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METALLOCENIC THIOKETONES AS TWO-ELECTRON LIGANDS.

IV *. *E–Z* ISOMERIZATION OF CYMANTRENE DERIVATIVES WITH AN ARYLCYMANTRENYL PHENYL THIOKETONE LIGAND

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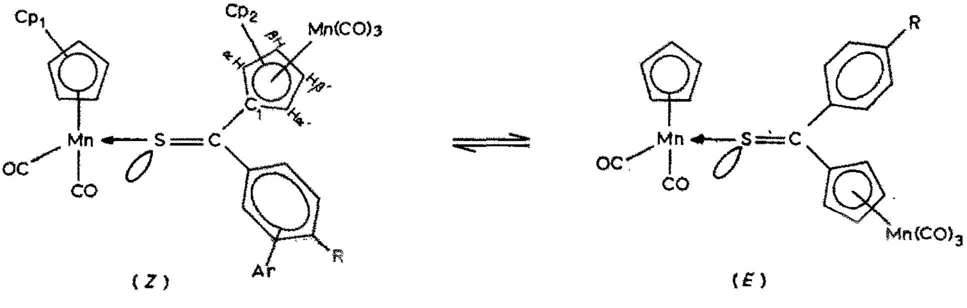
Summary

The ^1H NMR spectra of binuclear complexes of transition metals with cymantrenyl aryl thioketones have been studied. Temperature-dependence of the ^1H NMR spectra of these complexes indicates that the rotation about the C=S bond is restricted. The energetic parameters for this process have been determined.

Introduction

In our previous report [1] we assumed that a binuclear complex, obtained by the substitution of a CO ligand in cymantrene by cymantrenyl phenyl thioketone, $(\eta^5\text{-}C_5H_5)Mn(CO)_2S{=}C(Ph)(C_5H_4\text{-}\eta^5)Mn(CO)_3$ (I) is capable of existing as *E* and *Z* isomers. X-ray structure investigations have shown that in the crystalline state the



(I, R = H ; II, R = CH3)

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* For part III see ref. 1.

more stable *E* isomer is present, but, however, ^{13}C NMR spectra suggest the existence of another isomer in solution.

To observe spectrally both isomers and to quantitatively evaluate their stereochemical lability we investigated the ^{1}H NMR spectra of complex I and its methylhomologue II.

Results and discussion

The ^{1}H NMR spectral parameters of the binuclear complexes I and II are given in Table 1. It appeared that the spectra of I and II depended on the temperature and solvent. Thus, in diethyl ether the ^{1}H NMR spectrum of I displays two triplets with $J(\text{H–H}) = 2.5$ Hz from Cp_α and Cp_β coordinated to Mn(CO)_3 ($\Delta\delta_{\alpha\beta} = 10$ Hz) a broad signal from C_6H_5 and a narrow singlet from Cp(1) (Fig. 1). On lowering the temperature the signals change their multiplicity (Fig. 1A–C). Considering the fact that the protons of Cp(2) are pairwise equivalent both at 24°C and −98°C ($\delta_{\alpha(\beta)\text{H}} = \delta_{\alpha'(\beta')\text{H}}$) it may be assumed from the ^{1}H NMR spectra that the rotation about the C–C(1) bond in I in diethyl ester is free. The nonequivalence of the α and α' and β and β' protons is also not evident from the ^{1}H NMR spectra of I in $(CH_3)_2CO$, CS_2 and of II in CD_2Cl_2. It is noteworthy that at room temperature one singlet from Cp(1) of I in diethyl ester is found, while the low-temperature ^{1}H NMR spectrum (−65°C) shows two signals with ratio of intensities 3.8 : 1.

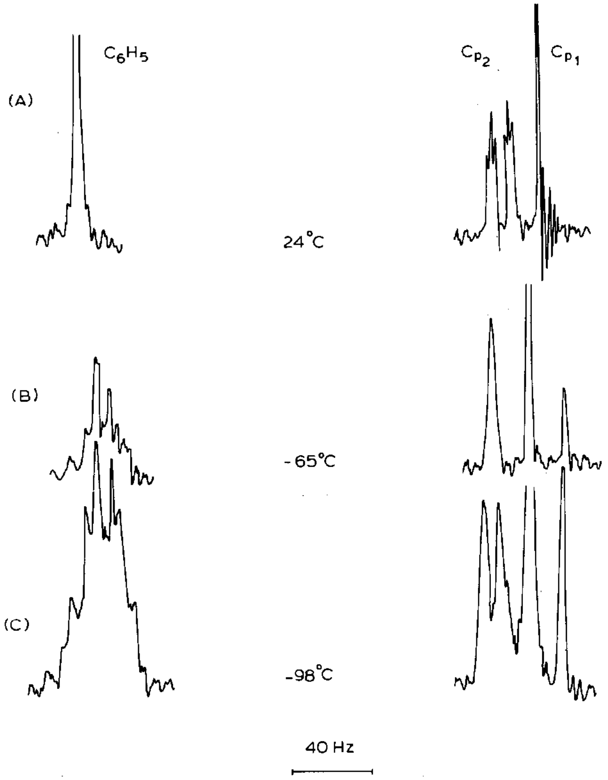


Fig. 1. Temperature dependence of the ^{1}H NMR spectrum of I in diethyl ether.

