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π-COMPLEXES AS LIGANDS IN TRANSITION METAL COMPOUNDS

VIII *. METALLOCENYL FULVENES AS SIX-ELECTRON LIGANDS IN CHROMIUM COMPLEXES **

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Summary

New binuclear heterometallic complexes, viz. 6-ferrocenyl-6-phenylfulvenetricarbonylchromion (I) and 6-cymantrenyl-6-phenylfulvenetricarbonylchromium (II), in which fulvenes act as six-electron ligands at the chromium atom, were synthesized.

It was found that under conditions suitable for coordination to $Cr(CO)_6$ the dimer of cymantrenylphenylfulvene can be transformed into a monomer; under ordinary conditions, however, the monomer dimerizes readily.

Introduction

A search for π-complexes of transition metals able to play a rôle as a ligand at another metal atom attracts ever-increasing interest since such compounds can be used in synthesis of new binuclear systems with unexpected properties.

Continuing our research in this field we synthesized metallocenylfulvenes, 6-ferrocenyl-6-phenylfulvene (III) and 6-cymantrenyl-6-phenylfulvene (IV) [1] (under ordinary conditions the latter forms a dimer (V)) and coordinated these π-complexes with chromium carbonyls.

In this paper we report the synthesis and physico-chemical properties of new heterometallic binuclear complexes, viz. 6-ferrocenyl-6-phenylfulvenetricarbonylchromium (I) and 6-cymantrenyl-6-phenylfulvenetricarbonylchromium (II), in which metallocenylfulvenes III and IV act as six-electron ligands at the chromium atom.

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* For part VII see ref. 7.

** Dedicated to Professor Oleg Reutov on occasion of his 65 birthday on September 5th, 1985.

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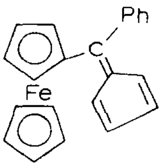
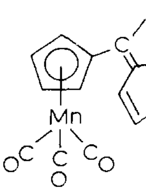


(III)



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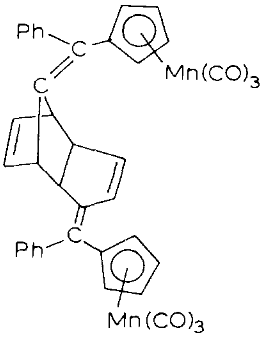


(V)

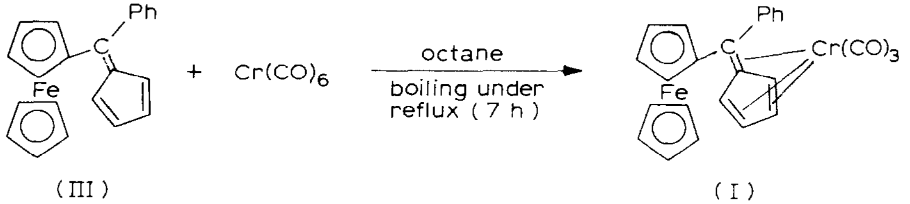
Results and discussion

Coordination of pentafulvenes with transition metals can follow different routes involving (i) isolated double bonds, (ii) two double bonds, (iii) tree double bonds, and (iv) more complex ways [2].

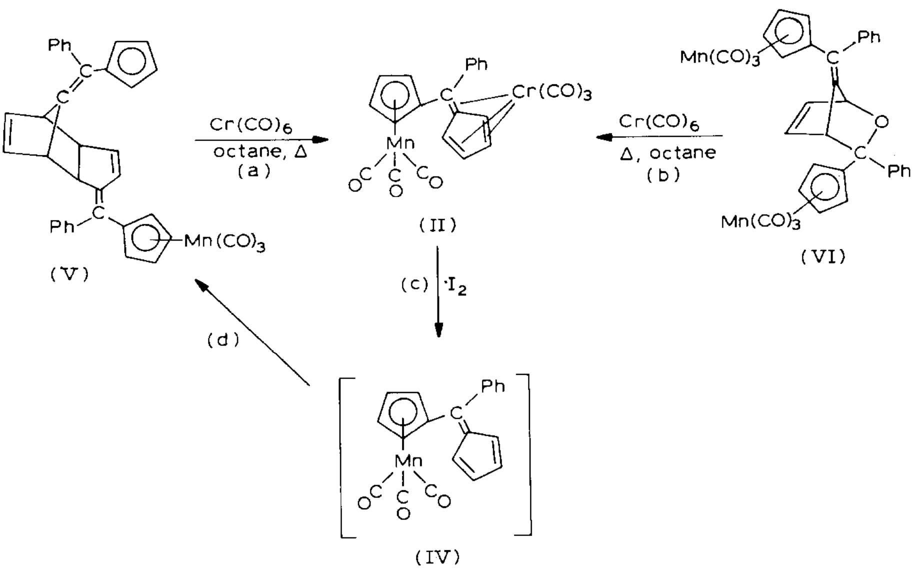
Complexes of pentafulvenes with chromium carbonyl are a typical example of six-electron coordination. In such compounds coordination of the chromium atom is realized via a butadiene system of a cyclopentadienyl ring and an exocyclic double bond [3,4]. On the basis of the above data we tried to carry out coordination of metallocenylfulvenes with chromium carbonyl in boiling octane, using the method of King and co-workers [5]. Under such conditions the reaction with the fulvene III yielded I (about 60%; Scheme 1).

