Journal of Organometallic Chemistry, 277 (1984) 75–84
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

INDENYL- AND FLUORENYL-TRANSITION METAL COMPLEXES

XI *. INTRAMOLECULARITY OF THE HAPTOTROPIC $\eta^6 \rightleftharpoons \eta^5$ REARRANGEMENTS IN FLUORENYLCHROMIUM TRICARBONYL ANIONS BY CROSSOVER EXPERIMENTS

N.A. USTYNYUK*, L.N. NOVIKOVA,

A.N. Nesmeyanov Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, 28 Vavilov St., 117813, Moscow (U.S.S.R.)

Yu.F. OPRUNENKO, S.G. MALYUGINA and Yu.A. USTYNYUK

Department of Chemistry, Moscow State University, 117234, Moscow (U.S.S.R.)

(Received June 27th, 1984)

Summary

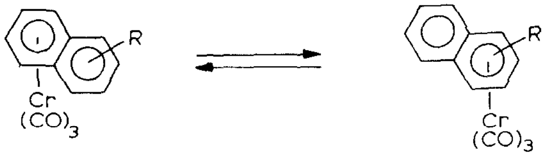
The intramolecular character of equilibrium and reversible isomerization of η^6- and η^5-fluorenylchromium tricarbonyl anions (IXa, IXb) is proved using crossover experiments. The rearrangement IXa $\rightleftharpoons$ IXb in the presence of 9-methylfluorenyl anion does not yield mixed products, i.e. η^6- or η^5-9-methylfluorenylchromium tricarbonyl anions. Similarly, under conditions of equilibrium between η^6- and η^5-(2,7-dideuterofluorenyl)chromium tricarbonyl anions (XIIa, XIIb) in the presence of non-deuterated fluorenyl anion, redistribution of the chromium tricarbonyl group among deuterated and deuterium-free fluorenyl anions does not take place.

Introduction

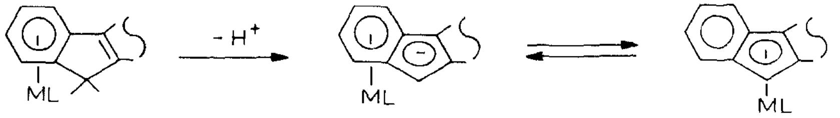
Rearrangements where the metal with its ligand surroundings shifts along the plane of the π-electron system from one ring to another have recently been found in the chemistry of transition metal π-complexes with polycyclic aromatic ligands. Albright et al. [1] classify such shifts as haptotropic rearrangements. As typical examples, we can cite isomerization of chromium tricarbonyl complexes of substituted naphthalenes [2,3] (eq. 1), and a general representation of $\eta^6 \rightleftharpoons \eta^5$ isomerization, II $\rightleftharpoons$ III (eq. 2), which takes place during deprotonation of transition metal π-complexes with indene, fluorene and their analogues [4–14].

---

* For part X see ref. 28.



(1)

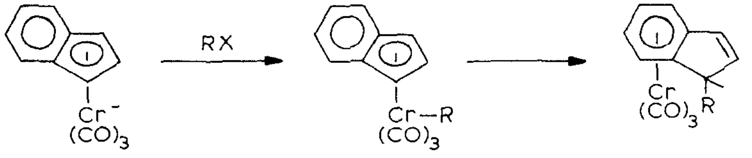


(I) (II) (III)

(2)

In some cases, for instance during deprotonation of dication indene-, indole-, 2-methylindene- and 1,5-dihydro-*s*-indacene-(pentamethylcyclopentadienyl)-iridium and -rhodium complexes, the intermediate deprotonated η^6-form (II) was not observed; rather, the product of isomerization (III) with an η^5-structure was generated [8,14]. At the same time, during deprotonation of fluorenechromium tricarbonyl [9–11] and fluorenemanganese tricarbonyl cation [6,15], both isomeric forms were certainly observed.