TABLE 1

PARAMETERS OF ^{1}H NMR SPECTRA OF COMPLEXES I AND II (δ, ppm from TMS [a])

Compound	Temperature (°C)	Cp(1)	Cp(2)	Ar	CH_3	Solvent
I	24	4.73	5.03	7.44	-	$(CH_3)_2CO$
	−60	4.79 and 4.62	5.10	7.44	-	
	24	4.59	4.91 and 4.79	7.36	-	$(C_2H_5)_2O$
	−98	4.80 and 4.62	5.07 and 4.96	7.36	-	
II	24	4.61	4.92 and 4.74	7.22	2.37	CD_2Cl_2
	−54	4.66 and 4.35	4.93 and 4.76	7.22	2.36	

[a] Chemical shifts from that of the solvent, then recalculated with respect to TMS.

The trend of the temperature dependence of these signals (Fig. 2A–D) implies exchange between them (all the temperature changes are reversible). In accordance with this the chemical shift of Cp(1) protons at 24°C is a mean value of the chemical shifts of both signals observed for Cp(1) at −65°C corrected for the populations. The same results were obtained for I in $(CD_3)_2CO$ and for II in CD_2Cl_2, for which the ratio of integral intensities of the Cp(1) signals observed is 3.1 : 1 (−59°C) and 5.0 : 1 (−54°C), respectively. The results from ^{13}C NMR spectra of complexes I [1] and II are in full agreement with the ^{1}H NMR data (Table 2). Thus, on lowering the temperature from 30°C to 5°C, as is the case with the ^{1}H NMR spectra, the signal of the ^{13}C carbon nuclei of Cp(1) ligand is broadened, and on cooling to −60°C and

TABLE 2

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

Temperature (°C)	Cp(1)	Cp(2)		Ar	CH_3	CO	CS
		C(1)	H(β, β')				
30	85.14	n.d.	83.06	128.35 129.07	21.14	224.58	231.14
5	85.47	n.d.	82.93	128.15 128.87	21.21	224.45	231.27
−60	84.76 89.50	106.9	82.87	127.31 128.41	20.80	223.37	230.62
−80	84.64 89.37	105.3	82.67	127.51 128.29	20.88	224.20 202.04	230.69

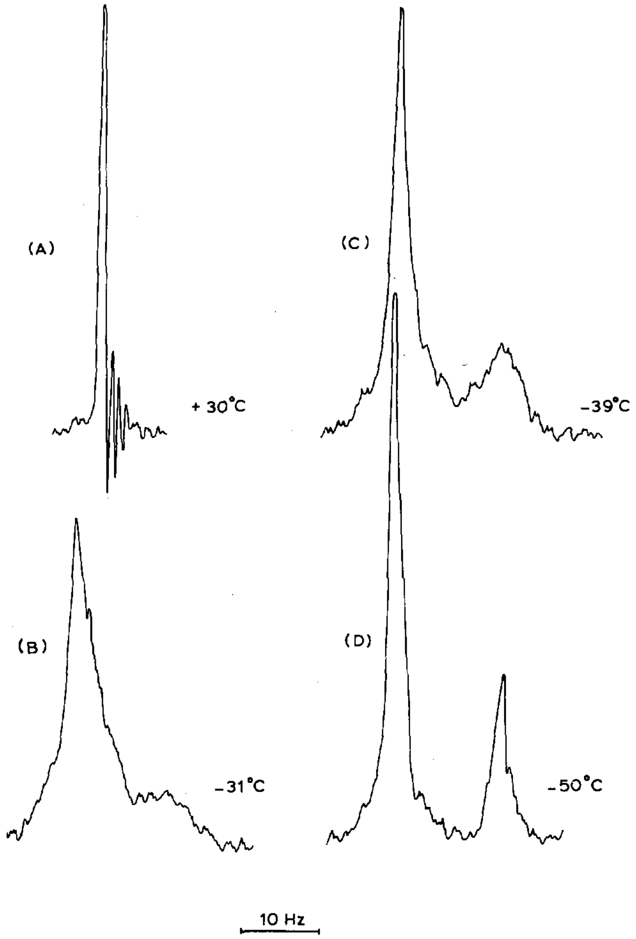


Fig. 2. Temperature dependence of the ^{1}H NMR spectrum of the cyclopentadienyl ring Cp(1) of I in diethyl ether.

