Journal of Organometallic Chemistry, 294 (1985) 31–44
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

INDENYL AND FLUORENYL TRANSITION METAL COMPLEXES

XIII *. DETERMINATION OF GEOMETRIC CONFIGURATION OF (9-SUBSTITUTED FLUORENES)CHROMIUM TRICARBONYL COMPLEXES BY ASIS-EFFECT IN ^{1}H NMR SPECTRA

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(Received April 23rd, 1985)

Summary

A method to determine the geometric configuration of chromium tricarbonyl complexes of 9-substituted fluorenes (η^6-9-RC$_{13}$H$_9$)Cr(CO)$_3$ which allows one to distinguish between *exo*-isomers (IIIa–e) and *endo*-isomers (Va–e) is proposed; a, R = CH$_3$; b, R = CH$_2$C$_6$H$_5$, c, R = D; d, R = t-C$_4$H$_9$; e, R = C$_6$H$_5$. This method is based on measuring chemical shifts induced in ^{1}H NMR spectra by aromatic solvents when passing from CDCl$_3$ to C$_6$D$_6$ solutions (ASIS effect). The validity of the criterion is confirmed by X-ray analysis of IIIb. *Exo*-isomers, IIIb,c, were obtained by alkylation of the η^6-fluorenylchromium tricarbonyl anion (I) with the corresponding halides RX in tetrahydrofuran (THF) at low temperature. *Endo*-isomers (Vb,c) have been obtained by alkylation of the η^5-fluorenylchromium tricarbonyl anion (II) with subsequent thermal rearrangement of intermediate σ-organometal derivatives (IV) without their isolation. *Endo*-isomers, Vd,e, have been formed by stereoselective protonation of substituted complex anions [(η^6-9-RC$_{13}$H$_8$)Cr(CO)$_3$]$^-$.

Introduction

As was previously shown by us [1,2], chromium tricarbonyl complexes of 9-substituted fluorenes (η^6-9-RC$_{13}$H$_9$)Cr(CO)$_3$ produced by interaction of η^6-fluoren-

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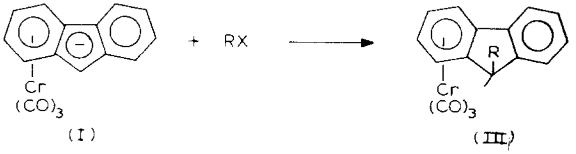
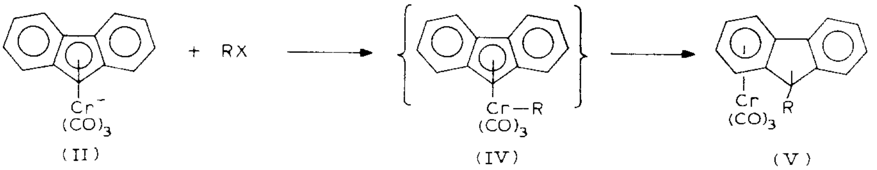
* For part XII see Ref. 23.

0022-328X/85/$03.30

ylchromium tricarbonyl anion I and its isomer, η^5-fluorenylchromium tricarbonyl anion II with alkyl halides differ in their geometrical configuration. Electrophilic attack of RX on the anion I proceeds stereoselectively from the outer side opposite to the coordinated $Cr(CO)_3$ group (eq. 1) yielding *exo*-isomers, III. Alkylation of the isomeric anion II takes place at the metal atom. The intermediate σ-derivatives, IV, undergo thermal "ricochet" rearrangement to yield *endo*-isomers, V.



(1)



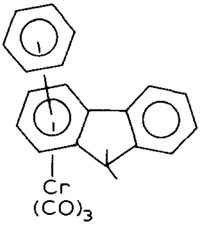
(2)

These conclusions were drawn from X-ray analysis of the rearrangement product in the case of η^5-$C_9H_7(CO)_3CrCH_2C_6H_5$ and spectral differences between IIIa and Va. Though X-ray analysis presents the most reliable method for determining the structure of this type of complexes, it cannot be used always because of the difficulties in obtaining crystals of the required quality or because of the instability of the complexes. X-ray methods also fail to analyse the isomeric mixtures which cannot be quantitatively separated. To study the reactions involving pure I and II and their tautomeric mixtures, a fast and convenient quantitative method for determining the geometric configuration of III and V type complexes is required. This paper reports the synthesis of new complexes IIIb–e and Vd,e and the general method for determining their configuration using ASIS effect in ^1H NMR spectra.

