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η^5-6-*N*-DIMETHYLAMINO-2,3-BENZOFULVENCHROMIUM TRICARBONYL

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Summary

η^5-6-*N*-Dimethylamino-2,3-benzofulvenchromium tricarbonyl has been synthesized. The rotational isomerism of the complex and the parent fulvene and the kinetic parameters of the barriers to rotation about the $C(6)\overset{\cdots}{-}N$ bond have been determined by dynamic ^1H NMR spectroscopy. π-Coordination increases the free energy of the rotational barrier, i.e. increases the degree of double-bond character between the C(6) and N atoms and, hence, enhances the π-electron polarization of the exocyclic double bond. Electron impact mass spectra of the complex and the parent fulvene have been investigated.

Introduction

Donating six π-electrons to coordinate to the metal atom, cyclopentadienylides and pentafulvenes easily form π-complexes with transition metal carbonyls. π-Complexes of cyclopentadienylides with S, P and As atoms, π-complexes of 6-dimethylamino- and 6,6-bis(dimethylamino)fulvenes, and also π-complexes of pentafulvenes bearing alkyl and aryl substituents at the exocyclic carbon have been described [1]. Up to now, however, no information is available on metal carbonyl π-complexes of pentafulvenes containing condensed bicyclic systems, the fulvene part of which serve as a 6π-electron donor.

To investigate the effect of π-coordination on the structure and reactivity of pentafulvenes [2] serving as π-ligands, the reaction of 6-*N*-dimethylamino-2,3-benzofulvene (I) with chromium carbonyl has been studied. The paper describes the synthesis, structure and some properties of the resulting η^5-6-dimethylamino-2,3-benzofulvenchromium tricarbonyl (II).

Results and discussion

η^5-6-*N*-Dimethylamino-2,3-benzofulvenchromium tricarbonyl (II) was prepared from 6-*N*-dimethylamino-2,3-benzofulvene (I) and the acetonitrile complex of chro-

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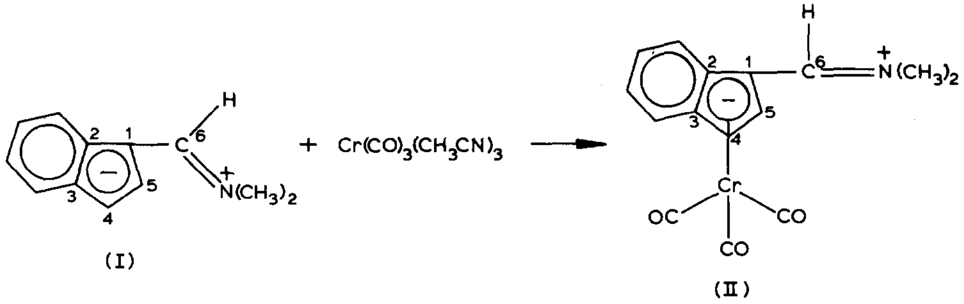
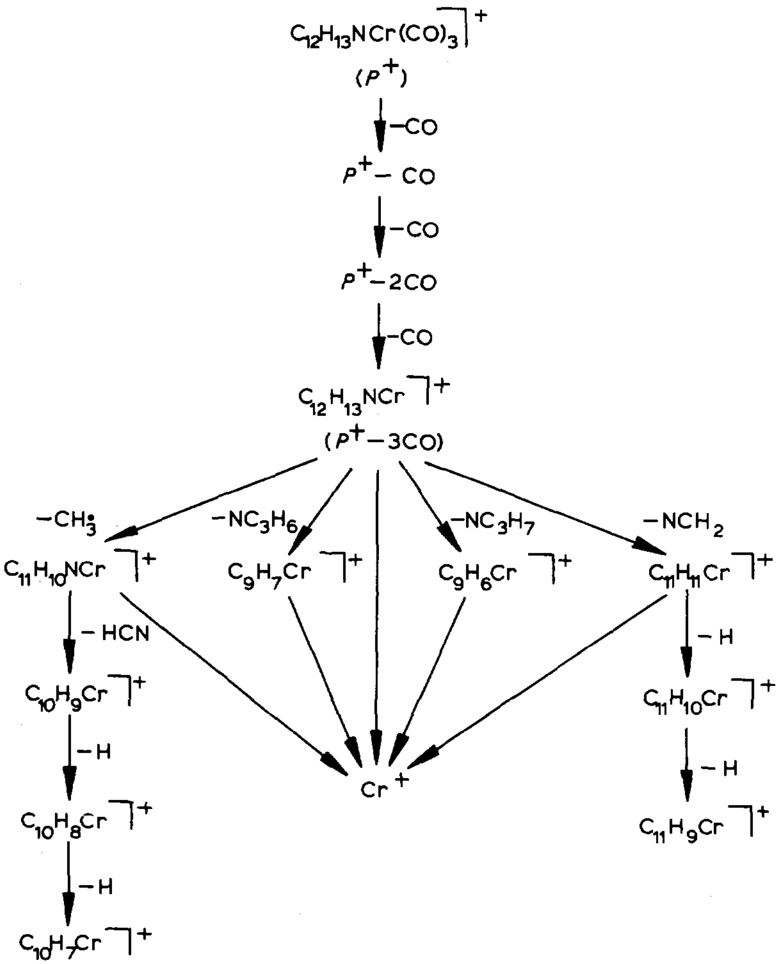
mium carbonyl. The reaction proceeds in diglyme at room temperature. Complex II was isolated as a dark ruby, finely crystalline powder. Complex II is only slightly