It was shown earlier [1], that, in contrast with ferrocenylfulvene (III), its cymantrenyl analogue IV dimerizes readily to give the dimer V. Assuming that dimerization is a reversible process, we used dimer V in the reaction with $Cr(CO)_6$. In fact, it turned out that under such conditions II was formed in 40% yield (Scheme 2, a).

It is noteworthy that the binuclear complex II can also be obtained when in reaction with Cr $(CO)_6$ an addition product of cymantrenyl phenyl ketone to fulvene IV is used (compound VI, Scheme 2,b). The formation of complex II from the products of cycloaddition of fulvene IV (dimer V and compound VI) indicates the ability of these compounds to produce, under certain conditions, monomeric fulvene IV.



SCHEME 1



SCHEME 2

A reverse reaction, transformation of fulvene IV into dimer V, takes place when complex II interacts with iodine. In this case the chromium–π-bond is readily cleaved with formation of a free ligand [6]. The splitting of II gave dimer V (about 55%) rather than monomer IV (Scheme 2, c,d).

New heterometallic binuclear complexes I and II are coloured crystalline compounds readily soluble in polar solvents (acetone, THF), and less soluble in benzene and saturated hydrocarbons; in the solid state they are stable in air. The compounds are characterized by IR, ^{1}H NMR, and mass spectra.

In the IR spectrum of complex I (in CH_2Cl_2) are two absorption bands at 1900 and 1975 cm^{-1} in the carbonyl frequencies region typical for $Cr(CO)_3$ groups. In this region the IR spectrum of complex II shows four bands at 1905, 1940, 1985, and 2025 cm^{-1} (the bands at 1905 and 1940 cm^{-1} are poorly resolved).

We assign the bands at 1940 and 2025 cm^{-1} to the vibrations of the CO groups in the $Mn(CO)_3$ fragment since for the initial fulvene these bands are similar (ν(CO) of fulvene V 1945 and 2030 cm^{-1}) and the bands at 1905 and 1985 cm^{-1} are similar to the vibrations of the CO groups in the $Cr(CO)_3$ fragment. Hence, coordination of fulvene IV with a $Cr(CO)_3$ group does not result in a noticeable change in the stretching band position of the terminal CO groups at the manganese atom.

The ^{1}H NMR spectra of compounds I and II clearly reveal the upfield shift of signals for protons of the pentafulvene ring ($\Delta\delta \sim 1$–1.4 ppm) *. These data show that in the binuclear complexes I and II the pentafulvene ring is coordinated with the $Cr(CO)_3$ group.

The PMR spectral data of I and II are given in Table 1. For comparison the values of chemical shifts for fulvenes III and IV and for dimer V are also listed.

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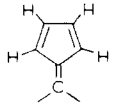
* It is interesting that chemical shifts of the protons of phenyl and cyclopentadienyl fragments of I–III change little upon coordination with the $Cr(CO)_3$ group ($\Delta\delta$(I–III) ~ 0.05–0.15 ppm).

TABLE 1

CHEMICAL SHIFTS IN THE ^{1}H NMR SPECTRA OF COMPLEXES I–IV IN (CD$_3$)CO (δ, ppm from TMS)

Compound	Unsubstituted C_5H_5	Substituted C_5H_5		C_6H_5
I	4.12(s,5H)	4.37(br.s.IH) 4.64(br.s.IH)	4.75(m,1H) 5.52(m,2H) 5.77(m,IH)	7.57(m5H)
III	4.17(s,5H)	4.51(t,2H) 4.54(t,2H)	5.78(dt,IH) 6.34(dt,IH) 6.61(dt,IH) 7.10(dt,IH)	7.44(m,5H)
IV	–	5.07(t,2H) 5.27(t,2H)	5.69(ddd,IH) 6.39(ddd,IH) 6.57(ddd,IH) 6.89(ddd,IH)	7.37(m,5H)
II	–	5.39(m,2H) 5.55(m,2H)	4.60(m,1H) 4.88(m,IH) 5.06(m,IH) 5.77(m,IH)	7.41(m,5H)