Inter-ring haptotropic rearrangements which are accompanied by the migration of one electron group (R) from the metal to the ligand take place during alkylation of η^5-indenyl- and η^5-fluorenyl-chromium tricarbonyl anions. This is illustrated by eq. 3 for the indenyl system [16]:



(IV) (V) (VI)

(3)

The intermediate (V) in the indenyl series has been obtained ($R = CH_3$) and characterized using IR spectra ($R = CH_2C_6H_5$); for fluorenyl analogues, it was only registered using IR spectra. In the η^6-isomer (VI), the alkyl group is in the *endo*-position to the chromium atom [16]. Protonation of η^5-fluorenylchromium tricarbonyl anion is similar (see below). The pronounced stereochemical result indicates that the "ricochet" V → VI rearrangement is an intramolecular process. It is possible that protonation of bis-(η^5-indenyl)iron [17,18], fluorenylmanganese tricarbonyl [19] and the monocation $[C_5(CH_3)_5M(\eta^5\text{-L})]^+$ (where M = Ir, Rh and η^5-L = indenyl or indolyl [8]) follows similar patterns, although no proof that the η^5-isomer is primarily formed after protonation at the metal was obtained for any of these systems.

A study of the mechanisms of inter-ring haptotropic rearrangements is important for a better understanding of the nature of the metal–ligand bond and the catalytic processes which incorporate organometallic π-complexes. It is particularly important to establish whether processes 1 and 2 are intermolecular or intramolecular. The possibility of haptotropic rearrangements being intermolecular processes is illustrated by the reaction of arene ligand exchange (eq. 4) in arenechromium tricarbonyl complexes, which takes place faster with coordinating solvents. In such solvents, these processes can proceed as pseudo-monomolecular reactions if replace-

$$\mathrm{AreneCr(CO)_3 + Arene' \rightleftharpoons Arene'Cr(CO)_3 + Arene} \qquad (4)$$

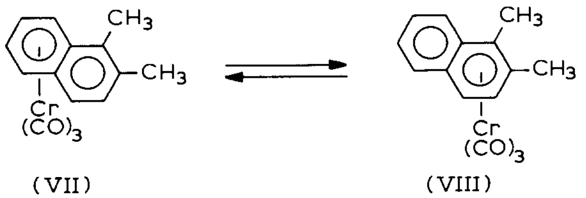
ment of the arene ligand by solvent molecules is the rate-determining step [20] (eq. 5, 6).

$$\mathrm{AreneCr(CO)_3 + 3Solv \overset{slow}{\rightleftharpoons} Arene + (Solv)_3Cr(CO)_3} \qquad (5)$$

$$\mathrm{Arene' + (Solv)_3Cr(CO)_3 \overset{fast}{\rightleftharpoons} Arene'Cr(CO)_3 + 3Solv} \qquad (6)$$

Both possible mechanisms of haptotropic rearrangement have recently been subjected to theoretical analysis by Albright et al. with the extended Hückel method. They found that in the case of naphthalenechromium tricarbonyl and indenyl(cyclopentadienyl)iron, the intramolecular shift of $Cr(CO)_3$ or the CpFe group according to least-motion transit over the centre of the inter-ring C–C bond, from the centre of one ring to the other, is symmetry-forbidden. The intramolecular shift with the least barrier may occur through a transition state which is closely related structurally to complexes of the η^4-trimethylenmethane or η^3-allyl type. Such a "roundabout" route demands 27.4 kcal/mol activation energy for degenerate inter-ring migration in naphthalenechromium tricarbonyl. In the case of indenyl(cyclopentadienyl)iron, the η^5-isomer is more stable and the least barrier intramolecular $\eta^6 \rightarrow \eta^5$ shift requires 35 kcal/mol. According to calculations, the dissociative path involves the least barriers (25 and 28 kcal/mmol, respectively). In this light, the authors prefer the intermolecular mechanism of haptotropic rearrangements 1 and 2 in coordinating media. It should be mentioned that the quantum chemical calculations used by the authors, while useful for qualitative studies, as a rule do not provide satisfactory quantitative energy estimates [21,22]. Therefore, the barrier values found for intramolecular migration and the dissociative path should be treated with some caution. To make a final assessment of the mechanism of inter-ring haptotropic rearrangement in fluorenylchromium tricarbonyl and naphthalenechromium tricarbonyl complexes, we carried out a number of additional studies, the results of which, for the first of these systems, are reported herein.

