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INDENYL AND FLUORENYL TRANSITION METAL COMPLEXES

VII *. INNERSPHERE "RICOCHET" REARRANGEMENTS ON ALKYLATION OF η^5-INDENYL- AND η^5-FLUORENYLTRICARBONYLCHROMATE ANIONS

A N NESMEYANOV †, N A. USTYNYUK *, L N NOVIKOVA, V G ANDRIANOV,
Yu T STRUCHKOV,
Institute of Organo-Element Compounds, Vavilova St 28, Moscow 117813 (USSR)

Yu A USTYNYUK, Yu F OPRUNENKO and Yu N LUZIKOV
Moscow State University Leninskii Gory Moscow 117234 (USSR)

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Summary

Alkylation of K[η^5-$C_9H_7Cr(CO)_3$] (Xa) with CH_3I and $C_6H_5CH_2Br$ leads to σ-alkyl derivatives of η^5-$C_9H_7Cr(CO)_3Alk$ type. These complexes undergo innersphere "ricochet" rearrangement, with the alkyl group being shifted to the *endo* position at C(1) and the chromium tricarbonyl group shifted to the benzene nucleus The structure of the product of such a rearrangement in the case of η^5-$C_9H_7(CO)_3CrCH_2C_6H_5$, i.e. (1-benzyl-3a,4-7,7a-η^6-indene)chromium tricarbonyl (XVIII), is established by a low temperature X-ray study, indicating an *endo* position for the benzyl radical

On alkylation of equilibrium tautomeric mixtures of η^5- and η^6-fluorenylchromium tricarbonyl anions XIa $\rightleftharpoons$ XIb under similar conditions, the η^5-anion (Xa) yields a σ-alkyl derivative, which is rearranged to (9-*endo*-alkyl-1-4,4a,9a-η^6-fluorene)chromium tricarbonyl Electrophilic attack of the η^6-anion (XIb) takes place on the outer side at C(9) and leads to a corresponding 9-*exo*-alkyl derivative.

Introduction

Many types of π-complexes are known to undergo innersphere rearrangements in which the R group σ-bonded to the metal migrates to the π-ligand.

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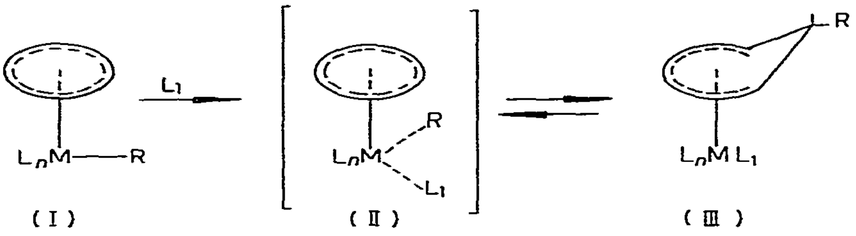
* For part VI see ref 29, for part V see ref. 24
† Deceased

Some of these rearrangements were called "ricochet" rearrangements by A N. Nesmeyanov [1,2]. Cases of R group migration from the π-ligand to the metal are also known [3,4].

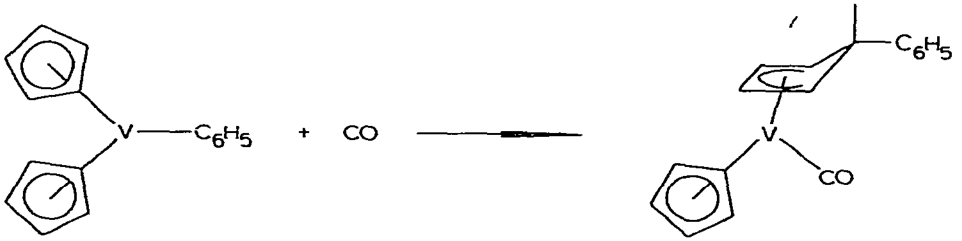
Migrations of σ-bonded groups from the metal to the π-ligand proceed under the influence of an external agent or thermal conditions In the former case the process may be illustrated as in Scheme 1.