SCHEME 1
Main fragmentation pathways of II under electron impact.



stable in the air, is moderately soluble in polar solvents (ether, tetrahydrofuran, diglyme, acetone, nitromethane, dimethylformamide), and is insoluble in nonpolar and hydrocarbon solvents.

The IR-spectrum of II contains two intense CO-group absorptions at 1920 and 1800 cm^{-1} and an intense band at 1628 cm^{-1} characteristic of the C=N bond.

The mass spectrum of II shows the molecular ion (P^+) peak. Decomposition of the ion is accompanied by successive decarbonylations to produce the most intense peak for the ion $P^+ - 3CO$ (Scheme 1). Further fragmentation of the ion proceeds with cleavage of the chromium–fulvene bond and partial decomposition of the π-bonded ligand. As follows from the Scheme, the main fragmentation pathways of the molecular ion of II involve cleavage of metal–CO bonds. The total intensity of the resulting chromium-containing ions is ca. 85% of that of all metal-containing ions produced in the complex fragmentation under electron impact. A characteristic of the η^5-6-*N*-dimethylamino-2,3-benzofulvenchromium tricarbonyl (II) fragmentation is the intense decomposition of π-bonded fulvene with the elimination of methyl radical and a number of nitrogen-containing particles (Scheme 1). The fragmentation routes of the ion ($P^+ - 3CO$) are completely analogous to the dissociation of uncoordinated fulvene I, although the fragmentation of I proceeds via some additional decomposition pathways (Table 1). It should be noted that this pattern of behavior is not characteristic of the substituted benzenechromium tricarbonyls under electron impact: as a rule, the free and π-bonded ligands fragment differently [3].

Figure 1 shows the ^1H NMR spectra of the parent fulvene I and its chromium tricarbonyl complex II in acetone-d_6 at −25°C. The spectrum of II shows signals at

TABLE 1

RELATIVE INTENSITIES OF ION PEAKS IN THE MASS SPECTRUM OF η^5-6-*N*-DIMETHYLAMINO-2,3-BENZOFULVENCHROMIUM TRICARBONYL (II) AND 6-*N*-DIMETHYLAMINO-2,3-BENZOFULVENE (I) [a]