First of all, we should like to point out the results of a kinetics study of both rearrangements 1 and 2 mentioned earlier [2]. Deubzer found that isomeric chromium tricarbonyl complexes of 2,3-dimethylnaphthalene, VII and VIII, are interconverted when heated in decane in the range from 90 to 120 °C. The process follows the kinetics law of a first-order reversible reaction. The activation energy constitutes approximately 30 kcal/mol. It is regrettable that these results that are so pertinent to the intramolecular nature of the process have been published only in Deubzer's



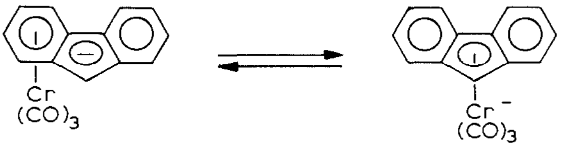
(7)

(VII) (VIII)

dissertation. The results that we obtained during studies of reactions of this kind, which on the whole confirm Deubzer's results, will be published separately.

The kinetics of reversible $\eta^6 \rightleftharpoons \eta^5$-isomerization of fluorenylchromium tricarbonyl anions were the subject of our earlier study [9,23], as well as that of Ceccon et al. [10] for tetrahydrofuran solutions. In both cases, it was proved that the process also follows the kinetics of a first-order reversible reaction. The reaction rate constants found turned out to be similar in both investigations notwithstanding the fact that the initial potassium salt (IXa) concentration used by Ceccon et al. [10] was about 200 times greater than that used by us [9]. The values of the activation enthalpies cited in Table 1 are similar. Ceccon et al. obtained values that are intermediate, as compared to our results, for rearrangements in the presence and absence of crown ether. These differences are probably explained by the differences in ion pair structure in solution.

The coinciding kinetic data obtained by us [9] and Ceccon et al. [10] for different concentrations indirectly point to the intramolecular mechanism of isomerization (eq. 8). Another fact in favour of this is that the rate of rearrangement is approximately the same in THF, benzene and heptane *. But in these media, anion IXa was generated by the reaction of initial fluorenechromium tricarbonyl (IX) with excess potassium solution in hexamethyltriamidophosphate (HMPA), which, like THF, can also facilitate the rupture of Arene–Cr bonds (eq. 5,6). Also, the appearance of a solvated particle, $(Solv)_3Cr(CO)_3$, in benzene solution should have led to the formation of benzenechromium tricarbonyl in considerable amounts, which, however, did not occur [24].



(IXa) (IXb) (8)

TABLE 1

ACTIVATION PARAMETERS FOR ISOMERIZATION: IXa $\rightleftharpoons$ IXb

Isomerization conditions (solvent, anion concentration, solvating additive)	$\Delta H^{\#}$ (kcal/mol)		$\Delta S^{\#}$ (e.u.)		Ref.
	$\eta^6 \rightarrow \eta^5$	$\eta^5 \rightarrow \eta^6$	$\eta^6 \rightarrow \eta^5$	$\eta^5 \rightarrow \eta^6$	
Pure THF, 6.7×10^{-3} *M*	15.7 ± 2.04	13.8 ± 2.2	-19.6 ± 2.55	-29.9 ± 4.8	9
THF + dicyclohexyl-18-crown-6; 6.7×10^{-3} *M*	21.3 ± 2.1	17.8 ± 3.2	0.2 ± 0.02	-13.7 ± 2.5	9
THF-d_8, 3×10^{-1} *M*	19.4 ± 1.0	15.1 ± 1.0	-6.8 ± 1.5	-25.4 ± 1.5	10

---

* Kinetic analysis of isomerization (eq. 8) in benzene and heptane is impossible due to the low solubility of the isomer anions IXa and IXb.

Finally, we should like to point out an important result obtained by Nekrasov and co-workers [25] in the course of studying the mass spectra of negative ions of indenechromium tricarbonyl. It is a characteristic feature of the fragmentation of the molecular ion of this compound that the loss of the hydrogen atom leads to $[M-\mathrm{H}]^-$ ions which are formed in two resonance regions at 0.4 and 3.0 eV. We believe that the ion formed at weak electron energy has the η^5-structure, since the energy expended on disrupting the C–H bond, in this case, is partially compensated for by the gain due to the formation of a more stable η^5-isomer. The second maximum corresponds directly to a scission in the C–H bond (the ion has the η^6-structure). Therefore, fragmentation of indenylchromium tricarbonyl anion indicates the possibility of an inter-ring haptotropic rearrangement in the gaseous phase, i.e. under conditions precluding intermolecular interaction.