SCHEME 1

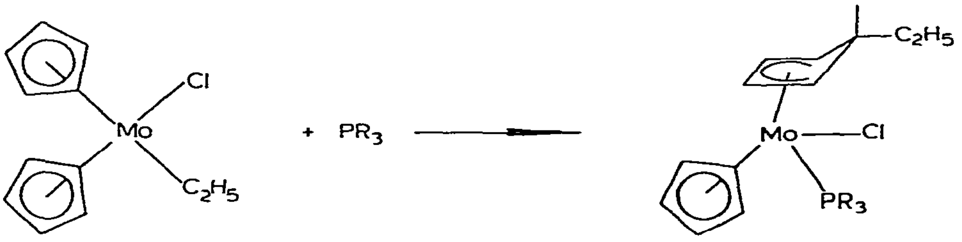


In complex III the cyclic ligand uses one π-electron less for metal bonding as compared to complex I. In the starting complex I the π-ligand is a planar cyclic π-electron system, while in III the cycle is not planar and the carbon atom bonded to the R-group is removed from the ring plane, and the group itself occupies an *endo* position to the metal.

Rearrangements of the type shown in Scheme 1 may be illustrated by the following reactions



[5]

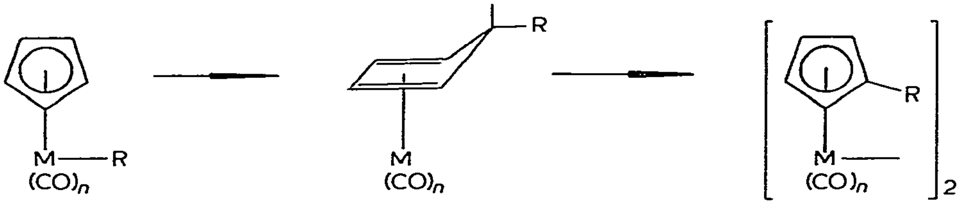


[3]

PR_3 = PEt_3, PMe_2Ph, $PMePh_2$

Complex III is in many cases unstable and undergoes further conversions. These reactions are often very fast and the presence of III as an intermediate is assumed by indirect data. Most often stabilization of III is achieved through a hydrogen and, more seldomly, through a substituent being eliminated from the π-ligand; the process being accompanied by recovery of the planar structure.

The following processes are examples:

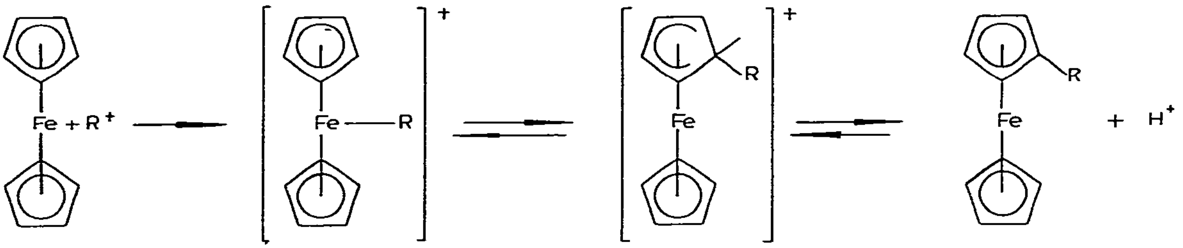


R = $CH_2C_6H_5$ M = Fe n = 2 [6]
M = Mo W n = 3 [6]
R = C_2H_5, M = Mo n = 3 [7]
R = C_6H_5, M = Mo, W n = 3 [8 9]

The thermal conversion of $(\eta^5\text{-}C_5H_5)_2VR$ complexes into the vanadocene derivatives $(\eta^5\text{-}C_5H_5)V(\eta^5\text{-}C_5H_4R)$ [10], the unusual transfer of the group $(C_6H_5)_3B$ from iron to the cyclopentadienyl ring [11] and some other reactions involve similar rearrangements

The formal scheme of "ricochet" rearrangements has been used to describe electrophilic replacement reactions or hydrogen isotopic exchange in acid media in ferrocene and some other π-complexes [12—14]. The system is stabilized in these reactions by a proton or some other electrophilic particle being eliminated from the cationic intermediate (Scheme 2).

