Journal of Organometallic Chemistry, 248 (1983) 161–169
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

STUDY OF THE PHOTOLYSIS OF ARENETRICARBONYLCHROMIUM COMPLEXES BY IR, UV AND ^{1}H AND ^{13}C NMR SPECTROSCOPY

E.A. DOMOGATSKAYA, V.N. SETKINA*, N.K. BARANETSKAYA, V.N. TREMBOVLER, B.M. YAVORSKII, A.Ya. SHTEINSHNEIDER and P.V. PETROVSKII

A.N. Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Moscow (U.S.S.R.)

(Received January 11th, 1983)

Summary

The mechanism of photolysis of arenetricarbonylchromium complexes is investigated by a number of spectral techniques. Experimental data are obtained in favour of the formation during the $ArCr(CO)_3$ photolysis of a multicenter complex, photodecay of which leads to the formation of chromium hexacarbonyl. A mechanism for the photolysis of arenetricarbonylchromium complexes is proposed.

The present study is one of a series [1–3] on the photolysis of the $ArM(CO)_3$ (M = Cr, Mo, W) complexes. Previously, a number of features of the process was established by UV spectroscopy, and it was also shown that Ar and $M(CO)_6$ are the photodecomposition products for the complexes under study. This article deals with the study of the mechanism of the photodecomposition reaction of the arenetricarbonylchromium complexes by the IR, UV and ^{1}H and ^{13}C NMR spectroscopic methods.

Results and discussion

The IR study of the $ArCr(CO)_3$ photolysis was carried out in the spectral region from 1600–2100 cm^{-1}. In Fig. 1(1) the IR spectrum of $C_6H_6Cr(CO)_3$ in cyclohexane is presented. According to the local C_{3v} symmetry of the tricarbonylchromium fragment, the high-frequency band $\nu = 1985$ cm^{-1} is assigned to a symmetric A_1 vibration, whereas the more intense one with $\nu = 1915$ cm^{-1} is assigned to the two-fold degenerate E_1 [4]. The bands of low intensity, denoted in Fig. 1(1) by asterisks, are assigned to the bands of the ^{13}CO group vibrations of the benzenetricarbonylchromium complex; the natural abundance of the latter bands amounts to about 1%. It has been established [4–6] that the ^{13}CO vibrations' bands are shifted to the low-frequency region with respect to the ^{12}CO group bands in the benzenetricarbonylchromium complex.

0022-328X/83/$03.00

As the photodecomposition of the initial compound proceeds (which was followed the decrease in the optical density of bands with $\nu = 1915$ and $1985\ \mathrm{cm}^{-1}$), there appears a band with $\nu = 1794\ \mathrm{cm}^{-1}$ (Fig. 1(1,2)). We assign this band to the complex (containing bridging C=O groups), which is formed under photolysis of the initial compound. The vibrational bands of such C=O groups are shifted to the low-frequency region as compared with the terminal CO groups in the complex [7,8].

One may assume that the complex formed with bridging C=O groups is a multicenter one. Thus, it was previously assumed [9] (although not confirmed by experiment) that elimination of Ar from $ArCr(CO)_3$ takes place not in a direct way but rather in a more complicated manner, namely, with a simultaneous formation of a long-lived multicenter complex, photodecomposition of which may lead to the formation of $Cr(CO)_6$. It is of interest that in the course of thermal reaction of the $C_6H_6Cr(CO)_2NCCH_3$ complex in benzene the formation of a dimer complex was established [10], chromium atoms of the latter being bonded by the bridging C=O groups.

As the presumed multicenter complex (with bridging C=O groups) accumulates, the formation of chromium hexacarbonyl is seen. The increase in the band at $1985\ \mathrm{cm}^{-1}$ intensity (Fig. 1(3–5)) is accounted for by the coincidence of the frequency of the symmetric A_1 vibration of CO groups in $C_6H_6Cr(CO)_3$ with that of the three-fold degenerate symmetric T_{1u} vibration of CO groups in $Cr(CO)_6$. Fig. 1(6) shows an instant of the complete photodecomposition for both the initial compound