Results and discussion

For the purpose of obtaining additional data on the mechanism of isomerization represented by eq. 8, we conducted a number of crossover experiments.

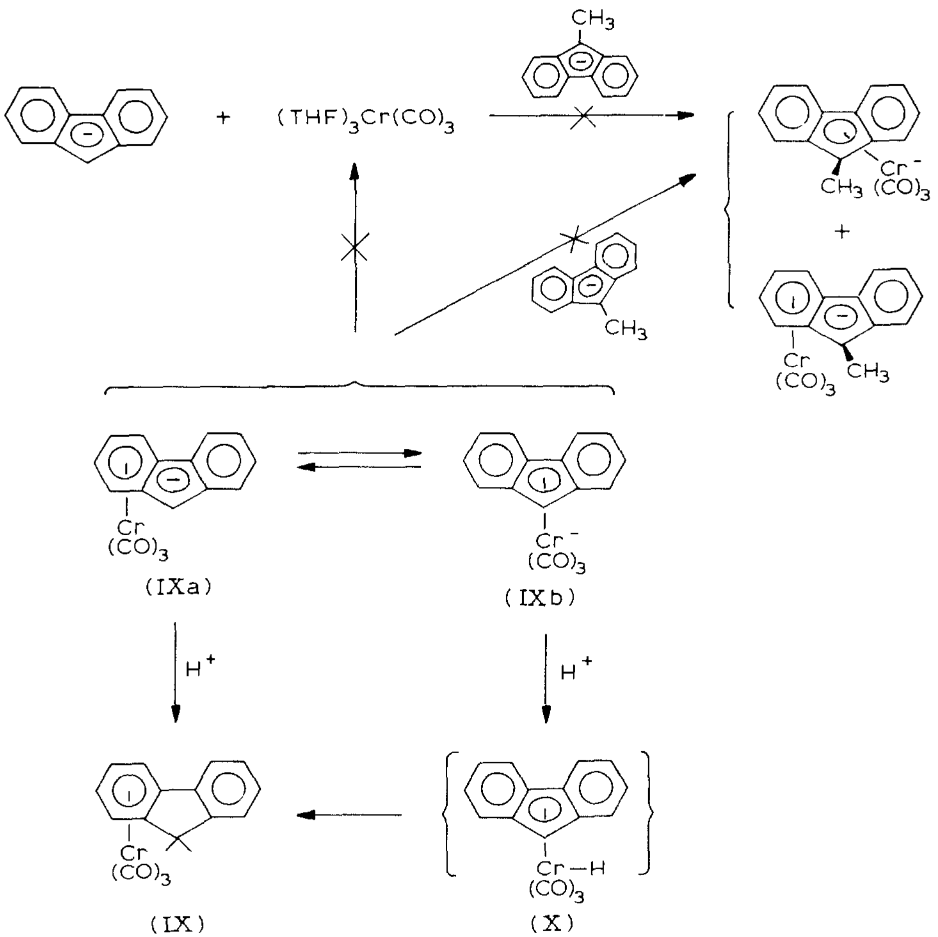
Deprotonation of η^6-fluorenechromium tricarbonyl (IX) with potassium solution in HMPA leads to an equilibrium mixture of η^6- and η^5-fluorenylchromium tricarbonyl anions (IXa, IXb), eq. 8, in a ratio of 1/2.46, as described earlier in ref. 24. The addition of 9-methylfluorenylpotassium solution * to this tautomeric mixture, keeping the mixture at 25 °C for 15–60 min, and treatment with acetic acid yields the following main products: fluorenechromium tricarbonyl (45%), 9-methylfluorene (100%), and fluorene (40–45%). The main result of this experiment is the fact that no mixed product, i.e. η^6-9-methylfluorenechromium tricarbonyl, is formed at all, i.e. no redistribution of the chromium tricarbonyl group between π-fluorenyl and π-9-methylfluorenyl ligands takes place. These processes may be represented as shown in Scheme 1.