Complex II		Fulvene I	
Ion	Relative intensity (%)	Ion [b]	Relative intensity (%)
P^+	14.1	P^+	100.0
$P^+ - CO$	0.5	$P^+ - H$	37.1
$P^+ - 2CO$	26.0	$P^+ - 2H$	1.1
$P^+ - 3CO$	100.0	$P^+ - 3H$	2.2
$C_{11}H_{10}NCr^+$	11.6	$C_{11}H_{10}N^+$	9.7
$C_{11}H_{11}Cr^+$	1.1	$C_{11}H_{11}{}^+$	6.3
$C_{11}H_{10}Cr^+$	0.5	$C_{11}H_{10}{}^+$	3.4
$C_{11}H_9Cr^+$	1.4	$C_{11}H_9{}^+$	10.3
$C_{10}H_9Cr^+$	14.9	$C_{10}H_9{}^+$	36.6
$C_{10}H_8Cr^+$	6.0	$C_{10}H_8{}^+$	89.1
$C_{10}H_7Cr^+$	3.9	$C_{10}H_7{}^+$	22.8
$C_9H_7Cr^+$	4.9	$C_9H_7{}^+$	5.1
$C_9H_6Cr^+$	3.6	$C_9H_6{}^+$	3.4
Cr^+	86.1		

[a] Ion composition was determined by measuring exact masses. [b] Other ions: $C_{12}H_{11}{}^+$ (2.8), $C_{11}H_9N^+$ (8.0), $C_{11}H_8N^+$ (10.8), $C_{10}H_{10}N^+$ (10.3), $C_{10}H_9N^+$ (2.8), $C_{10}H_{10}{}^+$ (16.0), $C_9H_8N^+$ (5.5), $C_2H_4N^+$ (83.4).

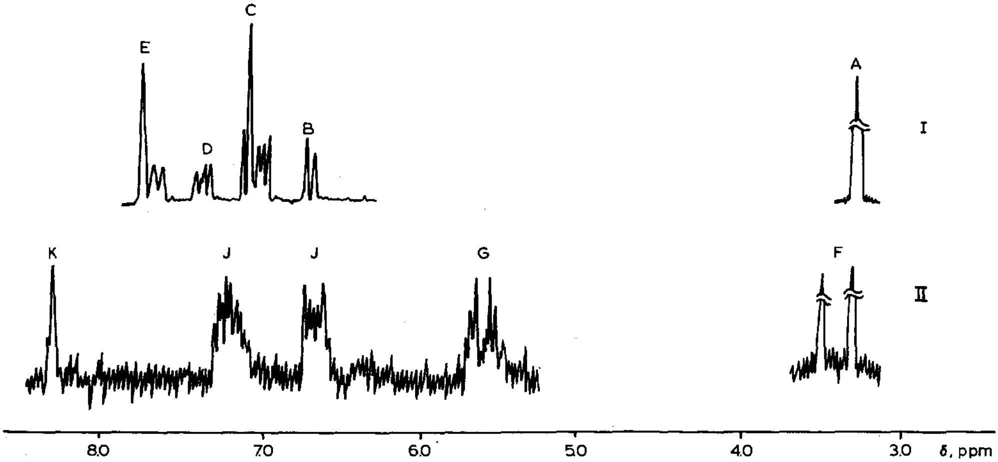


Fig. 1. ^{1}H NMR spectra of 6-*N*-dimethylamino-2,3-benzofulvene (I) and η^5-6-*N*-dimethylamino-2,3-benzofulvenchromium tricarbonyl (II) in acetone-d_6 at −25°C. I: A, $N(CH_3)_2$ group protons, 6H; B, Cp ring proton, 1H; C, Cp and benzene ring protons, 3H; D, benzene proton, 1H; E H(6) and benzene proton, 2H. II: F, $N(CH_3)_2$ group protons, 3H + 3H; G, Cp ring protons, 1H + 1H; J, benzene protons, 2H + 2H; K, H(6), 1H.