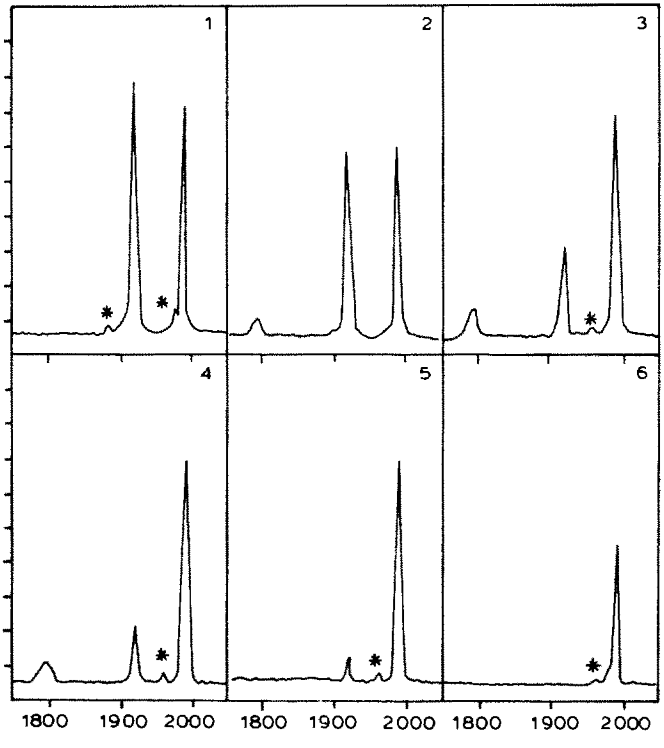


Fig. 1. The IR spectra of $C_6H_6Cr(CO)_3$ in cyclohexane during its photodecomposition ($c = 4 \times 10^{-3} M$; $d = 0.01$ cm). Times of irradiation (min): 1(0), 2(2), 3(11), 4(17), 5(27), 6(43).

and the intermediate multicenter complex, as well as the presence of $Cr(CO)_6$ (ν 1985 cm^{-1}), which is formed under photolysis of $C_6H_6Cr(CO)_3$ from the intermediate multicenter complex.

Substitution of the C_6H_6 ligand by biphenyl (BPh) in $C_6H_6Cr(CO)_3$ allows one to clarify some features of the $ArCr(CO)_3$ photolysis (Fig. 2). In the region of the bridging C=O group vibrations there appear two bands (Fig. 2(2)) at $\nu = 1741$ and 1791 cm^{-1}. The bands at 1914 and 1979 cm^{-1} are related to the valent CO vibrations of the $BPhCr(CO)_3$ complex, whereas the band at 1985 cm^{-1} is due to $Cr(CO)_6$ formed. The variation of the absorption in the region of the bridging C=O groups against the type of Ar in the initial $ArCr(CO)_3$ indicates that Ar enters into the intermediate multicenter complex with bridging C=O groups.

Significant variations with increasing irradiation time of the $C_6H_6Cr(CO)_3$ solution are observed in the ^1H and ^{13}C NMR spectra. In fact, in the ^1H NMR spectrum of the irradiated $C_6H_6Cr(CO)_3$ solution (in which the multicenter chromium complex has been formed according to the IR data), along with the sharp singlet signal of coordinated benzene ($\delta = 4.42$ ppm) there is observed an additional sharp singlet shifted into the low-field region by 0.06 ppm (Fig. 3). We note that this signal is not seen in the ^1H NMR spectrum of the irradiated $C_6H_6Cr(CO)_3$ solution, in the IR spectra of which the vibration band in the region of 1974 cm^{-1} is missing.

Increase in the integrated intensity of the uncoordinated benzene signal ($\delta = 7.24$ ppm) indicates the formation of the multicenter complex occurring with arene separation.