On the other hand, the rather high fluorene yield attracts attention. It is expedient to note that protonation of the tautomeric mixture IXa $\rightleftharpoons$ IXb also leads to IX and fluorene with approximately the same yield [6], i.e. the presence of 9-methylfluorenyl anion in the mixture has no apparent effect on the yield of IX and fluorene. We believe that the main process of decomposition that led to the appearance of fluorene in the system, and to the decrease in the yield of IX to 40–45%, occurred in the stage of "ricochet" inter-ring haptotropic isomerization of the η^5-hydride isomer X to IX. Such a supposition is confirmed by the fact that treating the same mixture with deuteroacetic acid resulted in a mixture of *exo*-d_1-IX (from IXa) and *endo*-d_1-IX (from IXb through d_1-X) in a ratio of 1/1, and not 1/2.5 as would be expected on the basis of the IXa/IXb ratio **. It is therefore obvious that the largest loss is the result of η^5-isomer X transformations. Besides d_1-IX, deuteration of the mixture by CH_3COOD also yielded 9-deutero-9-methylfluorene and traces of 9-methylfluorene. η^6-9-Methylfluorenechromium tricarbonyl was absent, as in the case of acetic acid.

---

* The same result is achieved with co-deprotonation of IX and 9-methylfluorene with a solution of potassium in HMPA.

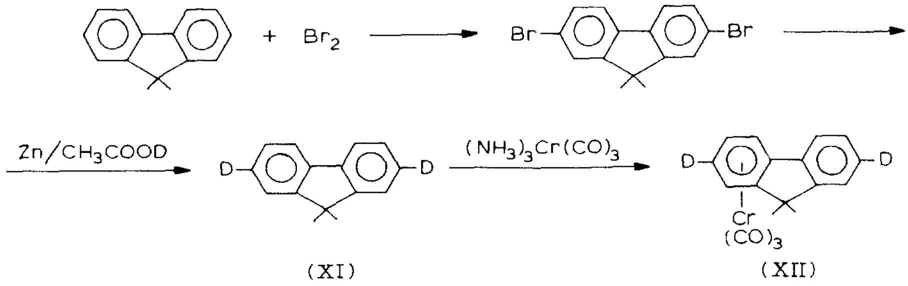
** The conclusions regarding the regio- and stereo-specificity of reactions of anions IXa and IXb that make up the tautomeric mixture with H^+ (D^+) are based on a study of the reaction of pure IXa and IXb with CH_3COOD, soon to be published.



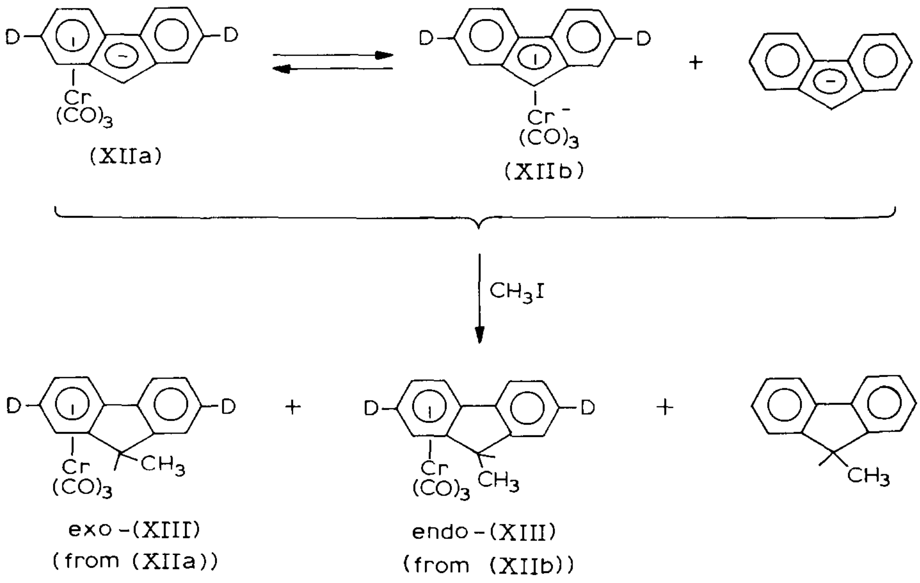
SCHEME 1

In order to neutralize the electron influence of the substituent label and therefore to improve the purity of the crossover experiment, we synthesized 2,7-d_2-fluorenechromium tricarbonyl according to Scheme 2.