δ 8.27 ppm (singlet, C(6)–H); 7.19 and 6.66 ppm (multiplets, benzene protons); 5.64 and 5.53 ppm (doublets, Cp-H); and 3.50 and 3.28 ppm (singlets, $N(CH_3)_2$ group) with the respective integral intensity ratio 1/2/2/1/1/3/3. The parent fulvene I shows signals at δ 7.72 ppm (singlet, C(6)–H); 7.68, 7.36 and 6.93 ppm (multiplets, benzene protons); 7.07 and 6.69 ppm (doublets, Cp-H); and 3.26 ppm singlet, $N(CH_3)_2$ group). ^{1}H chemical shifts for the Cp rings of I and II are given based on the analysis of the AB pattern in the AX approximation; relative intensities of the peaks being 1/1.89/1.89/1 and 1/1.35/1.35/1, respectively. The spin-spin coupling constants are equal to 3.4 and 5.1 Hz. The comparison of the ^{1}H NMR spectra of I and II shows that π-coordination of fulvene with chromium causes an upfield shift in the signals of Cp-ring hydrogen atoms of I (1.4 and 1.2 ppm), whereas signals from protons on the exocyclic carbon and from $N(CH_3)_2$-group protons are shifted 0.6 and 0.1 ppm downfield, respectively. The coordination of I with the $Cr(CO)_3$ group changes also the pattern of the spectrum of fulvene benzene protons: the spectrum of the parent fulvene I displays two triplets and one multiplet, while the spectrum of complex II shows only two multiplets shifted upfield (ca. 0.3 ppm). This unambiguously demonstrates that fulvene coordinates to the $Cr(CO)_3$ group via the cyclopentadienyl ring. π-Coordination causes balancing of the electron density not only in the Cp ring but also probably in the fulvene benzene ring, as shown by the decrease in the Cp-protons spin-spin coupling constant (1.7 Hz) and changes in the nature of the benzene protons spectrum. The presence of two proton signals in the region of the $N(CH_3)_2$ group in the spectrum of II compared to one signal in the spectrum of the parent fulvene indicates that complexation increases the degree of double-bond character between the C(6) and N atoms. To determine the kinetic parameters for the barriers restricting the rotation about the $C(6)\underset{---}{\text{—}}N$ bond of the parent fulvene I and its chromium tricarbonyl complex II, the temperature dependence of the ^{1}H NMR spectra (in acetone-d_6) of these compounds was studied over

TABLE 2

KINETIC PARAMETERS OF BARRIERS TO ROTATION ABOUT THE C(6)$\underline{\cdots}$N BOND IN 6-*N*-DIMETHYLAMINOFULVENE (III), 6-*N*-DIMETHYLAMINO-2,3-BENZOFULVENE (I), η^5-6-*N*-DIMETHYLAMINO-2,3-BENZOFULVENCHROMIUM TRICARBONYL (II) AND 6-*N*-DIMETHYLAMINOFULVENTRICARBONYL-CHROMIUM (IV), -MOLYBDENUM (V) AND -TUNGSTEN (VI)

Compound	Temperature (°C)	$k_{rot.}$ (sec^{-1})	log A	E_{act} (kcal mol^{-1})	$\Delta H^{\neq}$, (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)	$\Delta G^{\neq}_{298}$, (kcal mol^{-1})
III	−28	1.2	12.6±0.8	13.9±0.2	13.3±0.2	−2.5±1.0	14.0±0.2
I	−25	222	9.8±1.6	8.4±0.4	7.9±0.4	−15.2±1.8	12.4±0.3
II	50	25.0	16.1±3.0	21.1±1.5	21.1±1.5	12.8±2.9	17.3±0.5
	42.5	13.9					
IV	52	3.2	–	–	–	–	17.9±0.2
V	42	14.5	18.7±4.1	25.3±0.7	24.7±0.7	25.0±2.0	17.3±0.4
VI	41	85.5	19.1±4.1	24.9±1.0	24.3±1.0	27.3±2.0	16.2±0.5

