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METALLOCENIC THIOKETONES AS TWO-ELECTRON LIGANDS

II *. ^{13}C NMR SPECTRA OF GROUP VI METAL CARBONYL COMPLEXES WITH FERROCENYLPHENYLTHIOKETONE AS LIGAND

P.V. PETROVSKII, V.N. SETKINA *, S.P. DOLGOVA and D.N. KURSANOV
Institute of Organo-Element Compounds, Academy of Sciences of the USSR Vavilova St., 28, Moscow, B-312 (U.S.S.R.)

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Summary

The ^{13}C NMR spectra of binuclear Group VI metal carbonyl complexes with ferrocenylphenylthioketone as a *n*-ligand have been studied. These complexes have an octahedral structure with the metallocenyl thioketone in the axial position. It was found that the carbon nuclei in the cyclopentadienyl rings of the thioketone are deshielded upon coordination to the M(CO)$_5$ group; the degree of deshielding depends on the central metal atom and decreases in the series W $\geqslant$ Mo > Cr.

Introduction

We have recently reported the preparation of a novel type of binuclear complex of transition metals, where metallocenyl thioketones act as two-electron ligands [1]. The synthesis of these complexes is carried out by photochemical substitution of the CO ligand in carbonyl-containing compounds of transition metals by metallocenyl thioketones via an intermediate formation of a tetrahydrofuran derivative.

Several binuclear complexes have been obtained by this method, where the transition metals M and M′ belong either to the same or different groups of the periodic system. Complexes A have been characterized by elemental analysis, and IR, PMR and mass spectra.

In the present paper the data from the ^{13}C NMR spectra of binuclear complexes of Group VI metals with ferrocenylphenylthioketone as a two-electron ligand (compounds I, II, III) are given. By using ^{13}C NMR we hoped to reveal

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* For part I see ref. 1.

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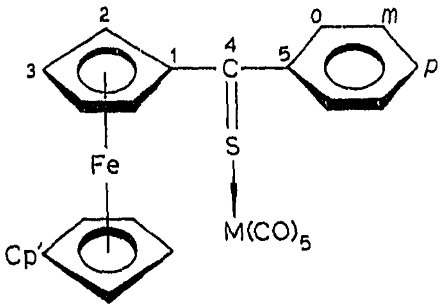
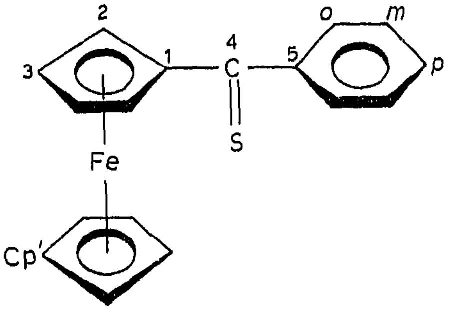
TABLE 1

^{13}C NMR CHEMICAL SHIFTS OF COMPLEXES I, II AND III AND FERROCENYLPHENYLTHIOKETONE IV IN CH_2Cl_2 AT 10°C (δ in ppm from TMS)



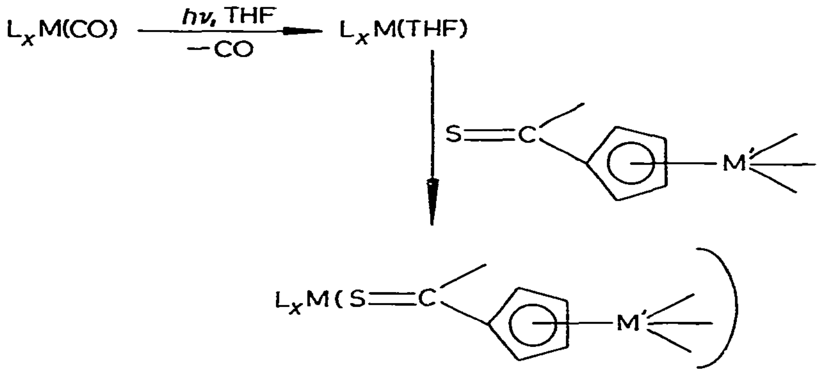
(I – III)



(IV)