The middle stage in this sequence is reductive debromination of 2,7-dibromofluorene to 2,7-dideuterofluorene (XI) by treatment with zinc powder and deuteroacetic



SCHEME 2



SCHEME 3

acid. This method was used for selective introduction of deuterium into the aromatic rings [26]. Using this method allowed 2,7-d_2-fluorene of high isotope purity to be obtained.

According to ^{1}H and ^{13}C NMR data, the non-deuterated fluorene content in various samples of XI did not exceed 10–15%. Keeping the tautomeric mixture obtained during deprotonation of XII in the presence of fluorenylpotassium in THF at 25°C for 15–60 min with subsequent treatment with methyl iodide leads to the processes shown in Scheme 3.

Methylation of the tautomeric XIIa $\rightleftharpoons$ XIIb mixture follows the trends found previously for the IXa $\rightleftharpoons$ IXb system [13,16]. The only chromium tricarbonyl complex obtained was a mixture of *exo-* and *endo-*(9-methyl-2,7-dideuterofluorene)chromium tricarbonyls (XIII) (40% yield), while according to the ^{1}H NMR spectra, the isotopic purity of XIII equalled that of the starting XII. This points to the fact that in this system, as in those studied previously, there is no redistribution of the chromium tricarbonyl group between the deuterated and deuterium-free fluorenyl anions. Among the metal-free products, 9-methylfluorene is the main one, accompanied by 9,9-dimethylfluorene and fluorene. These compounds were not subjected to deuterium-content studies.

Our study used crossover experiments to establish the nature of the "planar" inter-ring haptotropic rearrangement in IXa $\rightleftharpoons$ IXb and showed it to be an intramolecular process. In the course of rearrangement, the chromium tricarbonyl group retains its bonding to the fluorenyl ligand.

Experimental

All manipulations were performed in pure argon atmosphere. THF was purified by prolonged refluxing over a K/Na alloy, and was distilled just before use. ^{1}H and

^{13}C NMR spectra were recorded with XL-100 Varian and FT-80A spectrometers. IR spectra were taken with a UR-20 spectrometer. Silica gel L 40/100 and L 100/160μ (Chemapol, CSSR) were used for chromatography. 2,7-Dibromofluorene was obtained by fluorene bromination as described in ref. 27.

Synthesis of 2,7-dideuterofluorene (XI)

Zn powder (10.6 g, 163 mmol) was refluxed with benzene for 2 h, then benzene was distilled off and Zn powder was refluxed with D_2O (99%) for 17 h. Water was decanted, and 3.88 g (12 mmol) of 2,7-dibromofluorene, 7 ml of freshly distilled acetic anhydride and 50 ml of D_2O were added. The mixture was refluxed for 18 h. 2,7-Dideuterofluorene was extracted with ether. The ether extract was washed with water, dried over $MgSO_4$ and, after ether had been distilled off, the residue was sublimed in a water pump vacuum at 120 °C. Yield 0.402 g (20%). ^{13}C NMR ($CDCl_3$): 36.78, (C(9)); 119.72, (C(4) + C(5)); 124.75, (C(1) + C(8)); 126.53, (C(3) + C(6)); 141.56, (C(9a) + C(8a)); 143.06, (C(4a) + C(8b)). (Signals of carbon atoms that are connected to deuterium do not appear in the spectrum under registration conditions.)

Synthesis of 2,7-dideuterofluorenechromium tricarbonyl (XII)