the temperature range −65 to 50°C. The kinetic parameters for the barriers restricting the rotation about the C(6)$\overset{\cdot\cdot}{-}$N bond were determined from a complete analysis of the shapes of the lines of the proton signals of the methyl groups bounded to the nitrogen atom [4]. The experimental data are shown in Table 2 in comparison to the kinetic parameters for the rotation about the C(6)$\overset{\cdot\cdot}{-}$N bond of unsubstituted 6-dimethylaminofulvene (III) and its π-complexes with carbonyls of chromium, molybdenum, and tungsten (IV–VI) [2]. As follows from the analysis of these data, π-coordination of I with the $Cr(CO)_3$ group as with the unsubstituted fulvene III, decreases the rate of rotation about the C(6)$\overset{\cdot\cdot}{-}$N bond. This is brought about by an increase in the degree of double-bond character between the C(6) and N atoms in the parent ligand, i.e. by an enhancement of the π-electron polarization of the exocyclic double bond. The free energy for the rotational barrier and, hence, the polarity of the fulvene ligand strongly depend on the nature of the substituents on the Cp ring: the presence of the condensed benzene ring in the fulvene fragment of I and II substantially lowers the barrier for rotation about the C(6)$\overset{\cdot\cdot}{-}$N bond as compared to unsubstituted fulvene III and complex IV, respectively. The comparison of $k_{\text{rot.}}$ of complexes II, IV–VI shows that the rate of rotation about this bond in complex II practically equals that in the complex of unsubstituted fulvene III with molybdenum carbonyl (V), which is indicative of a nearly equal degree of the π-electron polarization of the exocyclic double bond in these compounds.

An attempt to establish the dependence of the kinetic parameters for the rotation about the C(6)$\overset{\cdot\cdot}{-}$N bond on the nature of the solvent was unsuccessful since complex II turned out to be unstable in such polar solvents as nitromethane,

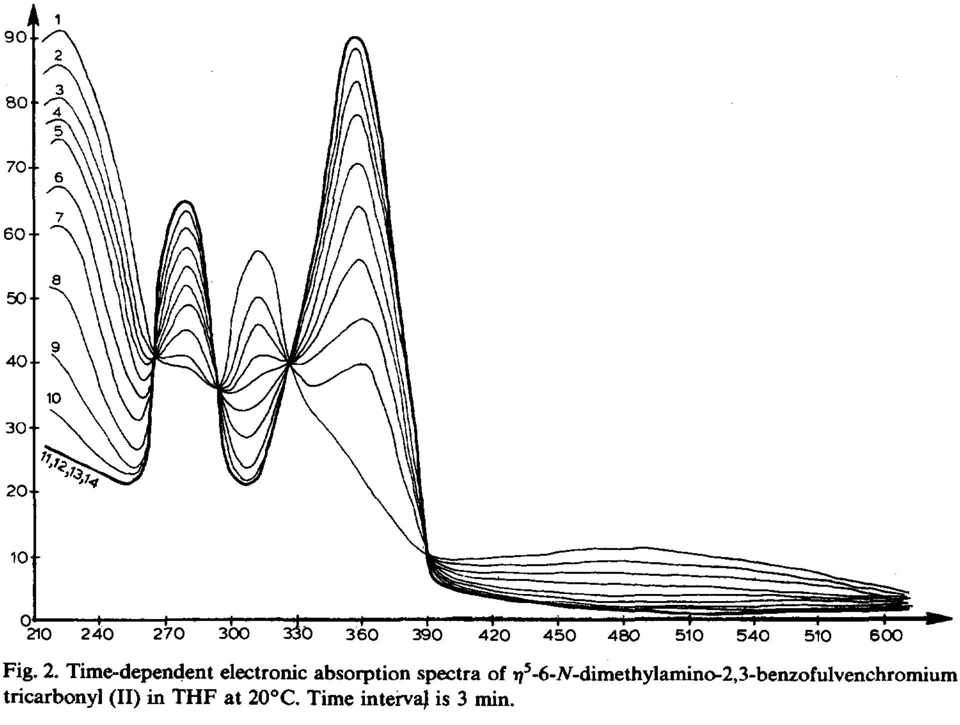


Fig. 2. Time-dependent electronic absorption spectra of η^5-6-N-dimethylamino-2,3-benzofulvenchromium tricarbonyl (II) in THF at 20°C. Time interval is 3 min.