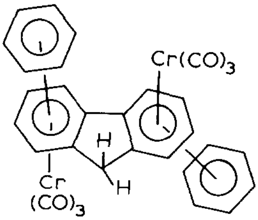
Results and discussion

Proton magnetic resonance spectra

Aromatic solvent induced chemical shifts in ^1H NMR spectra are widely used for studying the structure of many organic molecules and for simplifying intricate spectra. The use of aromatic solvents (C_6H_6, C_6D_6, $C_6H_5CH_3$, etc.) with flat disk-like molecules and high magnetic anisotropy instead of magnetic isotropic solvents such as CCl_4 or $CDCl_3$ results in the upfield shifting of all resonance signals. This shifting markedly depends on the structural environment of the protons and its value, i.e. the difference in chemical shifts of the same proton in two different solvents, $\Delta\delta_{ASIS} = \delta_{CDCl_3} - \delta_{C_6D_6}$, was termed the ASIS effect whose nature is discussed in a number of papers [3,4]. The molecules of the dissolved substance can form weak complexes ("collision complexes") with the molecules of the aromatic solvent due to the hydrogen bond formed with the π-electron system of the ring or as a result of electrostatic interaction between the polar groups and the induced dipoles of aromatic molecules, or, due to charge transfer. Though the lifetime of these complexes is quite short, in the NMR time scale, some average predominant mutual orientation of solvent and solute molecules results in additional screening for solute protons located near the benzene molecule 6th order axis due to the contribution of the ring current. Thus, according to [3], benzenechromium tricarbonyl can form weak charge transfer complexes with benzene whose molecule is placed above the plane of the coordinated ligand. Apparently, (η^6-fluorene)chromium tricarbonyl (VI) forms the same kind of complexes. Resonances from the protons of the coordinated benzene nucleus of this complex are correspondingly shifted upfield by 0.7–0.8 ppm. This effect is most pronounced, however, for the protons in the 9 position. Their diastereotopy is not exhibited in $CDCl_3$ solution, and only one signal is observed at δ 3.94 ppm. In benzene solution H^9(*exo*) and H^9(*endo*) give the expected AB spectrum with the chemical shifts 3.10 and 3.35 ppm and the characteristic $^2J(HH)$ 22 Hz. Thus, the ASIS effect for these two protons in 0.84 and 0.59 ppm, respectively, and the upfield signal should be assigned to H^9(*exo*) since it is located closer to the solvent molecule.



A similar phenomenon was observed by us [2] also for (η^6-9,9-dimethylfluorene)chromium tricarbonyl (VII). The induced shift of the coordinated nucleus proton signals for this compound is 0.7–0.8 ppm, and 0.38 ppm for those of the non-coordinated nucleus. The methyl group signals appeared at 1.44 and 1.62 ppm in $CDCl_3$ solution; after benzene addition they were gradually shifted upfield and were observed in pure benzene at 1.02 and 1.42 ppm, respectively. The upfield signal with a higher induced shift, $\Delta\delta_{ASIS}$ can be attributed to *exo*-methyl group protons. This assignment is reinforced by the fact that in the spectra of the binuclear complex (η^6,η^6-fluorene)bis(chromiumtricarbonyl) (VIII) the methylene protons at position 9 give a singlet irrespective of the solvent type. When passing from chloroform to deuterobenzene the induced shift value reaches 0.84 ppm which is indicative of the effective complex formation with both coordinated rings and clearly confirms the *trans* structure of the compound; an AB type spectrum should be expected for a *cis* complex. The ^1H NMR spectra for these and all other complexes considered in this paper are presented in Table 1.



(VIII)

All previous work used different criteria for establishing the geometric configuration of the substituted complexes of polycyclic ligands with transition metals. The

(*Continued on p. 36*)

TABLE 1

^1H NMR SPECTRAL PARAMETERS OF COMPLEXES IIIa–e AND Va–e

Complex	Solvent	Chemical shifts and signal multiplicity [a]			
		Coordinated nucleus [b]	Non-coordinated nucleus (ABCD-multiplet centers)	H^9	Other groups
IIIe	C_6D_6	4.63(H^2); 4.47(H^3); 5.02(H^1); 5.70(H^4).	7.07 (9H)	5.02 (*endo*)	the signals of phenyl group protons coincide with the signals of non-coordinated nucleous protons
IIIe	$CDCl_3$	multiplet 5.1-5.38 (H^2+H^3); 5.60 (H^1); 6.00 (H^4)	7.31 (9H)	5.28 (*endo*)	the signals of phenyl group protons coincide with the signals of non-coordinated nucleous protons
Ve	C_6D_6	4.95 (H^1+H^2); 4.16 (H^3); 5.20 (H^4)	7.23 (9H)	4.49 (*exo*)	
Ve	$CDCl_3$	5.62(H^1+H^2); 4.92(H^3); 5.80 (H^4)	7.45 (9H)	5.06 (*endo*)	
IIIa	C_6D_6	5.38 (H^4); 5.12 (H^1); 4.66 (H^2+H^3)	7.00 (4H)	3.68 q	1.00 d (CH_3)
IIIa	$CDCl_3$	6.01(H^4); 5.85 (H^1); 5.44 (H^2+H^3)	7.38 (4H)	4.15 q	1.40 d (CH_3)
Va	C_6D_6	5.02, d(H^1), 4.94, d(H^4) 4.70, t(H^3), 4.20, t, (H^2)	7.00 (4H)	3.18 q	1.23 d (CH_3)
Va	$CDCl_3$	5.82, d, (H^1), 5.74, d(H^4) 5.50, t, (H^3), 5.00, t, (H^2)	7.38 (4H)	4.13 q	1.59 d (CH_3)
IIIb	C_6D_6	5.26 d(H^4); 4.92 d(H^1); 4.52 t(H^3); 4.44 t(H^2)	6.90 (9H)	4.15 (*endo*)	Signals of phenyl group protons coincide with the signals of non-coordinated ring protons; CH_2Ph: AB part of ABX system ($X = H^9$) 2.60(H_A); 2.76 (H_B)