SCHEME 2

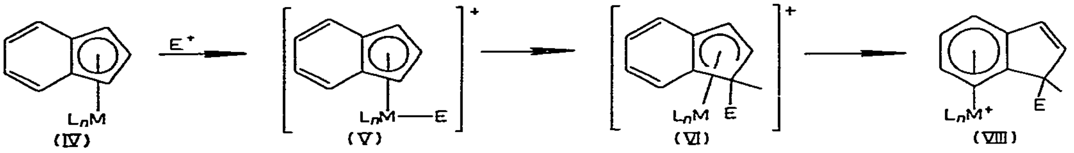


So far the "ricochet" reactions have been illustrated mainly for cyclopentadienyl complexes But similar rearrangements are known to occur with cyclobutadiene [15], cycloheptatriene [16] and cyclooctatetraene [17] transition metal complexes.

Some metal complexes with cyclic conjugated dienes show fast and reversible hydrogen migration between metal and diene fragments, accompanied by diene fragment transfer along the whole cycle, i.e. "diene—enyl" tautomerism [18,19].

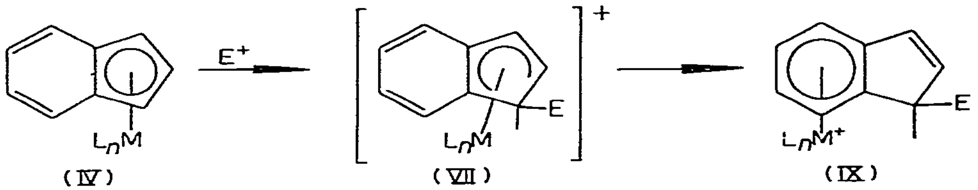
A new means of stabilizing is seen in ricochet rearrangements with polycyclic planar π-ligand complexes; the ligands using only some of their π-electrons for ring—metal bonding. Stabilization of III may be effected through shift of the organometallic group to the neighbouring cycle. The process may be thermodynamically more favoured than rupture of a C—H or C—E bond Such a "ricochet" process with metal shift is illustrated in Scheme 3.

SCHEME 3



There may be another variant of the process, i.e. electrophilic attack at a carbon atom with subsequent or synchronous shift of the organometallic group (Scheme 4)