tetrahydrofuran and dimethylformamide even at room temperature. As ^1H NMR spectroscopy shows, the complex decomposes to produce the initial fulvene I. This was confirmed by the data from electronic absorption spectra (EAS) of I and II taken in THF solution. Figure 2 shows the changes in the EAS of II in time. The spectrum of the initial complex contains absorption bands at λ_{max} 220 nm (log $\varepsilon = 4.77$), 314 nm (log $\varepsilon = 4.38$), and 480 nm (log $\varepsilon = 3.68$). The intensities of the bands decreases with time and new bands appear at λ_{max} 278 and 358 nm, the intensity of which increases synchronously with a decrease in that of the complex absorption bands: as a result, four isobestic points appear at 257, 286, 328 and 390 nm. The new absorption bands are characteristic of the initial fulvene I (λ_{max} 220 nm, log $\varepsilon = 4.65$; 278 nm, log $\varepsilon = 4.34$; and 358 nm, log $\varepsilon = 4.49$).

Within the temperature range −65 to 50°C, ^1H NMR spectra of II taken in acetone show no changes indicative of the metallotropic rearrangement of the complex by the type of reversible isomerization of the $\eta^6 \rightleftarrows \eta^5$-fluorenylchromium tricarbonyl anions or the corresponding indenyl analogs [5].

Experimental

IR spectra were recorded on a Zeiss UR-20 spectrometer, EA-spectra were run on a Hitachi EPS-3T instrument, and ^1H NMR spectra were taken on a RYa 2309 spectrometer at 90 MHz (internal standard was TMS). The temperature was maintained accurately to ±0.5°C. The lifetimes τ of the rotamers of I and II were estimated by comparing the experimental and computed spectra of the $N(CH_3)_2$ indicator groups. The difference in the chemical shifts $\Delta\delta$ [$N(CH_3)_2$], used for calculating the spectra, was found by extrapolating the observed temperature dependences of the given parameters in the absence of transitions to the region of rapid exchange [4]. The spectra of the $N(CH_3)_2$ groups were computed on a PDP12 computer using a program composed in Arnold's formalism [6]. The solutions were prepared and ampoules filled under dry argon.

Mass spectra were recorded on an MS-30 spectrometer equipped with a DS-50 data processing system. The temperature of the direct inlet probe was 200°C (II) and 60°C (I), temperature of ionization chamber: 250°C, emission current: 100 μA, ionizing voltage: 70 V.

6-Dimethylamino-2,3-benzofulvene (I) was obtained in a 65% yield by a method analogous to that for preparing 6-dimethylaminofulvene [7], m.p. 90–91°C (literature data 90–91°C [8]).

η^5-6-N-Dimethylamino-2,3-benzofulvenchromium tricarbonyl (II)

A two-necked flask was charged at room temperature under argon with a solution of $Cr(CO)_3(CH_3CN)_3$, prepared from 2.2 g (0.01 mol) chromium carbonyl and 85.5 g (110 ml, 2.1 mol) acetonitrile, in 30 ml diglyme and a solution of 1.2 g (0.007 mol) of I in 10 ml dry diglyme was added at room temperature. The mixture was left overnight. Then, 100 ml of dry n-hexane were added and after two hours the precipitate was filtered off, washed on the filter with 100 ml of n-hexane, and dried in vacuum at 50°C (1 mmHg); yield 0.4 g (18.6%), dec. p. 120°C.

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