	SC(16)C(17)	123.1(4)
C(1)Mn(1)C(2)	89.7(3)	C(7)C(8)C(9)	107.7(6)	C(11)C(16)C(17)	117.5(5)
C(3)Mn(2)C(4)	93.7(3)	C(8)C(9)C(10)	107.8(6)	C(16)C(17)C(18)	122.5(5)
C(3)Mn(2)C(5)	92.5(3)	C(6)C(10)C(9)	108.4(6)	C(16)C(17)C(22)	119.2(5)
C(4)Mn(2)C(5)	93.4(3)	C(12)C(11)C(15)	106.3(5)	C(18)C(17)C(22)	118.2(5)
Mn(1)SC(16)	123.1(2)	C(12)C(11)C(16)	129.2(5)	C(17)C(18)C(19)	119.9(6)
Mn(1)C(1)O(1)	178.5(6)	C(15)C(11)C(16)	124.6(5)	C(18)C(19)C(20)	121.4(6)
Mn(1)C(2)O(2)	172.9(6)	C(11)C(12)C(13)	108.9(5)	C(19)C(20)C(21)	119.2(6)
Mn(2)C(3)O(3)	178.2(6)	C(12)C(13)C(14)	108.5(6)	C(20)C(21)C(22)	120.5(6)
Mn(2)C(4)O(4)	177.2(6)	C(13)C(14)C(15)	107.9(6)	C(17)C(22)C(21)	120.8(6)
Mn(2)C(5)O(5)	178.4(6)	C(11)C(15)C(14)	108.5(5)		

lone pair electrons. On the other hand, molecule I can be regarded as an example of a system where a π-complex, in the present case  $(\eta^5\text{-}C_5H_4C{\overset{Ph}{\underset{S}{\lessgtr}}})Mn(CO)_3$, acts as a *n*-ligand to the second Mn atom.

Both Mn atoms are bonded symmetrically to the planar cyclopentadienyl ligands, the average Mn—C distances of 2.142 (7) and C—C of 1.414 (9) Å are consistent with those found in cymantrene, $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ [3], and its

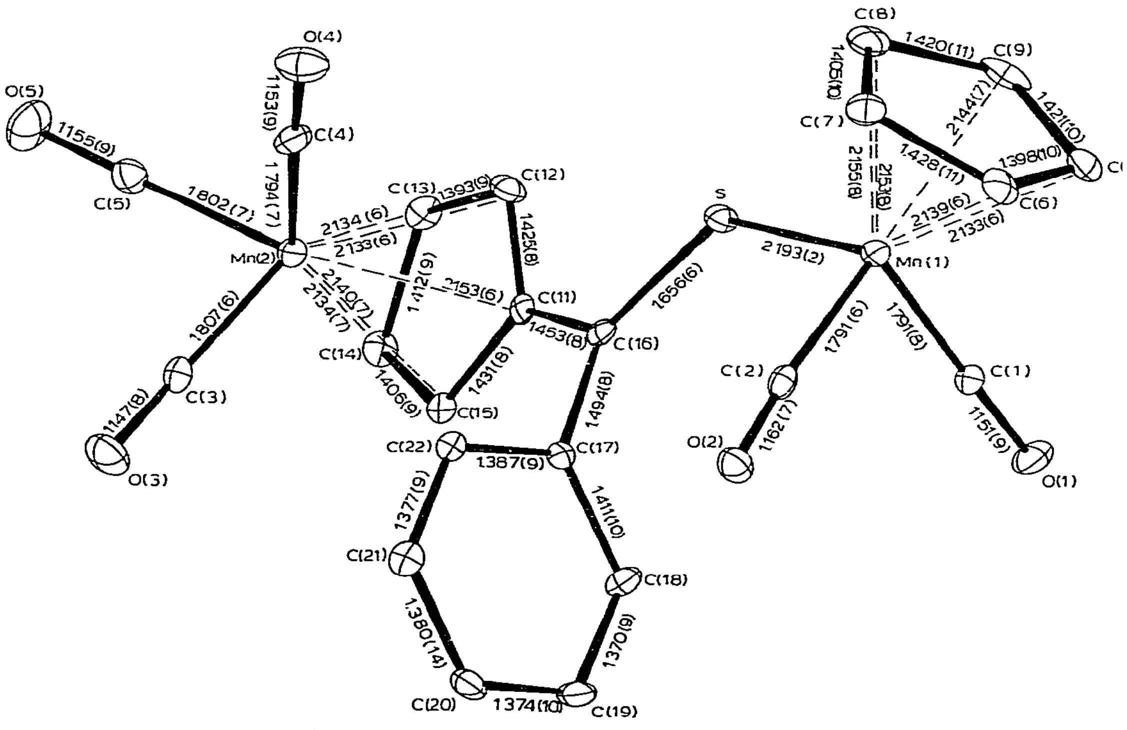


Fig. 1. The structure of complex I.