0.4 g of dideuterofluorene (2.4 mmol) and 0.51 g $(NH_3)_3Cr(CO)_3$ (2.4 mmol) were refluxed for 3.5 h in 30 ml of absolute dioxane. After the solvent had been distilled off in vacuo, the residue was chromatographed on a 15 × 2 cm column with silica gel L100/160μ. The wide yellow band containing XII was eluted with a 1/3 benzene/petroleum ether mixture. In the final stages of eluting, with no interface between the bands, a mixture of XII and the corresponding binuclear complex, 2,7-dideuterofluorenebis(chromium tricarbonyl) (XIV), was washed out [11]. Further separation of these complexes was performed on silica gel plates in the same mixture with two-fold plate exposure in the chromatographic vessel. Net yield of XII 0.29 g (40%). Binuclear complex XIV was discarded. ^{1}H NMR of XII (acetone-d_6, δ, ppm): AB-system, centre 4.05, J_{AB} 22 Hz, 2H; coordinated ring: 5.69, br.doublet, ^3J 6.8 Hz, 1H (H(3)); 6.23 br.singlet, 1H (H(1)); 6.53, doublet, ^3J 6.8 Hz, 1H (H(4)); non-coordinated ring: 7.43, br.doublet, ^3J 7.5 Hz, 1H (H(6)); 7.59, br.singlet, 1H (H(8)); 7.84, doublet 7.5 Hz, 1H (H(5)). ^{13}C NMR ($CDCl_3$, δ, ppm): 36.37; C(9); coordinated ring: 86.33 C(4), 90.08, C(1); 90.47, C(3); 110.67, C(4a), 112.68, C(9a); non-coordinated ring: 119.87, C(5); 124.80, C(8); 127.11, C(6); 138.35, C(8b); 141.77, C(8a), 233.08, C≡O. (Signals of C(2) and C(7) are not discernible in the spectrum under registration conditions.)

Investigation of IXa $\rightleftarrows$ IXb equilibrium by crossover experiments

1. IXa $\rightleftarrows$ IXb + 9-methylfluorenyl anion system. To a solution of IXa obtained by treating 0.3 g (1 mmol) of fluorenechromium tricarbonyl in 50 ml of THF with excess potassium solution in HMPA (2.5 ml) at −50 °C, and gradually heated to room temperature was added a solution of 9-methylfluorenyl anion, prepared by treating 0.36 g (2 mmol) of 9-methylfluorene in 30 ml of THF with 5 ml of potassium solution in HMPA. The mixture was stirred at room temperature for 10–60 min, after which it was cooled to 0 °C. A THF solution of acetic acid was then added. After gradual heating to 25 °C, the solvent was evaporated in vacuo and the residue extracted with benzene, washed with water, dried over $MgSO_4$ and subjected to chromatography on a 3 × 15 cm column with silica gel 40/100μ. A 1/1 Petroleum ether/benzene mixture was used to elute 9-methylfluorene and fluorene (ratio 4/1). The mixture of aromatics was analysed by ^{1}H NMR spectroscopy. IX was eluted with benzene. Yield 45%.

A similar experiment was carried out with CH_3COOD being used in the final stage instead of CH_3COOH. After chromatographic separation, the organic fraction contained a mixture of 9-deutero-9-methylfluorene, 9-deuterofluorene and 9-methylfluorene.

The only metal-containing product was benzene-eluted 9-deuterofluorene-chromium tricarbonyl in the form of an *exo*- and *endo*-isomer mixture. The yield varied from 0.11 to 0.13 g (37–44%).

2. XIIa $\rightleftarrows$ *XIIb system in the presence of fluorenyl anion.* To a solution of 2,7-dideuterofluorenechromium tricarbonyl (XII) 0.1 g (0.33 mmol) in 5 ml of THF at −20 °C, was added potassium solution in HMPA. A solution of fluorenylpotassium was prepared separately from 0.055 g of fluorene (0.33 mmol) in 5 ml of THF and potassium solution in HMPA. After both solutions had been mixed, they were stirred for 1 h after heating to 25 °C, following which excessive methyl iodide was added. After the solvent had been distilled off in vacuo, the residue was subjected to chromatography on a 15 × 2 cm column with silica gel 100/160μ, as described in the previous experiment. The colourless band contained a mixture of 9-methyl-, 9,9-dimethyl-fluorene and fluorene (^{1}H NMR). The yellow band containing 9-methylfluorenechromium tricarbonyl (XIII) in the form of mixed *exo*- and *endo*-isomers was eluted with benzene. Yield 0.042 g of XIII (40%).