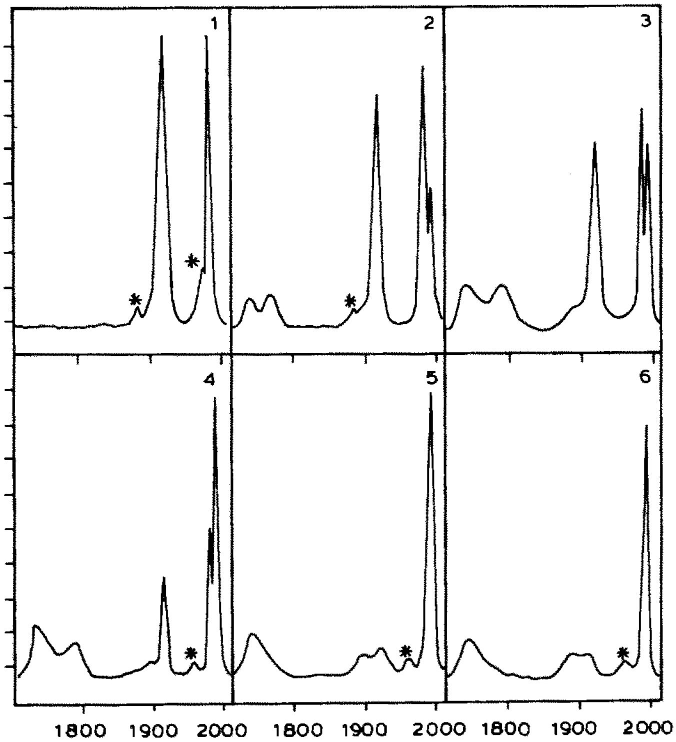


Fig. 2. The IR spectra of $(C_6H_5)_2Cr(CO)_3$ in cyclohexane during its photodecomposition ($c = 8 \times 10^{-3}M$; $d = 0.01$ cm). Times of irradiation (min): 1(0), 2(3), 3(7), 4(15), 5(35), 6(55).

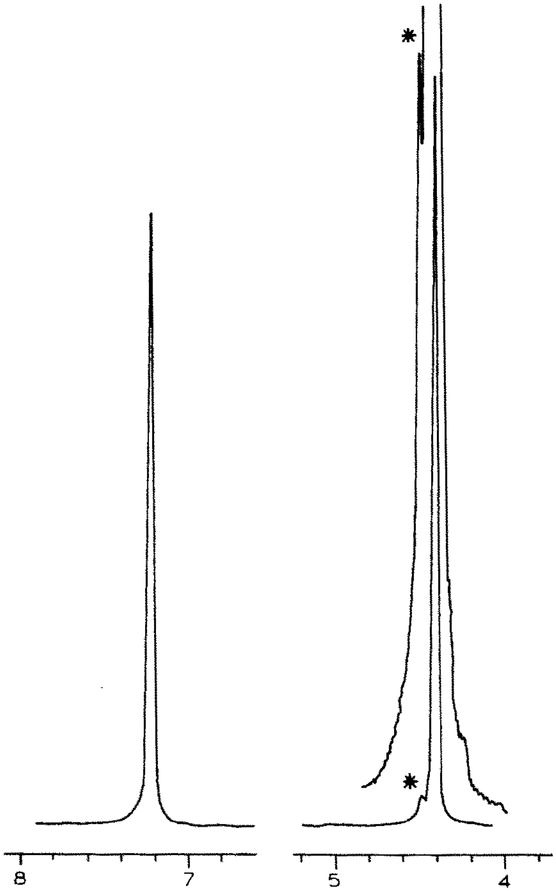


Fig. 3. The ^1H NMR spectrum of the irradiated $C_6H_6Cr(CO)_3$ in C_6D_6.

In the ^{13}C-{^1H} NMR spectrum of the irradiated $C_6H_6Cr(CO)_3$ solution besides the two signals (Fig. 4(3,4), $\delta = 92.50$ and 233.82 ppm) corresponding to carbon nuclei of coordinated benzene and the CO groups (which are directly bonded to the metal atom of the initial complex), there appear two signals in the region characteristic of coordinated arene (Fig. 4(2), $\delta = 92.35$ and 92.31 ppm), as well as at least four signals in the region of the CO groups of the complex (Fig. 4(1), $\delta = 233.84$; 233.83; 233.61; 233.51 ppm).