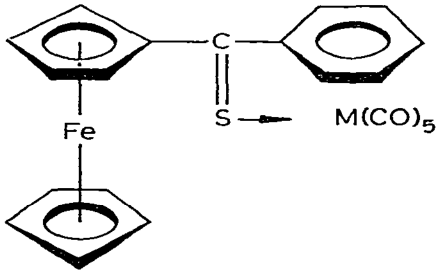
Compound	Cp'	Cp [a]			Ph				C(4)	CO		$M(CO)_6$ [b]
		C(1)	C(2)	C(3)	C(5)	C_o	C_m	C_p				
I, M = Cr	72.54	91.06	71.82	76.63	145.77	128.35	127.38	130.11	237.84	224.13	214.71	212.5
II, M = Mo	72.80	90.34	72.34	77.09	146.72	128.42	127.25	130.30	236.28	214.12	204.11	202.0
III, M = W	72.86	90.47	72.34	77.28	146.35	128.48	127.18	130.37	233.61	202.42	196.90	192.1
IV	72.34	89.30	72.73	75.27	149.01	127.70	127.05	130.17	238.69	—	—	—

[a] The signal assignments are according to Koridze et al. [3]. [b] See ref. 4.



(A)

M,M′ = Group VI, VII and VIII transition metals ; L = CO, π—Cp etc.



(I, M = Cr ;
II, M = Mo ;
III, M = W)

the changes in electron density distribution occurring in ferrocenylphenylthioketone (IV) upon its coordination to transition metals, as well as the relationship between these changes and the nature of the central atom M (M = Cr, Mo, W).

Furthermore, it was expected that the combination of ^{13}C NMR data and other spectral data would make it possible to obtain detailed information on the structure of these compounds.

Results and discussion

The ^{13}C-$\{^1H\}$ NMR spectral parameters of the binuclear complexes I—III and the starting thioketone IV are given in Table 1. Nine signals are found in the ^{13}C NMR spectrum of thioketone IV, including 4 high-field signals from the carbon nuclei of the cyclopentadienyl rings (C(Cp′), C(1), C(2), C(3); δ = 72 to 89 ppm), 4 signals from the carbon nuclei of the phenyl ring (C(5), C_o, C_m, C_p); δ = 127 to 149 ppm) and one signal from the thiocarbonyl group (C(4)) located at low field (δ = 238.68 ppm from TMS). It should be noted that signals from the carbon nuclei (C(1) and C(5)) directly bonded to the thiocarbonyl group are deshielded to a greater extent than the remaining carbon nuclei of the same fragments, similar to what is observed, e.g. in α-ferrocenylcarbenium system [2]. Upon coordination of thioketone IV to the $M(CO)_5$ group, an increased shielding of the carbon nucleus in the thiocarbonyl group (C(4)) is observed. However, the carbon nuclei (C(1) and C(5)) bonded directly to C(4) are shielded differently.

The carbon nuclei in the ferrocenyl fragment (C(1)) are deshielded, while the shielding of the phenyl group (C(5)) is increased. This fact demonstrates the different abilities of the C(4)—C(1) and C(4)—C(5) bonds to transfer electronic effects. The remaining carbon nuclei of both the phenyl and ferrocenyl fragments (except C(2) in the substituted cyclopentadienyl ring) in complexes I—III are deshielded as compared to the starting thioketone, thus pointing to the electron-acceptor character of $M(CO)_5$ groups coordinated to ferrocenylphenylthioketone.

Within the range characteristic of the signals from the carbon nuclei of carbonyl group two signals are clearly distinguished for all three complexes I—III, the signal located at higher field being about four times greater in intensity than the low field signal. These data show that two types of CO group are present (in the ratio of 1 : 4). This feature of the ^{13}C NMR spectra suggest that molecules of compounds I—III have the structure of a substituted octahedron. This conclusion is in agreement with the data of IR spectra to the effect that complexes I—III have C_{4v} symmetry [1]. Four CO ligands are located in the equatorial positions (values of chemical shifts for derivatives of Cr, Mo and W are 214.71 ppm, 204.11 ppm and 196.90 ppm, respectively). In one of the axial positions there is the remaining CO ligand (chemical shifts for the same derivatives are 224.13 ppm, 214.12 ppm and 202.42 ppm, respectively), and in the other the ferrocenylphenylthioketone acting as a two-electron ligand (Fig. 1).