IIIb	$CDCl_3$	5.87 d(H^4); 5.50 d(H^1); 5.28 t(H^3); 5.22 t(H^2)	7.20 (9H)	4.35 (*endo*)	AB part of ABX system 2.90 (H_A); 3.10 (H_B) (CH_2Ph)
Vb	C_6D_6	5.10 d(H^1); 4.96 d(H^4); 4.80 t(H^3); 4.20 t(H^2)	6.95 (9H)	3.88 (*exo*)	AB part of ABX system 3.27 (H_A), 3.07 (H_B) (CH_2Ph)
Vb	$CDCl_3$	5.84 d(H^1); 5.60 d(H^4); 5.48 t(H^3); 5.02 t(H^2)	7.30 (9H)	4.53 (*exo*)	AB part of ABX system 3.38 (H_A); 3.21 (H_B)(CH_2Ph)
VII	C_6D_6	5.12 d(H^1); 5.02 d(H^4); 4.86 t(H^3); 4.44 t(H^2)	7.06 (4H)	–	1.02 (CH_3 (*exo*)) 1.42 (CH_3 (*endo*))
VII	$CDCl_3$	5.93 d(H^1); 5.74 d(H^4); 5.59 t(H^3); 5.12 t(H^2)	7.44 (4H)	–	1.44 (CH_3 (*exo*)) 1.62 (CH_3 (*endo*))
IIId	C_6D_6	5.41 d(H^4); 5.37 d(H^1); 4.65 t(H^3); 4.53 t(H^2)	7.18 (4H)	3.55 (*endo*)	0.67 (t-Bu)
IIId	$CDCl_3$	6.04 d(H^4); 6.00 d(H^1); 5.40 t(H^3); 5.28 t(H^2)	7.48 (4H)	3.77 (*endo*)	1.00 (t-Bu)
Vd	C_6D_6	5.57 d(H^1); 4.88 d(H^4); 5.10 t(H^3); 4.24 t(H^2)	7.24 (4H)	3.30 (*exo*)	1.12 (t-Bu)
Vd	$CDCl_3$	6.22 d(H^1); 5.67 d(H^4); 5.86 t(H^3); 5.04 t(H^2)	7.60 (4H)	3.96 (*exo*)	1.25 (t-Bu)
VI	C_6D_6	5.29 (H^4); 4.96 (H^1) 4.53 (H^2+H^3)	7.00 (4H)	AB system 3.10 (H^9(*endo*)) 3.35 (H^9(*endo*)) $J(AB) = 22$ Hz	–
VI	$CDCl_3$	6.08 (H^4); 5.85 (H^1); 5.38 (H^2+H^3)	7.36 (4H)	3.94 (H^9(*exo*)+ H^9(*endo*))	
IIIc	C_6D_6	5.29 (H^4); 4.96 (H^1) 4.53 (H^2+H^3)	7.00 (4H)	H^9(*endo*) 3.35 (1H)	–
Vc	C_6D_6	5.29 (H^4); 4.96 (H^1) 4.53 (H^2+H^3)	7.00 (4H)	H^9(*exo*) 3.13	–
VIII	C_6D_6	4.80 (H^4); 4.59 (H^1) 4.30 (H^2+H^3)	–	3.09 (H^9), s	–
VIII	$CDCl_3$	5.83 (H^4); 5.73 (H^1) 5.19 (H^2+H^3)	–	3.93 (H^9), s	–

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[a] s, singlet; d, doublet; q, quadrouplet; t, triplet. [b] The signals of coordinated ring protons were assigned on the basis of double resonance spectra.

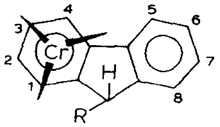
ASIS data were most successfully used by French authors [5] for studying substituted indanechromium tricarbonyl complexes. According to them, the signals of the *exo*-proton or the *exo*-substituent are shifted upfield to a much greater extent than those of the *endo*-proton.

To determine the stereochemistry of α-hydroxy-1,2-tetramethyleneferrocenes and (2-hydroxyindane)chromium tricarbonyls the data on ν(OH) in IR spectra were used under the assumption that the lower value corresponded to the *endo*-isomer due to hydrogen bonding with the metal atom or carbonyl group [6–8]. In [9] X-ray analysis was used to establish stereochemistry, but no correlation with spectral data was presented.

For chromium tricarbonyl complexes of cyano- and carbomethoxy-substituted indanes the assignment to *exo*- and *endo*-isomers was made on the basis of dipole moments which are higher for *endo*-isomers [10]. To assign *exo*- and *endo*-configurations to the 9,10-dihydro-9,10-dimethylanthracene complexes, Sutherland et al. [11,12] used the interrelations between proton and carbon chemical shifts in ^{1}H and ^{13}C NMR spectra.

For determination of *exo*- and *endo*-configurations in monocyclic ligand π-complexes where the only sp^3 carbon atom which has a substituent and which is not involved in bonding with the metal is located at the same ring as the coordinated carbon atoms (cycloheptatriene, cyclohexadienyl and other complexes) the most reliable information is provided by the analysis of vicinal constants of spin–spin coupling [13]. The ASIS effect can also be used for this purpose [14,15], but it should be borne in mind that for Ir and Rh complexes the signals of *exo*-protons appear to be in the lower field in relation to the signals from *endo*-protons [16]. In some cases the ASIS effect cannot be used for determining the *exo*- or *endo*-configuration [17].

Another possibility for assigning *exo*- and *endo*-configurations to these complexes is given by analyzing ^{1}H NMR spectra in the range of coordinated aromatic ring protons (δ 4.5–6.0 ppm), which was first demonstrated by Jackson [18] for chromium tricarbonyl complexes of 1-substituted indanes. For *endo*-isomers, V, the substituent R is oriented in the direction of $Cr(CO)_3$ group which apparently favours the formation of the preferred conformation, A *, where carbonyl groups are mostly located under C^1 and C^3 carbon atoms. This results in further additional downfield shift of H^1 and H^3 signals, as compared to those from H^2 and H^4, under the influence of the CO groups magnetic anisotropy. Therefore, the spectra of coordinated nucleus protons (100 MHz) of *endo*-isomers, Vb and Vd can be analyzed in the first order approximation. In the spectra of the corresponding *exo*-isomers IIIa–e for which there is no preferred conformation of this type the difference in the chemical shifts of H^1–H^4 protons is not so large and such simple analysis is impossible.



(A)

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* This very conformation takes place in the crystal of (η^6-1-*endo*-benzylindene)chromium tricarbonyl [1].