Occurrence of the new signals in the ^1H and ^{13}C-{^1H} NMR spectra in the region corresponding to coordinated benzene, and the shift of the latter to high field with respect to the corresponding signal of initial $C_6H_6Cr(CO)_3$ seem to be related to a slight increase of the electron density on the carbon nuclei of the coordinated benzene in the multicenter complex formed, the chromium atoms of which are bonded by bridging C=O groups. It is known that terminal CO groups in $ArCr(CO)_3$ are strong π-acceptors [11]. As for the bridging CO group of the complex, the backdonation of electron density from the occupied *d* orbitals of the metal to the CO π^*-orbitals is absent due to the high energy of the π^*-orbital [7]. On this ground, for the multicenter complex, in which chromium atoms are bonded to Ar and, e.g., to

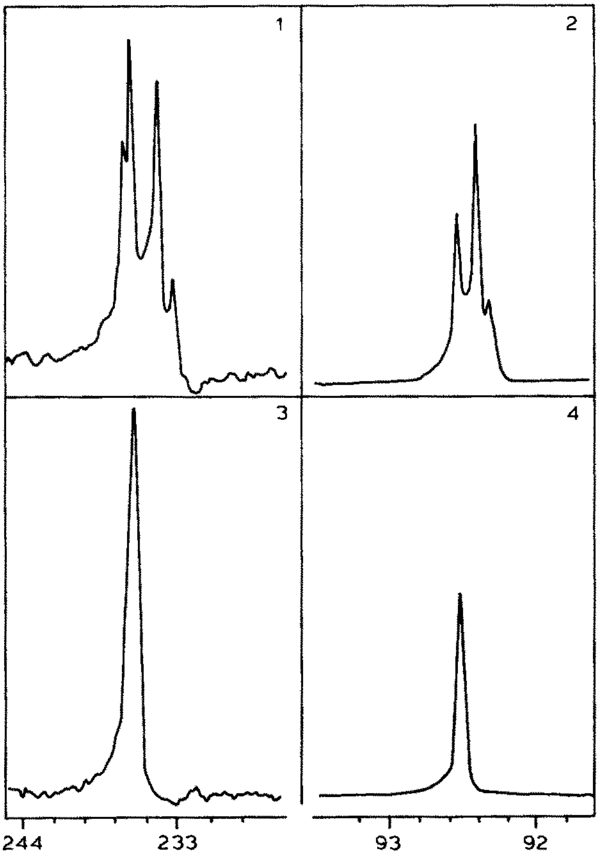
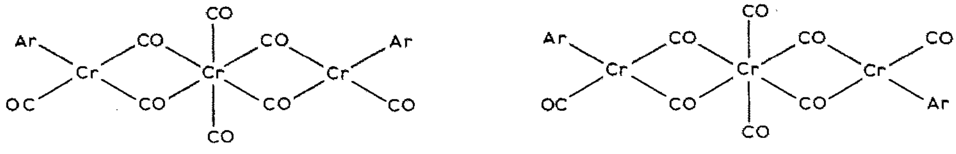


Fig. 4. The $^{13}C\text{-}\{^1H\}$ NMR spectrum of the unirradiated (3,4) and irradiated (1,2) $C_6H_6Cr(CO)_3$ in C_6D_6 in the region which is characteristic of the coordinated arene (2,4) and the CO groups(1,3) of the complex.

one of the terminal CO group and to two bridging CO groups, one would expect an increase in the electron density on the arene ligand, and, as a result, a shift of the corresponding signals to the high-field region. The presence of two signals in the region, which is typical of the coordinated benzene's carbon nuclei, may be attributed to the *cis* and *trans* forms of the intermediate multicenter complex (Scheme 1). Occurrence of four signals for the carbonyl carbons appears to result from the presence in the multicenter complex of bridging C=O groups, bonded to the metal atom, and of terminal CO groups, bonded to metal atoms which are either coordinated or un-coordinated to the arene (Scheme 1).