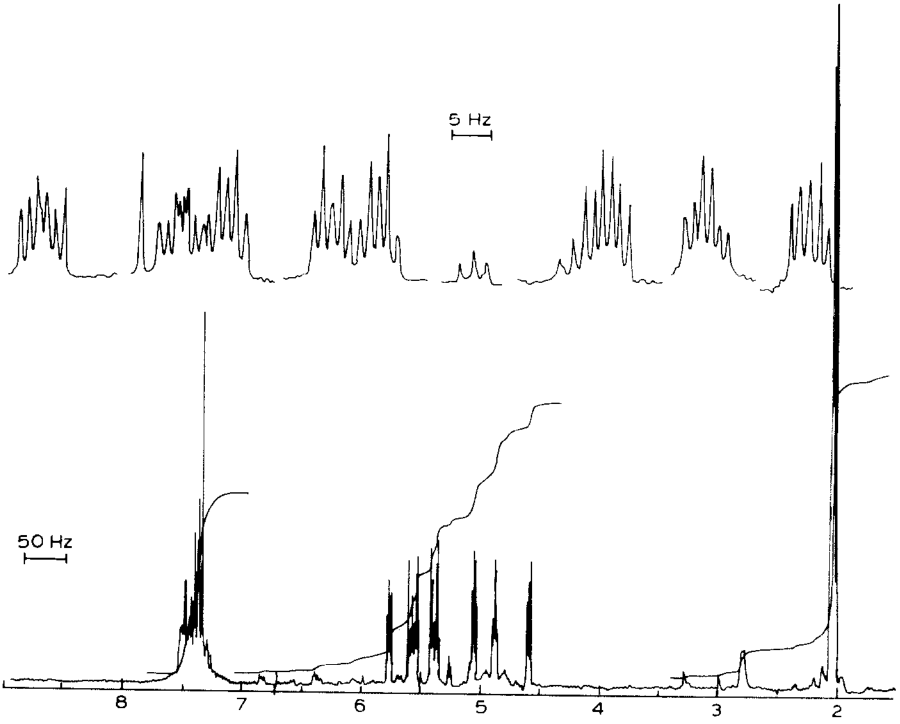


Fig. 1. ^{1}H NMR spectrum of II in (CD$_3$)$_2$CO (δ, ppm from TMS).

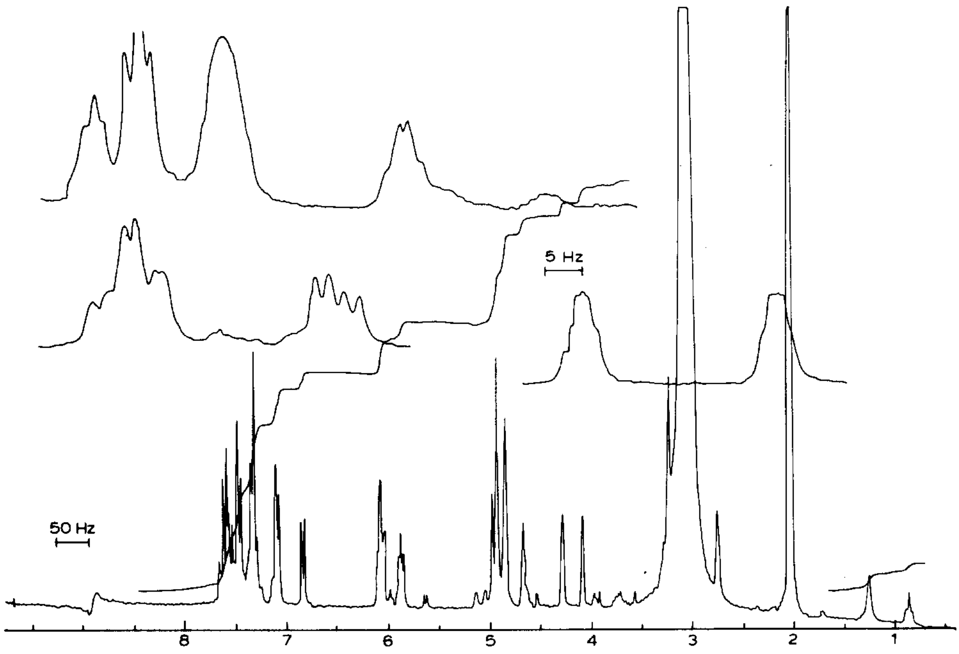


Fig. 2. ^1H NMR spectrum of V in $(CD_3)_2CO$ (δ, ppm from TMS).