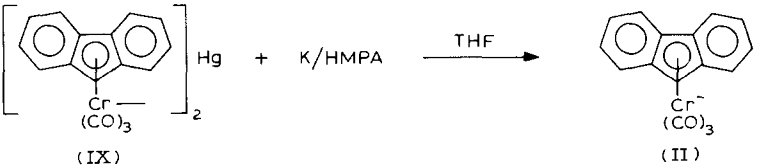
To check these assumptions *exo*- and *endo*-isomers of (η^6-9-substituted fluorene)chromium tricarbonyls with known configuration were synthesized, their ^{1}H NMR spectra in $CDCl_3$ and C_6D_6 were studied, and IIIb was subjected to X-ray analysis.

Synthesis of isomers with known configuration

The complexes with *exo*-configuration IIIb and IIIc were obtained according to eq. 1 by treating I with $C_6H_5CH_2I$ and CH_3COOD, respectively. To obtain the starting anion I, free from the admixture of II, it was produced in THF at temperatures not higher than $-40°C$ which prevented isomerization of I into II [19].

^{1}H NMR spectra of an *exo*-derivative of IIIc in C_6D_6 showed a broadened and slightly distorted triplet with J(HD) 3.5 Hz. Broad band decoupling from deuterium ^{1}H{^{2}D} resulted in the triplet collapsing to a narrow singlet with a chemical shift of δ 3.35 ppm equal to the *endo*-proton shift in VI which points to an *exo*-orientation of deuterium. The admixture of the *endo*-deuterium isomer Vc does not exceed 5%. Therefore, the selectivity of reaction 1 with CH_3COOD is about 95%. Reaction 1 with benzyl iodide seems to be completely stereospecific.

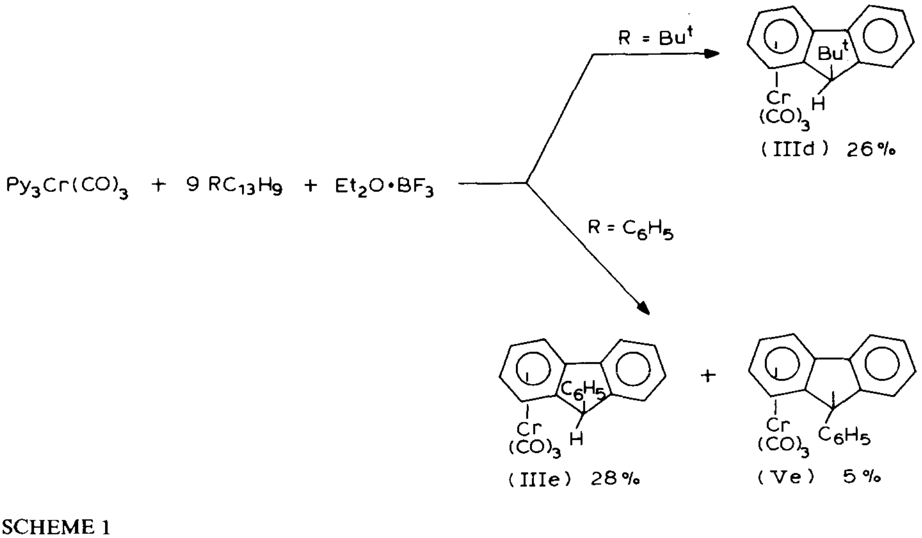
The corresponding *endo*-isomers Vb and Vc were obtained by reacting II with CH_3COOD and $C_6H_5CH_2X$, respectively, eq. 2. To minimize the admixtures of the isomeric anion I, II was obtained as in eq. 3



(3)

When the saturated potassium solution in HMPA was used for reducing the mercury compound (IX), the process time could be shortened to 10 min.

The ^{1}H{^{2}D} NMR spectrum of the *endo*-deutero derivative Vc obtained as in eq.



SCHEME 1

2 shows the singlet at δ 3.10 ppm (C_6D_6) which corresponds to the *exo*-proton in VI and indicates an *endo*-orientation of deuterium. The admixture of *exo*-deutero derivative IIIc does not exceed 5%. Stereoselectivity of the reaction, II, with CH_3COOD is 95%.

Reactions of 9-substituted fluorenes with $Py_3Cr(CO)_3$

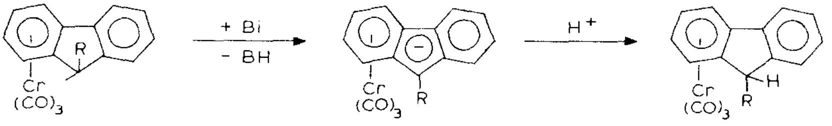
Interaction between 9-phenylfluorene and $Py_3Cr(CO)_3$ in ether using the technique suggested by Öfele [20] gave the mixture of IIIe and Ve with the yields 28 and 5%, respectively. According to ^{13}C NMR spectra the chromium tricarbonyl group was coordinated to the fluorene ring, rather than to the phenyl group. Unlike other pairs of isomers, IIIe and Ve were separated by chromatography. Interaction of 9-t-butylfluorene with $Py_3Cr(CO)_3$ in similar conditions yielded exclusively the *exo*-isomers IIId (see the reaction Scheme 1).

Heating 9-phenylfluorene with $Cr(CO)_6$ to 140°C in diglyme/heptane mixture gave IIIe and Ve with yields of 14 and 1%, respectively.

Different stereochemical reaction results with 9-substituted fluorenes seem to be due to the steric requirements of the substituents. The reaction of 9-methylfluorene with $(NH_3)_3Cr(CO)_3$ yields a mixture of *exo*- and *endo*-9-methylfluorenechromium tricarbonyls in the ratio of about 1/1 [21], while 9-t-butylfluorene yields a chromium tricarbonyl complex with only an *exo*-configuration.

Inversion of configuration IIId,e to Vd,e

The possibility of this conversion is due to the stereospecificity of the reaction of I with electrophiles. Deprotonation of *exo*-isomers IIId and IIIe results in the corresponding η^6-anions whose protonation leads to *endo*-complexes Vd and Ve (eq. 4).