SCHEME 1



cis form

trans form

In analysing the electronic absorption spectra of the irradiated $BPhCr(CO)_3$ solution an increase in the optical density in the region $\lambda > 375$ nm was observed, which took place synchronously with increase in the intensities of bands assigned to the multicenter complex in the IR spectra. Figure 5 shows the variation of the $BPhCr(CO)_3$ electronic absorption spectrum in the course of its photodecomposition. The presence of the isobestic point in the region $\lambda \approx 310$ nm stems from the fall in the concentration of initial $BPhCr(CO)_3$ ($\lambda_{max} = 327$ nm, $\log\varepsilon_{max} = 4.0$), and the simultaneous increase in its photodecomposition products: $Cr(CO)_6$ ($\lambda_{max} = 230$ nm, $\log\varepsilon_{max} = 4.8$; $\lambda_{max} = 281$ nm, $\log\varepsilon_{max} = 4.2$), and in-coordinated BPh ($\lambda_{max} = 245$ nm, $\log\varepsilon_{max} = 4.4$). Taking into account the fact that the known intermediates do not absorb in the 375 nm region we believe that in the specified region the absorption band of the chromium multicenter complex is located.

Calculation of concentrations of intermediates of the $BPhCr(CO)_3$ photodecomposition, which was accomplished using IR and UV spectral data, enabled us to determine the approximate shape of the multicenter complex electron absorption spectrum (Fig. 6).

Thus, on the basis of the IR, UV and ^1H and ^{13}C NMR data we obtained experimental evidence in favour of the hypothesis [9] on the formation under photolysis of $ArCr(CO)_3$ of a chromium multicenter complex, having *cis* and *trans* forms (Scheme 1), metal atoms of which are bonded by bridging C=O groups. In the absence of irradiation the complex under study practically does not undergo decomposition. Thus, its optical density in the IR spectra at room temperature is unaffected for 24 h, the complex's lifetime being significantly increased at low temperatures.

The formation of $Cr(CO)_6$ under irradiation of the supposed multicenter complex

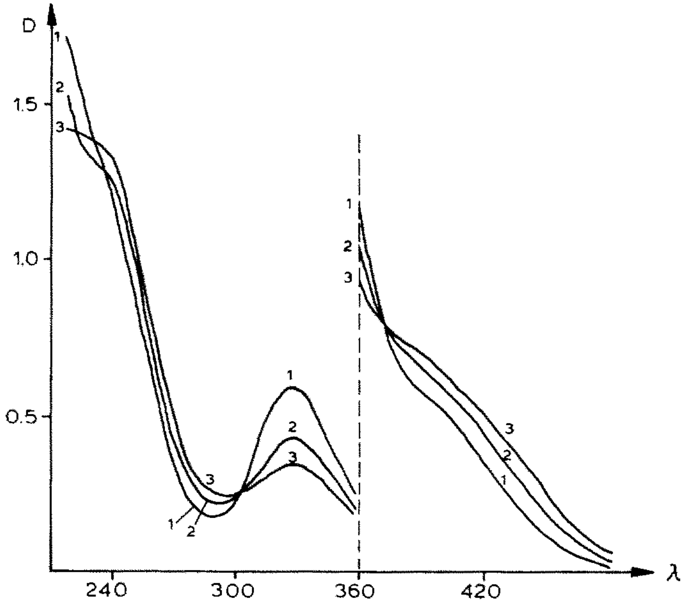


Fig. 5. The change of the electronic absorption spectra of $(C_6H_5)_2Cr(CO)_3$ in cyclohexane during its photodecomposition ($c = 15.5 \times 10^{-3}M$, $d = 0.04$cm).

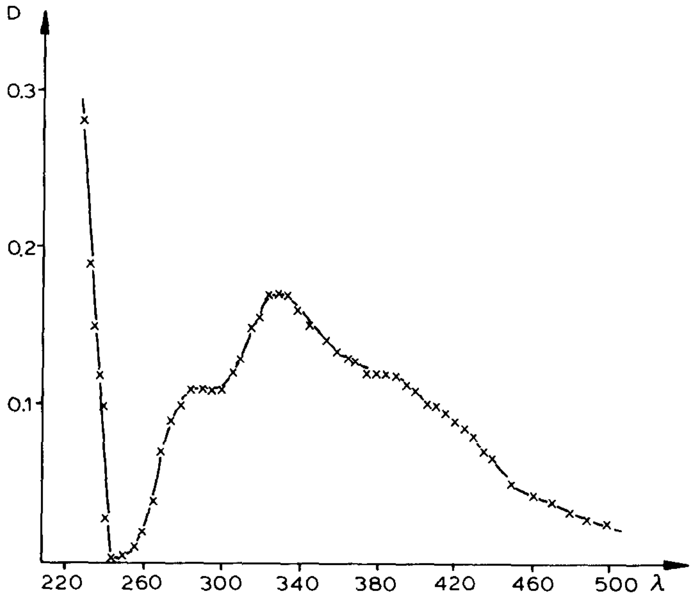


Fig. 6. Approximate shape of the electron absorption spectrum of the intermediate multicenter complex.