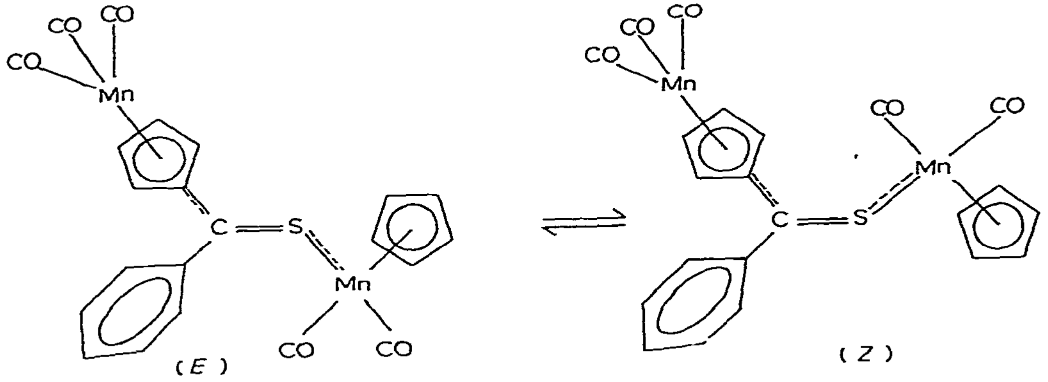


Fig. 2. The *E* and *Z* isomers of complex I.

derivatives, though a noticeable difference is found in the geometry of the $Mn(CO)_3$ and $Mn(CO)_2S$ fragments. While the $Mn(CO)_3$ moiety is almost undistorted and has a C_{3v} local symmetry (the bond angles (O)C—Mn—C(O) are in the range of 92.5—93.7°), in the second fragment the bond angle S—Mn(1)—C(2) is increased to 103.1 (2)° and both other angles are close to 90°. This difference is explained by the presence of ligands of different volumes in the coordination sphere of Mn(1) and, hence, a steric stress resulting in short intramolecular contacts, in particular between the C(2) atom of the carbonyl group and the C(17) atom of the phenyl ring at a distance of 3.182(8) Å (Fig. 1).

The above-mentioned steric crowding is also increased by the unusually short Mn—S bond of 2.193(2) Å which is smaller not only than the sum of the covalent radii of Mn (1.38 Å [4]) and S (1.04 Å [5]) by 0.23 Å, but also than the lengths of normal Mn—S bonds (2.3—2.4 Å) found in manganese complexes with sulphur-containing ligands [6]. This decrease in bond length indicate an increased Mn—S bond order, which is also supported by a noticeable elongation of the S=C bond to 1.656(6) Å, whereas the length of a typical double S=C bond (e.g. in CS_2) is equal to 1.553 Å [7].

The thiobenzoylcyclopentadienyl ligand is as a whole not planar: the phenyl and cyclopentadienyl rings form dihedral angles of 83.5° * and 15.6°, respectively, with the SC(16) C(11) C(17) plane **; the Mn(1) atom is displaced from this plane by 0.385 Å. Only the cyclopentadienyl ring is likely to take part in conjugation with the double C=S bond, which is also in agreement with the shortening of the C(16)—C(11) bond to 1.453(8) Å as compared to the C(16)—C(17) bond of 1.494(8) Å (the latter is even longer than the standard value for a normal $C(sp^2)$—$C(sp^2)$ bond length of 1.476 Å [7]).

The geometry of the metal carbonyl fragments is quite unexceptional with the normal bond length Mn—C of 1.797(8) and C—O of 1.154(9) Å.

Comparing data from the X-ray structural analysis and the results obtained from the ^{13}C NMR spectra of complex I, we come to the conclusion that in

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* This large dihedral angle corresponds fully to the NMR data (see above) excluding participation of this substituent in redistribution of electron density.

** The C(16) atom has a maximum deviation from this mean squares plane (0.027(6) Å).

solution isomers of this compound exist as a result of different positions of the substituents relative to the double C=S bond (*E*, *Z* isomers) (Fig. 2).

The data from the X-ray structural analysis show that in the crystalline state the more stable *E* isomer is present. However, definite conclusions about the isomeric behaviour of the complex studied necessitate further experimental substantiation.

Experimental

Thioketone II and complex I were prepared following the previously described procedures [8 and 1, respectively]. All solvents were distilled under argon before use. IR spectra were recorded with a IR-20 spectrophotometer in CCl_4 solution. Mass spectra were measured with a AE MS-30 mass-spectrometer using a DS-50 automatic data-processing system at an ionization voltage of 70 V. ^{13}C NMR-$\{^1H\}$ spectra were recorded with a Bruker HX-90 spectrometer with the working frequency of 22.63 MHz in the Fourier transform mode under proton decoupling and noise modulation.

The X-ray structural study of I was carried out with an Syntex $P2_1$ automatic diffractometer (λMo-K_α, graphite monochromator, $\theta/2\theta$ scan, $2^\circ \leqslant 2\theta \leqslant 50^\circ$, without absorption correction, $\mu(\lambda\text{Mo-}K_\alpha) = 14.5\ \text{cm}^{-1}$, 2418 reflections with $I \geqslant 2\sigma$ measured at —120°C). The structure was determined by the heavy-atom method and refined by the least squares method in the full-matrix anisotropic approximation (isotropic for H atoms with geometrically calculated positions), $R = 0.049$, $R_w = 0.045$.

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