(4)

(IIId, R = Bu^t;
IIIe, R = Ph)

(Vd, R = Bu^t;
Ve, R = Ph)

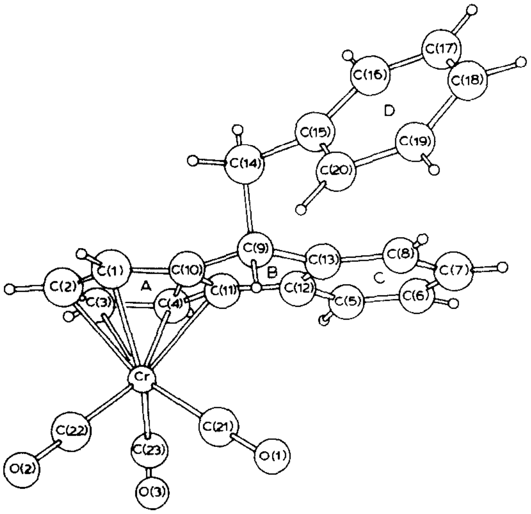


Fig. 1. The molecular geometry of IIIb.

TABLE 2

ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS IN IIIb (with e.s.d.'s in parentheses)

Atom	x	y	z	B
Cr	0.59976(5)	0.12140(2)	0.46894(4)	
O(1)	0.39529(31)	0.20791(10)	0.33871(21)	
O(2)	0.57967(35)	0.04223(11)	0.24767(23)	
O(3)	0.24843(30)	0.05603(11)	0.55504(23)	
C(1)	0.89649(35)	0.14653(12)	0.45518(26)	
C(2)	0.85596(36)	0.09130(11)	0.52134(31)	
C(3)	0.74644(37)	0.08807(11)	0.62359(28)	
C(4)	0.66986(37)	0.13957(12)	0.66156(24)	
C(5)	0.53699(34)	0.27436(11)	0.69866(23)	
C(6)	0.50187(37)	0.33378(13)	0.69477(26)	
C(7)	0.58108(34)	0.37386(11)	0.60746(25)	
C(8)	0.69694(32)	0.35509(10)	0.52199(22)	
C(9)	0.84976(34)	0.26265(11)	0.44195(22)	
C(10)	0.82340(34)	0.19795(11)	0.49341(23)	
C(11)	0.71100(32)	0.19489(11)	0.59665(22)	
C(12)	0.65197(32)	0.25508(11)	0.61397(22)	
C(13)	0.73323(32)	0.29512(11)	0.52522(22)	
C(14)	1.05032(34)	0.28990(11)	0.44152(24)	
C(15)	1.08256(33)	0.35560(11)	0.39984(25)	
C(16)	1.14868(36)	0.40216(12)	0.47952(26)	
C(17)	1.16797(45)	0.46278(14)	0.44381(33)	
C(18)	1.12288(44)	0.47765(13)	0.32810(38)	
C(19)	1.05834(39)	0.43252(13)	0.24765(28)	
C(20)	1.03921(37)	0.37159(13)	0.28324(25)	
C(21)	0.47384(37)	0.17343(12)	0.38864(26)	
C(22)	0.58918(37)	0.07228(11)	0.33260(26)	
C(23)	0.38470(35)	0.08019(11)	0.52027(26)	
				B_{iso}
H(1)	0.97338(419)	0.14893(143)	0.38341(301)	4.06(83)
H(2)	0.90284(457)	0.05576(157)	0.49500(330)	5.11(93)
H(3)	0.72313(467)	0.05138(157)	0.66556(351)	5.24(94)
H(4)	0.59422(473)	0.13996(158)	0.72786(340)	5.28(98)
H(5)	0.48397(466)	0.24721(161)	0.75586(338)	5.52(95)
H(6)	0.42248(413)	0.34849(143)	0.75163(300)	3.97(81)
H(7)	0.55793(453)	0.41391(156)	0.60631(323)	4.80(90)
H(8)	0.74764(397)	0.38208(137)	0.46237(301)	4.14(80)
H(9)	0.80042(401)	0.26380(137)	0.35514(287)	3.76(79)
H(141)	1.11081(413)	0.26497(142)	0.38556(302)	4.06(82)
H(142)	1.10188(422)	0.28671(142)	0.52367(314)	4.36(82)
H(16)	1.17428(443)	0.39014(149)	0.55930(316)	4.76(87)
H(17)	1.21071(545)	0.49285(187)	0.49978(387)	7.29(115)
H(18)	1.13425(503)	0.51837(174)	0.30398(372)	6.46(109)
H(19)	1.02545(472)	0.44209(161)	0.16964(346)	5.43(95)
H(20)	1.00014(460)	0.34111(160)	0.22865(327)	5.36(93)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	2.91(2)	2.42(2)	3.51(2)	0.37(1)	−0.44(2)	0.03(1)
O(1)	7.22(13)	5.72(11)	5.57(11)	3.10(10)	−1.73(10)	0.52(9)
O(2)	8.21(16)	6.02(12)	5.41(12)	2.23(11)	−1.05(11)	−2.11(10)
O(3)	3.79(12)	5.58(11)	7.89(15)	−0.45(9)	0.28(10)	0.52(10)
C(1)	2.72(12)	3.34(11)	4.87(14)	0.55(8)	−0.06(10)	−0.22(10)
C(2)	3.13(12)	3.00(10)	4.73(17)	0.94(8)	−1.19(12)	0.00(11)

(continued)

