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σ—π-REARRANGEMENT OF σ-CROTYLMANGANESE PENTACARBONYL WITH THE RETENTION OF THE GEOMETRIC CONFIGURATION OF THE ALLYLIC LIGAND

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Summary

The decarbonylation reaction of σ-crotylmanganese pentacarbonyl (σ-C_4H_7)-$Mn(CO)_5$ (I), in the presence of bis(diphenylphosphino)ethaneiridium chloride, [Ir(Diphos)$_2$]Cl (II), is described. At room temperature, II abstracts one molecule of CO from I, which results in the latter rearranging into the π-crotyl complex. The reaction is shown to proceed with the retention of the geometric configuration of the allylic ligand.

In 1961 McClellan et al. [1] discovered that at 85—95°C σ-allylmanganese pentacarbonyls give up one molecule of carbon monoxide to form π-allylmanganese tetracarbonyls. We analyzed the ^{1}H NMR spectrum of the π-crotylmanganese tetracarbonyl thus obtained and showed that the π-crotyl ligand is of *syn* configuration irrespective of the *cis*- and *trans*-structural forms in (σ-C_4H_7)-$Mn(CO)_5$ (I) [2]. This direction of the thermal decarbonylation may be due to *anti*—*syn* isomerization which readily occurs at high temperatures. To reduce the effect of this reaction during σ—π-rearrangement, we decided to make use of the ability of some transition metal complexes to adsorb carbon monoxide under mild conditions [3]. As the carbon monoxide acceptor, bis(diphenylphosphino)ethaneiridium chloride (II) obtained from $Ir(PPh_3)_2COCl$ and bis(diphenylphosphino)ethane was chosen [4].

To a suspension of 2 g (2 mmol) of [Ir(Diphos)$_2$]Cl (II) in 7 ml of tetrahydrofuran 0.22 g (1 mmol) of $C_4H_7Mn(CO)_5$ was added with stirring. After 5—10 min, the colour of the suspension changed from orange to cream. The reaction mixture was stirred for another 1.5—2 h and then the yellow solution was filtered off, leaving the precipitate behind. The reaction was followed by recording the IR spectra in the carbonyl stretching region. It has been found that the starting (C_4H_7)$Mn(CO)_5$ shows the most intense absorption at 2103