From a comparison of the ^{13}C NMR spectra of complexes I, II and III it follows that the degree of shielding of the carbon nuclei in the thioketone ligand is related to the nature of the central metal atom (Table 2). Thus, the maximum shift of the signals of the carbon nuclei in the unsubstituted cyclopentadienyl ligand (Cp') towards low field takes place for tungsten complexes, while the minimum is seen for chromium complexes ($\Delta\delta$ for C(Cp') = 0.20 ppm, 0.46 and 0.52 ppm for derivatives of Cr, Mo and W, respectively). The same

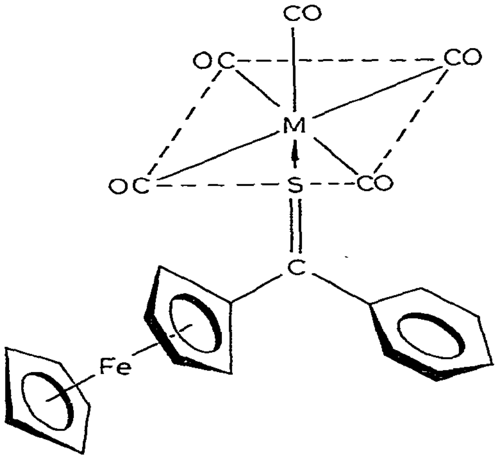


Fig. 1. The coordination geometry of complexes I—III (M = Cr, Mo, W).

TABLE 2

CHANGES IN ^{13}C NMR CHEMICAL SHIFTS ($\Delta\delta$ in ppm) OF FERROCENYLPHENYLTHIOKETONE UPON COORDINATION TO THE M(CO)$_5$ GROUP [a]

Compound	Cp'	Cp		Ph		
		C(1)	C(2), C(3) [b]	C(5)	C_o, C_m, C_p [c]	C(4)
I, M = Cr	−0.20	−1.76	−0.23	+3.24	−0.38	+0.84
II, M = Mo	−0.46	−1.04	−0.72	+2.29	−0.39	+2.40
III, M = W	−0.52	−1.17	−0.81	+2.66	−0.40	+5.07

[a] $\Delta\delta = \delta$ of thioketone IV — δ of complex (I, II or III), positive values for upfield shifts. [b] C(2), C(3) = averages value of chemical shift, $\Delta\delta$(C(2),C(3) = δ(C(2), C(3)) of IV — δ(C(2), C(3)) of I, II or III.
[c] C_o, C_m, C_p = average value of chemical shift, $\Delta\delta(C_o, C_m, C_p) = \delta(C_o, C_m, C_p)$ of IV — $\delta(C_o, C_m, C_p)$ of I, II or III.

trend is also observed for the average values of chemical shifts of carbon nuclei in the substituted cyclopentadienyl ring ($\Delta\bar{\delta}$(C(2), C(3))). In the phenyl fragment of the thioketone ligand the average value of the downfield chemical shifts of the *o*-, *m*- and *p*-carbon nuclei ($\Delta\bar{\delta}(C_o, C_m, C_p)$ is substantially the same for all the three complexes, whereas for C(5) the shielding increases in the series Cr > W ⩾ Mo. As has been mentioned, for C(1) not an increase in shielding, but a deshielding is observed, the same sequence being retained for the variation of the central metal atom: Cr > W ⩾ Mo.

The analysis of ^{13}C NMR spectra of the isostructural complexes I, II and III shows that the total effect of the metal—ligand donation and back-donation resulting in deshielding of the Cp rings of the ferrocenylthioketone ligand, is revealed to a lesser extent upon coordination to Cr(CO)$_5$ group and to a greater extent for the W(CO)$_5$ and Mo(CO)$_5$ derivatives, these effects being very similar for the latter compounds.

Experimental

Complexes I, II and III are prepared by the previously reported method [1]. Thioketone IV is prepared by a known method [5]. ^{13}C-{^{1}H} NMR spectra are recorded on a Bruker HX-90 spectrometer operated at 22.63 MHz with Fourier transform and ^{13}C-{^{1}H} noise decoupling. The spectra were recorded in CH$_2$Cl$_2$ solution under argon.

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