TABLE 2 (continued)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(3)	4.12(14)	2.99(10)	5.11(14)	0.08(9)	−1.40(11)	0.89(10)
C(4)	3.55(13)	3.71(11)	3.18(12)	−0.26(9)	−0.53(10)	0.87(9)
C(5)	3.45(12)	3.79(11)	3.19(11)	−0.15(9)	0.79(9)	−0.04(9)
C(6)	3.26(14)	4.45(12)	4.08(13)	0.61(10)	0.94(10)	−0.87(11)
C(7)	3.10(12)	3.15(10)	4.49(13)	0.76(8)	0.15(10)	−0.43(9)
C(8)	3.82(11)	2.97(9)	3.31(10)	0.36(8)	0.04(9)	0.27(8)
C(9)	2.76(12)	2.77(9)	3.01(11)	0.27(8)	0.46(8)	0.03(8)
C(10)	2.47(12)	2.82(9)	3.32(11)	0.21(8)	−0.02(8)	0.01(8)
C(11)	2.61(11)	2.91(10)	2.94(11)	−0.02(8)	−0.44(9)	0.11(8)
C(12)	2.59(11)	3.01(9)	2.42(10)	−0.06(8)	−0.13(8)	−0.15(8)
C(13)	2.27(11)	3.00(9)	2.69(10)	0.09(7)	−0.04(9)	−0.07(9)
C(14)	3.08(12)	3.47(10)	4.17(12)	0.37(8)	0.55(9)	0.33(9)
C(15)	2.38(12)	3.39(11)	3.92(13)	0.19(8)	0.85(9)	0.25(10)
C(16)	3.29(13)	4.47(12)	4.13(12)	−0.16(9)	0.17(10)	−0.11(10)
C(17)	4.62(17)	3.85(13)	6.27(20)	−0.19(11)	0.29(14)	−0.99(13)
C(18)	4.74(17)	3.31(13)	7.71(22)	0.47(11)	0.70(15)	0.72(14)
C(19)	4.21(14)	4.89(13)	4.88(14)	0.67(10)	0.36(11)	1.19(11)
C(20)	3.35(14)	4.12(12)	3.93(13)	−0.04(9)	0.52(10)	0.04(10)
C(21)	4.12(14)	3.40(11)	3.84(13)	0.78(9)	−0.64(11)	−0.21(10)
C(22)	4.27(14)	3.46(11)	4.57(13)	1.19(9)	−0.55(11)	−0.36(10)
C(23)	3.26(13)	3.24(10)	4.71(13)	0.20(8)	−0.79(10)	−0.05(10)

The molecular geometry of IIIb

Figure 1 shows the molecular structure of IIIb, Table 2 gives atomic coordinates and anisotropic thermal parameters, Tables 3 and 4 present interatomic distances and valent angles. Basic bond distances in IIIb are within the same range as for

TABLE 3

BOND DISTANCES (Å) FOR IIIb

Cr–C(21)	1.817(3)	Cr–C(22)	1.847(3)
Cr–C(22)	1.835(3)	O(1)–C(21)	1.165(4)
O(2)–C(22)	1.143(4)	O(3)–C(23)	1.155(3)
C(1)–C(2)	1.414(4)	C(1)–C(10)	1.392(4)
C(2)–C(3)	1.394(4)	C(3)–C(4)	1.406(4)
C(4)–C(11)	1.409(4)	C(5)–C(6)	1.371(4)
C(5)–C(12)	1.381(4)	C(6)–C(7)	1.384(4)
C(7)–C(8)	1.387(4)	C(8)–C(13)	1.386(3)
C(9)–C(10)	1.520(3)	C(9)–C(13)	1.518(4)
C(9)–C(14)	1.548(3)	C(10)–C(11)	1.415(4)
C(11)–C(12)	1.468(3)	C(12)–C(13)	1.400(3)
C(14)–C(15)	1.504(4)	C(15)–C(16)	1.389(4)
C(15)–C(20)	1.384(4)	C(16)–C(17)	1.379(4)
C(17)–C(18)	1.371(5)	C(18)–C(19)	1.369(5)
C(19)–C(20)	1.385(4)		
Cr–C(1)	2.236(3)		
Cr–C(2)	2.207(3)		
Cr–C(3)	2.213(3)		
Cr–C(4)	2.211(4)		
Cr–C(10)	2.228(3)		
Cr–C(11)	2.219(2)		

TABLE 4

VALENT ANGLES (°) FOR IIIb

C(21)-Cr-C(22)	89.4(1)	C(21)-Cr-C(23)	87.6(1)
C(22)-Cr-C(23)	89.9(1)	C(2)-C(1)-C(10)	118.7(3)
C(1)-C(2)-C(3)	121.1(2)	C(2)-C(3)-C(4)	120.5(2)
C(3)-C(4)-C(11)	118.7(2)	C(6)-C(5)-C(12)	119.1(2)
C(5)-C(6)-C(7)	120.4(3)	C(6)-C(7)-C(8)	121.1(2)
C(7)-C(8)-C(13)	118.9(2)	C(10)-C(9)-C(13)	102.0(2)
C(10)-C(9)-C(14)	110.9(2)	C(13)-C(9)-C(14)	114.8(2)
C(1)-C(10)-C(9)	129.3(2)	C(1)-C(10)-C(11)	120.5(2)
C(9)-C(10)-C(11)	110.1(2)	C(4)-C(11)-C(10)	120.5(2)
C(4)-C(11)-C(12)	131.0(2)	C(10)-C(11)-C(12)	108.5(2)
C(5)-C(12)-C(11)	130.4(2)	C(5)-C(12)-C(13)	121.2(2)
C(11)-C(12)-C(13)	108.4(2)	C(8)-C(13)-C(9)	129.6(2)
C(6)-C(13)-C(12)	119.4(2)	C(9)-C(13)-C(12)	111.0(2)
C(9)-C(14)-C(15)	113.0(2)	C(14)-C(15)-C(16)	120.6(2)
C(14)-C(15)-C(20)	121.1(2)	C(16)-C(15)-C(20)	118.2(2)
C(15)-C(16)-C(17)	120.8(3)	C(16)-C(17)-C(18)	120.0(3)
C(17)-C(18)-C(19)	120.3(3)	C(18)-C(19)-C(20)	119.8(3)
C(15)-C(20)-C(19)	120.9(3)	Cr-C(21)-O(1)	178.4(2)
Cr-C(22)-O(2)	178.7(3)	Cr-C(23)-O(3)	177.6(2)