References

1 T.A. Albright, P. Hofmann, R. Hoffmann, C.P. Lillya and P.A. Dobosh, J. Am. Chem. Soc., 105 (1983) 3396.
2 B. Deubzer, Ph.D. Dissertation, Technische Hochschule München, 1966.
3 K.H. Dötz and R. Dietz, Chem. Ber., 110 (1977) 1555.
4 N.A. Ustynyuk, Yu.A. Ustynyuk and A.N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 265 (1980) 127.
5 K.M. Nicholas, R.C. Kerber and E.I. Stiefel, Inorg. Chem., 10 (1971) 1519.
6 A.N. Nesmeyanov, N.A. Ustynyuk, L.G. Makarova, S. Andrae, Yu.A. Ustynyuk, L.N. Novikova and Yu.N. Luzikov, J. Organomet. Chem., 154 (1978) 45.
7 P.M. Treichel and J.W. Johnson, Inorg. Chem., 16 (1977) 749.
8 C. White, T.Thompson and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1977) 1654.
9 N.A. Ustynyuk, B.V. Lokshin, Yu.F. Oprunenko, V.A. Roznyatovsky, Yu.N. Luzikov and Yu.A. Ustynyuk, J. Organomet. Chem., 202 (1980) 279.
10 A. Ceccon, A. Gambaro, G. Agostini and A. Venzo, J. Organomet. Chem., 217 (1981) 79.
11 Yu.F. Oprunenko, Yu.N. Luzikov, Yu.A. Ustynyuk and N.A. Ustynyuk, J. Organomet. Chem., 231 (1982) 137.
12 A.N. Nesmeyanov, N.A. Ustynyuk, T. Thoma, N.S. Prostakov, A.T. Solodatenkov, V.G. Pleshakov, K. Urga, Yu.A. Ustynyuk, O.I. Trifonova and Yu.F. Oprunenko, J. Organomet. Chem., 231 (1982) 5.
13 A.N. Nesmeyanov, N.A. Ustynyuk, L.N. Novikova, T.N. Rybina, Yu.A. Ustunyuk, Yu.F. Oprunenko and O.I. Trifonova, J. Organomet. Chem., 184 (1980) 63.
14 P. Bickert and K. Hafner, Tetrahedron Lett., 23 (1982) 2309.
15 P.M. Treichel, K.P. Fivizzani and K.J. Haller, Organometallics, 1 (1982) 931.
16 A.N. Nesmeyanov, N.A. Ustynyuk, L.N. Novikova, V.G. Andrianov, Yu.T. Struchkov, Yu.A. Ustynyuk, Yu.F. Oprunenko and Yu.N. Luzikov, J. Organomet. Chem., 226 (1982), 239.
17 C.C. Lee, R.G. Sutherland and B.J. Thomson, J. Chem. Soc., Chem. Commun., (1971) 1071.
18 P.M. Treichel and J.W. Johnson, J. Organomet. Chem., 88 (1975) 207.
19 M.G. Yezernitskaya, B.V. Lokshin, V.I. Zdanovich, I.A. Lobanova and N.E. Kolobova, J. Organomet. Chem., 234 (1982) 329.

20 C.L. Zimmerman, S.L. Shaner, S.A. Roth and B.R. Willeford, J. Chem. Res., S, (1980) 108

21 V.I. Minkin, B.Ya. Simkin and R.M. Minaev, Theory of Molecular Structure. Moscow, Vyshaya Shkola, 1979, Ch.10.

22 G.A. Shembelov, Yu.A. Ustynyuk, V.M. Mamaev et al., Quantum Chemical Methods of Molecular Calculation. Khimia, 1980, Ch. 2,4.

23 A.N. Nesmeyanov, Yu.F. Oprunenko, N.A. Ustynyuk, B.V Lokshin and Yu.A Ustynyuk, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 1942.

24 Yu F. Oprunenko, Doctor's Thesis, MGU, Moscow, 1982.

25 V.I Khvostenko, Yu.S. Nekrasov, I.I. Furlev, N.I. Vasyukova and G.A. Tolstikov, J. Organomet Chem., 212 (1981) 369

26 B. Bak, D. Christensen, L Hansen-Nygaard and E Tannenbaum, J Chem. Phys., 26 (1957) 134.

27 A. Sieglitz, Chem. Ber., 53 (1920) 1232.

28 N.A. Ustynyuk, Yu. F. Oprunenko, S.G. Malyugina, O.I. Trifonova and Yu A Ustynyuk, J. Organomet Chem., 270 (1984) 185