is related to breaking of the Cr–CO (bridging) bond. Taking into consideration the high symmetry of the octahedral structure of hexacarbonyls [12,13], fission of this bond under irradiation of the multicenter complex is probable.

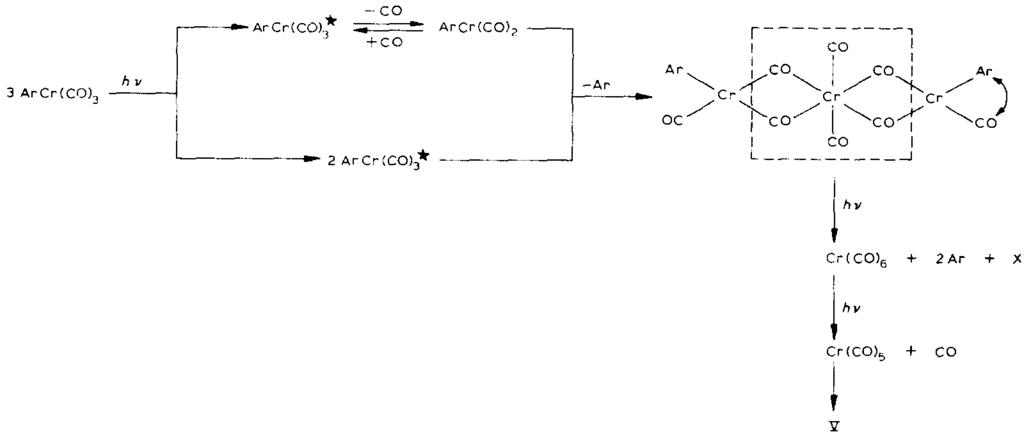
It is also necessary to establish the probable paths of the multicenter complex formation under photolysis of $ArCr(CO)_3$. The authors of a series of articles [9,14,15] propose that the primary photochemical event in $ArCr(CO)_3$ photolysis is the formation of the coordinatively unsaturated species $ArCr(CO)_2$ by loss of a CO group. This is concluded on the basis of the study of the Ar formation rate under photolysis of $ArCr(CO)_3$ in the presence of CO [9], and the comparison of quantum yields of the photoinduced exchange between CO and Ar in $ArCr(CO)_3$ [14,15]. When studying the photolysis of a series of isostructural complexes $ML(CO)_3$ ($ML = Cr(\eta\text{-}C_6H_6)$; $Mn(\eta\text{-}C_5H_5)$; $Fe(\eta\text{-}C_4H_4)$) within argon and methane matrices at $T = 12$ K the appearence of two additional bands was established in the IR spectra of these compounds, which were assigned to vibrations of terminal CO groups: of types A_1 and B_1 in accord with the local C_{2v} symmetry of the $M(CO)_2$ fragment. The following scheme of the photochemical process for $ML(CO)_3$ was proposed [5]:

$$[ML(CO)_3] \xrightarrow{h\nu} [ML(CO)_3]^{\star} \rightarrow [ML(CO)_2] + CO$$

Our investigations on the photolysis of $ArCr(CO)_3$ by the EPR spin trapping method [16] indicate also that the primary photochemical event of the $ArCr(CO)_3$ photolysis is the formation of the coordinatively unsaturated species $ArCr(CO)_2$ by loss of the CO group. Thus, the multicenter complex may be formed on complexation of the reactive $ArCr(CO)_2$ species with $ArCr(CO)_3^{\star}$ molecules.

Summing up the results obtained, as well as taking into account the photochemical activity of hexacarbonyl formed [13], we propose the mechanism for the photolysis of $ArCr(CO)_3$ shown in Scheme 2.