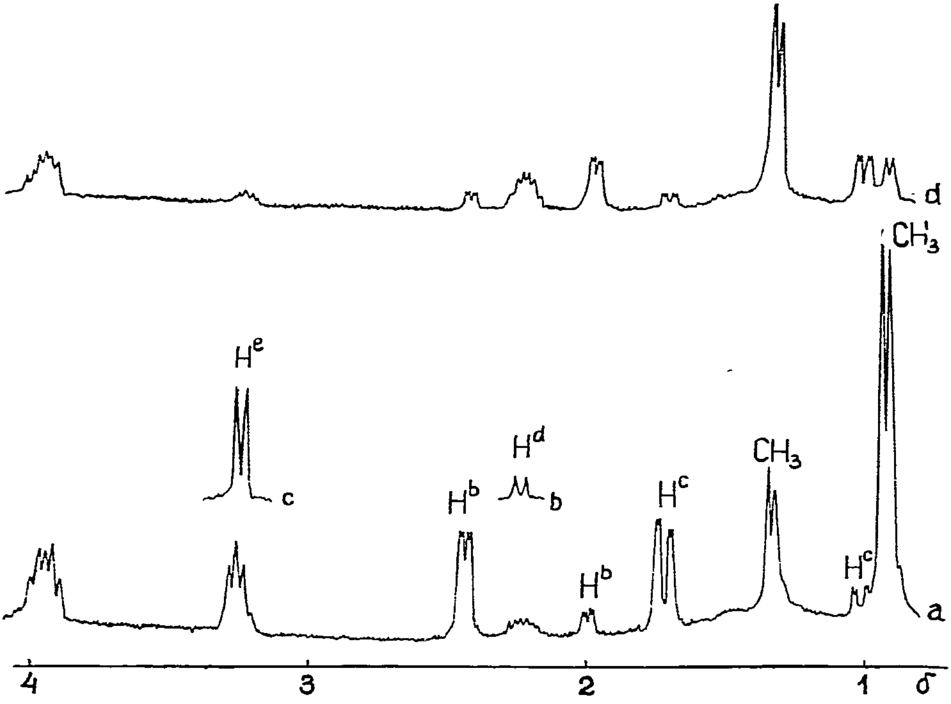


Fig. 1. The 270 MHz ^{1}H NMR spectra of (σ-C_4H_7)Mn(CO)$_4$.

cm^{-1} and 2008—1998 cm^{-1} while in the case of the reaction product ν(CO) appears at 2062, 1960 and 1944 cm^{-1}.

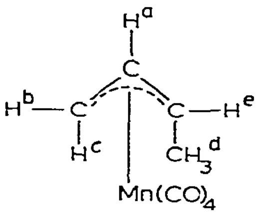
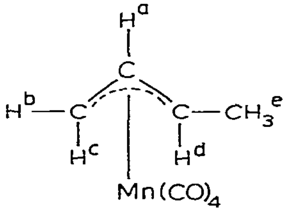
^{1}H NMR spectra of π-crotylmanganese tetracarbonyl were obtained in benzene solution using a Bruker HX-270 spectrometer. Chemical shifts were calculated in δ ppm relative to tetramethylsilane. In Fig. 1a, the spectrum is shown of (C_4H_7)Mn(CO)$_4$ obtained by decarbonylation of C_4H_7Mn(CO)$_5$ (consisting of a mixture of 85% *cis*- and 15% *trans*-isomers which results from the interaction between HMn(CO)$_4$ and butadiene [2]). In the double resonance spectra obtained by irradiation of the methyl protons at δ 1.32 and 0.91, the H^d and H^e protons appear in the spectrum as doublets at δ 2.23 and 3.26, respectively, the spin—spin coupling constants being J_{ad} = 12 Hz and J_{ae} = 7 Hz (Fig. 1b and 1c). The integral intensities ratio showed that the mixture of (π-C_4H_7)Mn(CO)$_4$ isomers contains 85% *anti*- and 15% *syn*-complexes. Parameters of the ^{1}H NMR spectra of (C_4H_7)Mn(CO)$_4$ are listed in Table 1.

A mixture of σ-crotylmanganese pentacarbonyls containing a small amount (19%) of *cis*-isomer, formed as a result of the interaction between NaMn(CO)$_5$ and crotyl chloride [2] during decarbonylation with irridium complex II under mild conditions, gives rise to π-crotylmanganese tetracarbonyls with approximately the same amount of the *anti*-isomer (18%). The ^{1}H NMR spectrum of the reaction product is presented in Fig. 1d.

The data obtained in the present study suggest that the σ—π-rearrangement of the crotyl ligand during decarbonylation under mild conditions occurs with the retention of its geometric configuration and point to the genetic relation-

TABLE 1

CHEMICAL SHIFTS AND SPIN—SPIN COUPLING CONSTANTS FOR $C_4H_7Mn(CO)_4$

		
H^a	3.95 *dt* $J_{ab} = J_{ae} = 7$ Hz $J_{ac} = 12$ Hz	4.00 *dt* $J_{ac} = J_{ad} = 12$ Hz $J_{ab} = 7$ Hz
H^b	2.44 *dd* $J_{bc} = 2$ Hz	1.99 *dd* $J_{bc} = 2$ Hz
H^c	1.72 *dd*	1.01 *dd*
H^d	0.91 *d* $J_{de} = 6$ Hz	2.23 *dq* $J_{de} = 6$ Hz
H^e	3.26 *dq*	1.32 *d*

ship between *cis*- and *trans*-structures of σ-crotyl ligands and *anti*- and *syn*-structures of π-allylic ligands.

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