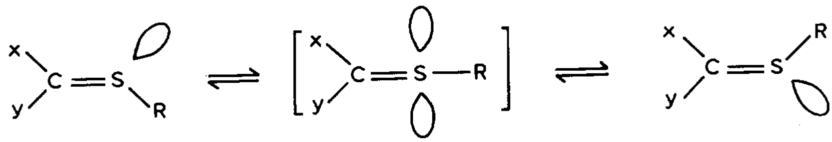
$-80°$C a new signal with a chemical shift of 89.50 and 89.37 ppm, respectively, appears, which is absent at room temperature. In the range of the CO ligands a new signal is also seen at high field when the temperature is lowered to $-80°$C ($\delta = 202.04$ ppm). Similar changes in the ^{13}C NMR spectra were observed previously for complex I [1].

The spectral behaviour of complexes I and II may be explained by restricted rotation about either Mn–S or C=S bonds. Considering the above ^{1}H NMR data concerning free rotation about the C–C(1) bond, as well as those of the X-ray structure analysis of I we suggest that at low temperatures isomers of I and II are fixed relative to the C=S bond, and that in the ^{1}H NMR spectra the high-field signal of lowered intensity belongs to the Cp(1) *Z*-isomer protons. The kinetic parameters of the *Z*–*E* isomerization (Table 3) were obtained by use of the standard programm for two-centre exchange with the aid of the NMR dynamic method [2]. The values of

TABLE 3

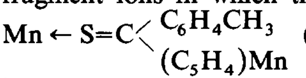
KINETIC PARAMETERS OF *E*–*Z* ISOMERIZATION OF COMPLEXES I AND II

Compound	Isomer	$10^2/t$ (°C) τ sec	log *A*	$E_{act.}$ (kcal mol^{-1})	ΔH^* (kcal mol^{-1})	ΔS^* (entr. un.)	ΔG^*_{298} (kcal mol^{-1})	Solvent
I	*E*	7.4(−13)	11.3±0.9	11.1±0.9	10.7±0.8	−8.4±1.5	13.2±0.3	$(C_2H_5)_2O$
	Z	1.9(−13)	11.9±0.9	11.1±0.9	10.7±0.8	−5.7±1.5	12.4±0.3	
	E	6.7(−11)	12.0±0.5	12.0±0.5	11.5±0.5	−5.0±1.0	13.0±0.3	$(CD_3)_2CO$
	Z	2.2(−11)	12.5±0.5	12.1±0.5	11.5±0.5	−2.8±1.0	12.3±0.3	
II	*E*	2.7(−25)	14.3±1.1	14.4±0.3	14.0±0.3	−5.2±1	12.5±0.3	CD_2Cl_2
	Z	0.55(−25)	14.9±1.1	14.4±0.3	14.0±0.3	−8.6±1.1	11.4±0.3	



the pre-exponential factor log A of 12 : 14 prove the intermolecular nature of the isomerization. It should be noted that the comparatively small values of $\Delta S^{\neq}$ are characteristic of the isomerization of I and II. However, it is known from the literature that thermal isomerization relative to double bonds accompanied by heterolytic decay of these bonds in the transition state is characterized by considerably larger negative values of $\Delta S^{\neq}$. Apparently, in our case Z–E isomerization proceeds via the inversion mechanism like that observed for C=N, N=N moieties [3].

Experimental

Complexes I and II were obtained by methods already described [4]. The previously undescribed II is a dark-blue crystalline substance, m.p. 155°C (decomp.). The IR spectra of II in the range of carbonyl frequencies display five absorption bands of different intensities: 1915s, 1945vs, 1955vs, 2000s, 2031s cm^{-1} (in $C_2H_2Cl_2$). The mass spectrum of II contains a peak of the molecular ion (P^+) ($m/e = 513.58$–515.62) with a relative intensity of 26.53%, as well as peaks of fragment ions typical for carbonyl π-complexes of transition metals ($P^+ - 2CO$; $P^+ - 5CO$). The most intense peak (100%) corresponds to the fragment ion ($P^+ - 5CO$; $m/e = 373.76$). It is noteworthy that the spectrum contains intense peaks of fragment ions in which the metal atom is directly bonded to the sulphur atom,  $\mathrm{Mn} \leftarrow \mathrm{S{=}C}\begin{matrix} \diagup\, C_6H_4CH_3 \\ \diagdown\, (C_5H_4)Mn \end{matrix}$ (13.51%), $(C_5H_5)MnS$ (10.06%), MnSH (6.75%), indicating a fairly stable Mn–S bond.

The IR spectra were recorded with a IR-20 spectrophotometer. The mass spectra were measured with a AEMS-30 mass-spectrometer with an automatic data-processing system (DS-50) at an ionizing voltage of 70 eV. The ^{13}C-{^1H} NMR spectra were recorded with a Bruker HX-90 spectrometer with an operating frequency of 22.63 MHz in the Fourier transform mode and ^{13}C-{^1H} noise decoupling. The ^1H NMR spectra were recorded with a RYa-2309 spectrometer with an operating frequency of 90 MHz. Thermostat accuracy was ±0.5°C. The dynamic ^1H NMR spectra were computed on a PDP-12 computer. All the solvents were distilled under argon.

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