SCHEME 2



Experimental

The study of the photolysis of $ArCr(CO)_3$ complexes ($Ar = C_6H_6$; C_6H_5–C_6H_5) in cyclohexane and C_6D_6 solutions was performed using IR, UV and ^1H and ^{13}C NMR spectroscopy. The IR and UV studies were based on the analysis of variations of the absorption spectra of $ArCr(CO)_3$ complexes in the course of their photodecomposition. The photolysis of complexes was accomplished directly in an airtight cuvette made of CaF_2 (which was employed to record IR spectra ($d = 0.1$ mm; 2.6 mm)) on irradiating with a DRT-375, 1000 mercury lamp with water filter at room temperature. UV spectra were recorded on a Hitachi EPS-3T spectrophotometer, whereas the IR spectra were recorded on a UR-20 spectrophotometer. The solution concentrations of the complexes studies varied from 4×10^{-3}–$1.6 \times 10^{-4} M$.

^1H and ^{13}C-{^1H} NMR spectra were recorded on a Brücker CXP-200 spectrometer under pulse operation conditions using Fourier transform within the working frequences 200 MHz and 50.3 MHz, respectively. The signal of C_6H_6 in C_6D_6 (δ(1H) 7.24 and δ(13C) = 128.5 ppm) was used as an internal standard. The irradiation of a 10% solution of $C_6H_6Cr(CO)_3$ in C_6D_6 was performed directly in a sealed ampoule for measurements of ^1H NMR spectra.

References

1 V.N. Trembovler, N.K. Baranetskaya, N.V. Fok, G.B. Zaslavskaya, B.M. Yavorskii and V.N. Setkina, J. Organometal. Chem., 117(1976)339.

2 B.M. Yavorskii, N.K. Baranetskaya, E.A. Domogatskaya, A.A. Tsoi, V.N. Trembovler and V.N. Setkina, Zh. Fiz. Khim., 54(1980)1307.

3 E.A. Domogatskaya, V.N. Trembovler, N.K. Baranetskaya and B.M. Yavorskii, Zh. Fiz. Khim., 55(1981)2975.

4 V.T. Aleksanyan and B.V. Lokshin, The Structure of Molecules and the Chemical Bond, No.5, Itogi Nauki i Tekhniki ("Advances in Science and Technology" series, in Russian), "VINITI", Moscow 1976.

5 A.J. Rest, J.R. Sodean and D.J. Taylor, J. Chem. Soc. Dalton, 6(1978)651.
6 A.M. English, K.R. Plowman and I.S. Butler, Inorg. Chem., 21(1982)338.
7 M. Orchin and H.H. Jaffé, The Importance of Antibonding Orbitals, Houghton Mifflin Co., Boston, 1967.
8 F.A. Cotton and G. Yagupsky, Inorg. Chem. 6(1967) 15.
9 C.H. Bamford, C.G. Al-Lamee and C.J. Konstantinov, J. Chem. Soc. Faraday Trans. I,73(1977)1406.
10 L. Knoll, K. Reiss, J. Schäfer and P. Klüfers, J. Organometal. Chem., 193(1980)C40.
11 N.M. Klimenko, The Structure of Molecules and the Chemical Bond, No.6, "Itogi Nauki i Tekhniki" ("Advances in Science and Technology" series, in Russian), "VINITI", Moscow, 1978.
12 I.B. Bersuker, Elektronnoe Stroenie i Svoistva Koordinatsionnykh Soedinenii (The Electronic Structure and Properties of Coordinated Compounds), Khimiya, Leningrad, 1976.
13 M. Wrighton, Chem. Rev., 74(1974)401.
14 A. Gilbert, J.M. Kelly, M. Budzwait and E. Koerner von Gustof Z. Naturforsch., B31(1976)1091.
15 M.S. Wrighton and J.L. Haverty, Z. Naturforsch., B30(1975)254.
16 R.G. Gasanov, E.A. Domogatskaya, V.N. Setkina, N.K. Baranetskaya, V.N. Trembovler and B.M. Yavorskii, Chimicheskaya physica, submitted for publication.