other arenechromium tricarbonyl complexes. The average Cr–C (cycle) distance is 2.219 Å, II, the distance from Cr to the ring plane equals 1.713(3) Å. The geometry of the chromium tricarbonyl group is also quite normal, with the average Cr–C(CO) and C–O distances equal to 1.833(15) and 1.154(12) Å, respectively. All the individual rings in the fluorene system are planar with the dihedral angles A–B 1.2, A–C 2.3, B–C 1.6, A–D 57.7; B–D 58.5; C–D 60.0 and ABC–D 58.9°.

The projection of the chromium tricarbonyl group to the plane A of the coordinated ring is shown in Fig. 2.

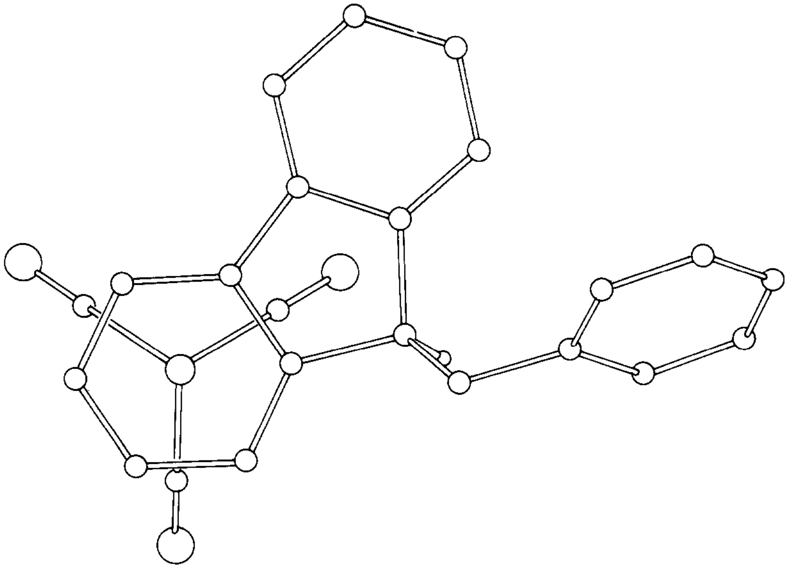


Fig. 2. The projection of chromium triarbonyl group on the A plane.

Thus, the X-ray analysis data unambiguously confirm the conclusions drawn from ^1H NMR spectra, which supports the use of the ASIS effect as a criterion for determining geometrical configurations of the complexes of 9-substituted fluorenes.

Experimental

All the operations, except for TLC, were carried out under an argon atmosphere. Ether and tetrahydrofuran were purified over sodium benzophenoneketyl. Silica gel Chemapol L 40-100 μ was used for chromatography. 9-phenylfluorene was obtained as described in [22]. ^1H NMR spectra were taken on XL-100 "Varian".

Interaction of I with benzyl iodide

0.07 g (1.1 mmol) of n-butyllithium in hexane solution was added to the solution of 0.3 g (1 mmol) of η^6-fluorenechromium tricarbonyl (VI) in 50 ml of ether at −20°C. The mixture was stirred for 30–40 min at −15°C and diluted with hexane to complete precipitation of a red-orange solid. The supernatant was removed and the precipitate was washed with cold hexane and dissolved in 20 ml of THF at −20°C. 0.26 g (1.2 mmol) of benzyl iodide was added to the resulting solution and the mixture was stirred at −20°C for 30 min. The THF was removed in vacuo and the precipitate dissolved in benzene and chromatographed on SiO_2 in a benzene/petroleum ether mixture. The basic yellow band showed 0.08 g (20%) (η^6-9-*exo*-benzylfluorene)chromium tricarbonyl (IIIb); M.p. 140–141°C, ν(CO) ($CHCl_3$) 1900, 1977 cm^{-1}.

The crystals of the quality required for X-ray analysis were obtained by slow crystallization of IIIb from the benzene/heptane mixture.

Synthesis of IIIc by reacting I with CH_3COOD

An excess of potassium solution in HMPA was added to a solution of 0.1 g (0.3 mmol) of VI in 25 ml THF at −20°C while stirring. The deprotonation degree was determined by IR spectra. Then the reaction mixture was cooled to −50°C and treated with CH_3COOD solution prepared from 3.2 g (32 mmol) $(CH_3CO)_2O$ and 10 g D_2O under reflux. After several minutes of stirring THF was removed in vacuo, the residue was extracted with benzene, washed with water and filtered through a silica gel layer. Heptane was added to the benzene solution, and the crystals formed after evaporating benzene in vacuo were collected and dried. The yield was 0.04 g (39.9%).

Synthesis of Vc by reacting II with CH_3COOD

A solution of 0.15 g (0.18 mmol) of $[\eta^5\text{-}C_{13}H_9(CO)_3Cr]_2Hg$ in 25 ml THF at −50°C was treated with an excess of potassium solution in HMPA, and the temperature was raised to −20°C. The end of the reaction (formation of II) was determined by IR spectra. The red solution was cooled to −78°C and CH_3COOD solution prepared as described above was added. The solution turned yellow. THF was removed in vacuo, the residue was extracted with benzene, washed with water and filtered through a silica gel layer, reprecipitated from benzene by heptane and then washed with pentane. 0.08 g (70%) of yellow crystals of Vc were collected. M.p. 162–163°C (dec), ν(CO)(THF) 1900, 1972 cm^{-1}.