Figures 1 and 2 present the ^1H NMR spectra of II and V.

The mass spectra of complexes I and II (Table 2) reveal the peaks of the molecular ions P^+ with masses 474 and 492, respectively, and the fragment ions $P^+ - (CO)_n$, where $n = 1, 2, 3$ for I and $n = 1, 2, 3, 4, 5, 6$ for II formed in successive decarbonylation of molecular ions. The spectra also display the peaks of the ions corresponding to the masses of the initial fulvenes III and IV formed when $Cr(CO)_3$ groups are cleaved from I and II.

TABLE 2

MASS SPECTRA OF BINUCLEAR COMPLEXES I AND II

Compound I		Compound II	
Ion	m/e	Ion	m/e
P^+	474	P^+	492
$P^+ - 3CO$	390	$P^+ - 3CO$	408
$P^+ - 3CO - C$	338	$P^+ - 4CO$	380
$P^+ - 3CO - Cr - Cp$	273	$P^+ - 5CO$	352
$P^+ - 3CO - Cr - Cp - Fe$	217	$P^+ - 6CO$	324
$P^+ - 3CO - Cr - Cp - Fe - C_5H_4$	153	$P^+ - 3CO - Cr$	356
Ph^+	77	$P^+ - 6CO - Mn$	269
Cp^+	65	$P^+ - 6CO - Mn\text{-}Cr$	217
Fe^+	56	$P^+ - 6CO - Mn - Cr - C_5H_4$	153
Cr^+	52	$P^+ - 6CO - Mn - Ph - C_5H_4$	117
		Ph^+	77
		Mn^+	55
		Cr^+	52

It is noteworthy that the mass spectrometric data indicated unambiguously that in complex II, obtained either from dimer V or from compound VI, monomeric cymantrenylphenylfulvene IV is a six-electron ligand coordinated to the chromium atom.

Thus, the set of spectral data (IR, ^{1}H NMR, and mass) obtained for complexes I and II shows that metallocenylfulvenes can act as six-electron ligands in coordination with transition metals. This property of metallocenylfulvenes opens a possibility for preparation of new heterometallic binuclear complexes.

Experimental

The ^{1}H NMR spectra were recorded on a Bruker WP-200 SU spectrometer with a working frequency of 200 MHz. The scan was chosen for ratios not more than 0.2 Hz per channel. The IR spectra were recorded on an UR-20 spectrometer and mass spectra on an AEI MS-30/DS-50 device. All operations for synthesis and isolation of the products were performed under argon. Initial III, IV, and V were synthesized by the procedure described earlier [1].

Synthesis of I

A mixture of ferrocenylfulvene III (0.3 g; 0.8 mmol) and $Cr(CO)_6$ (0.3 g; 1.4 mmol) in octane (50 ml) was boiled under reflux for 7 h. A dark violet percipitate separated out which was chromatographed on a silica gel column. The mixture was eluted with a hexane/benzene system (5/1) to remove initial $Cr(CO)_6$, and then with benzene. Benzene was distilled and the residue recrystallized from hexane. Complex I, m.p. 130°C, was obtained in 51% yield (0.25 g). The IR spectrum in CH_2Cl_2 (ν(CO), cm^{-1}) reveals bands at 1900 and 1975. The data of ^{1}H NMR and mass spectra are given in Tables 1 and 2.

Synthesis of II

Complex II was obtained similarly to I. (a) 54% (0.07 g) of II was prepared from V (0.1 g; 0.14 mmol) and $Cr(CO)_6$ (0.1 g; 0.45 mmol) after chromatography on an Al_2O_3 column (hexane/benzene 5/1) and recrystallization from hexane. (b) 54% (0.04 g) of II was prepared from IV (0.1 g; 0.15 mmol) and $Cr(CO)_6$ (0.1 g; 0.45 mmol); II, m.p. 130°C. The IR spectrum in CH_2Cl_2 (ν(CO), cm^{-1}) reveals bands at 1905, 1940, 1985, and 2025. The data of ^{1}H NMR and mass spectra are given in Tables 1 and 2.

Splitting the chromium–π-ligand bond in complex II [6]

Molecular iodine (0.1 g; 0.39 mmol) was added to the solution containing complex II (0.1 g; 0.20 mmol) in 20 ml of absolute ether. After 3 h the reaction mixture was treated with an aqueous solution of sodium bisulphite to remove iodine. The organic layer was dried over magnesium sulphate. Compound V (m.p. 138–139°C) was obtained in 43% yield (0.06 g); no lowering of melting point was observed for the mixture of compound V with the initial dimer of cymantrenylphenylfulvene. The IR and R_f data were identical to those for V.

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