Conversion of IIId to Vd

0.2 g (0.97 mmol) of dry t-BuOCs was added to a solution of 0.1 g (0.28 mmol) of

IIId in 15 ml of THF at 25°C, and the mixture was immediately cooled to -10°C. After deprotonation was complete, control by IR spectra, 0.4 g (7 mmol) of CH_3COOH in 5 ml THF was added to the red solution at the same temperature. The solution turned yellow. After solvent removal, in vacuo, the residue was chromatographed on a silica gel column (30 × 2.5 cm) in petroleum ether/benzene mixture under gradual increase of the benzene portion. The yellow zone gave 0.03 g (30%) of yellow crystals of Vd. M.p. 151–152°C, ν(CO) (CH_2Cl_2) 1892, 1968 cm^{-1}.

Conversion of IIIe into Ve

0.11 g of dry potassium t-butoxide was added to a solution of 0.2 g (0.52 mmol) of IIIe in 12 ml of THF at -40°C. The solution turned red. After 5 min stirring at -20°C 0.06 g (1 mmol) of CH_3COOH was added. The solvent was removed in vacuo and the residue was reprecipitated from benzene with heptane with a Ve yield of 0.173 g (87%).

Synthesis of IIId

0.69 g (4.9 mmol) of $(C_2H_5)_2O \cdot BF_3$ was added to a mixture of 0.24 g (1.1 mmol) of 9-t-butylfluorene and 0.40 g (1.1 mmol) of $(C_5H_5N)_3Cr(CO)_3$ in ether (30 ml) at 0°C with stirring. The reaction proceeded at room temperature for 30–45 min. Water was added to the mixture and the ether solution was dried over $MgSO_4$ and removed in vacuo. The residue was reprecipitated from a benzene/heptane mixture and washed with pentane. The yield of yellow crystals of IIId was 100 mg (26%). M.p. 147–149°C. ν(CO)(CH_2Cl_2) 1892, 1968 cm^{-1}. Found: C 66.92; H 5.18; Cr 14.50. $C_{20}H_{18}CrO_3$ calcd.: C 67.1; H 5.02; Cr 14.5%.

Interaction of 9-phenylfluorene with $Py_3Cr(CO)_3$

6.2 ml (38 mmol) of freshly distilled $F_3B \cdot OEt_2$ was added to a mixture of 3 g (12.5 mmol) of 9-phenylfluorene and 4.81 g (11.6 mmol) of $Py_3Cr(CO)_3$ in 150 ml of ether at 0°C. After stirring at 25°C for 30 min the solution was filtered, washed three times with water and the ether layer was dried over $MgSO_4$. After removing the ether in vacuo the residue was chromatographed on a silica gel column (3 × 40 cm). The *exo*-phenyl complex IIIe was eluted with benzene/petroleum ether mixture in a ratio 1/4. After evaporating the solvent in vacuo 1.37 g (28%) of IIIe was obtained as yellow crystals. M.p. 139–141° (dec). ν(CO) (THF) 1900, 1972 cm^{-1}. Found: C 70.10; H 3.96; Cr 13.67. $C_{22}H_{14}CrO_3$ calcd.: C 69.84; H 3.73; Cr 13.74%. The *endo*-phenyl complex Ve was eluted with benzene/petroleum ether mixture in a ratio 1/1. 0.24 g (5%) of yellow crystals of Ve was obtained.

Synthesis of η^6,η^6-fluorenebis(chromium tricarbonyl) (VIII)

A mixture of 0.5 g (1.65 mmol) of VI and 2 g (30 mmol) of $(NH_3)_3Cr(CO)_3$ in 30 ml of dioxane was boiled for 10 h. The reaction mixture was filtered off and the dioxane was removed in vacuo. The residue was chromatographed on silica gel plates in a 1/1 benzene/petroleum ether mixture with double exposure of the plates in the chromatographic chamber. Two yellow bands, without a distinct border between them, were developed. The upper band corresponded to the original VI and the lower one to VIII.

After extracting the lower band with CH_2Cl_2 and precipitating it with hexane 0.15 g (21%) of VIII was obtained. M.p. 179–180°C. ν(CO)($CHCl_3$) 1903, 1965 cm^{-1}. Found: C 52.16; H 2.20; Cr 23.65. $C_{19}H_{10}O_6Cr_2$ calcd.: C 52.05; H 2.28; C 23.74%.

To remove the admixture of VI from the product VIII it was washed with a small quantity of benzene.

X-Ray analysis of IIIb

Yellow crystals of dimensions 0.2 × 0.3 × 0.43 mm were used for this analysis which was carried out on an automated Syntex P1 diffractometer (λ(Mo-K_α)-irradiation, graphite monochromator, $\theta/2\theta$-scan up to $2\theta_{max}$ 60°. The total of 2921 independent reflections was collected, of which 2379 reflections with $I \geqslant 3\sigma(I)$ were used for further computation. The file of experimental reflections was corrected to Lorentz factors and polarization; no correction was made for absorbtion since its contribution was small (μ(MO) 6.8 cm^{-1}).

Basic crystallographic parameters: $C_{23}H_{16}O_3Cr$, mol.wt. = 392.4, $F(000) = 808$, a 7.547(1), b 22.012(9), c 11.023(2) Å, γ 98.04(1)°, V 1813.3(5) $Å^3$, $Z = 4$, d_{calc} 1.44 g/cm^3, space group $P2_1/a$.

The structure was solved by the Patterson method and refined by full-matrix least-squares in anisotropic (Cr, O, C) isotropic (H) approximations. The final value of R factor was 0.031. All computations were performed on the Nova-3 computer using the SHELXTL program complex in Nickolett-P3 system.

Acknowledgement

The authors wish to thank A.N. Kashin for supplying 9-t-butylfluorene.

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