SCHEME 4

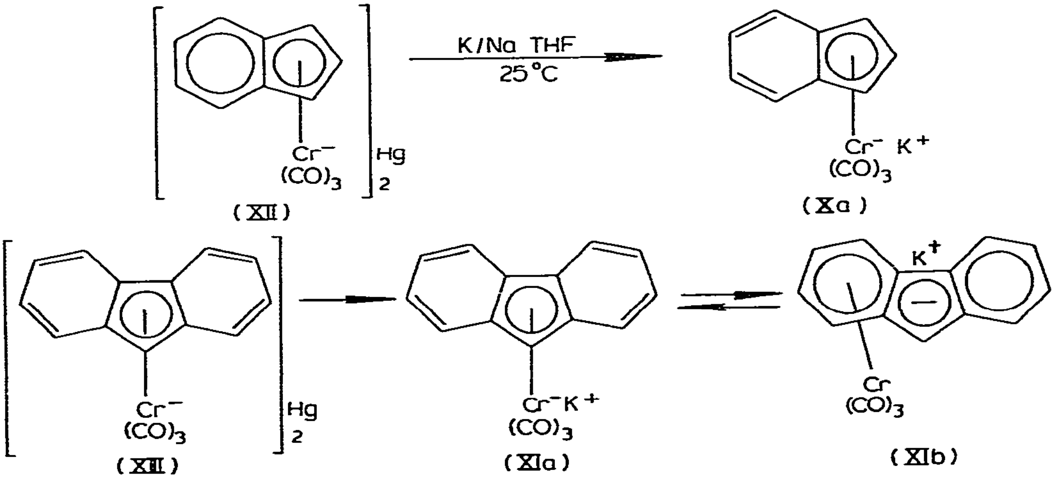


The difference between these two possible mechanisms is seen in the stereochemical result of the reaction. "Ricochet" mechanism always leads to an *endo* configuration in the complex (VIII), while the electrophilic attack on the ring (Scheme 4) yields *exo* complexes (IX). This may become a criterion for choosing between the mechanisms. But it is not always simple to define the stereochemistry of the reaction product Thus if E = D (Schemes 3 and 4) direct X-ray analysis does not show the difference between the *endo* and *exo* isomers, and signal assignment in the NMR spectrum is difficult, made worse because of possible reversibility. For the reasons given above it was not possible to determine the protonation stereochemistry of bis(η^5-indenyl)iron [20], although the authors are in favour of the "ricochet" type process (Scheme 3) The stereochemical result of protonation of $[\eta^5\text{-}C_9H_7M(\eta^5\text{-}C_5Me_5)]^+$ (M = Ir, Rh) [21] is not clear either. Interactions of η^5-indenyl- (Xa) and η^5-fluorenyl-tricarbonylchromate anions (XIa) with methyl iodide and benzyl bromide (iodide) are good subjects for the study of the ricochet processes shown in Scheme 3 by determining the stereochemical result of the reaction.

Discussion

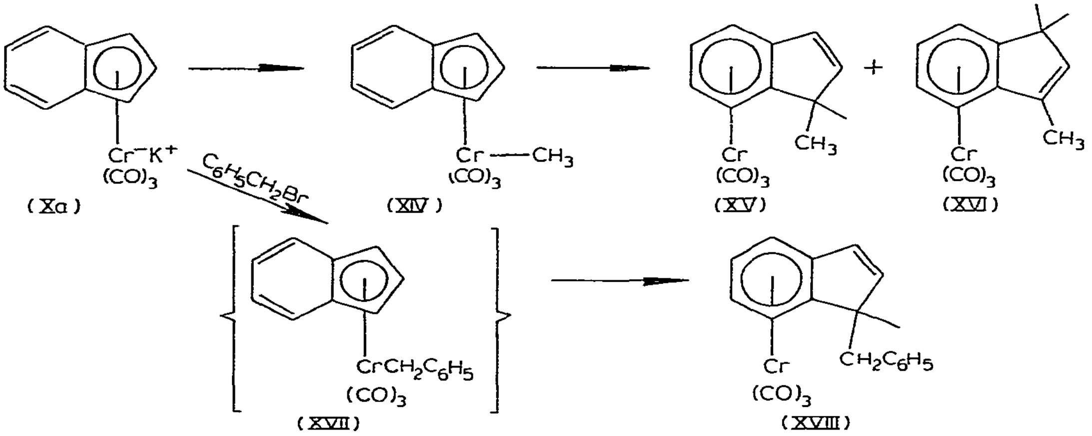
Preliminary results from application of NMR techniques for determining the methylation stereochemistry of Xa and XIa have already been published by us [22,23]. In this work we have performed a direct X-ray analysis of the η^5-indenyltricarbonylchromate anion benzylation product.

η^5-Series anions Xa and XIa are generated by reduction of the corresponding mercury compounds XII and XIII with K/Na alloys [23], as illustrated below:



Anion Xa is not isomerized to the η^6-anion, and the η^5-fluorenyl anion XIa, as we have shown [24], exists as an equilibrium mixture with the η^6-isomer appearing as a result of metallotropic rearrangement (K_{equil} = [XIa]/[XIb] ≈ 7, THF, 25°C). The σ-methyl complex formed through methylation of Xa was characterized by elemental analysis, and IR and ^{1}H NMR data (Scheme 5).

SCHEME 5



Heating of XIV in hexane to 50°C for an hour leads to a mixture of two η^6-isomers in a 1 : 2 ratio [22] The same substances may be derived without intermediate isolation of XIV, but in the latter case the yield is much lower. Structures XV and XVI are determined by ^{1}H NMR, but we failed to produce crystals for an X-ray study. Benzyl chloride does not react with Xa in THF even at 40—50°C The use of benzyl bromide promotes the process considerably, requiring 20 minutes at 30°C. The intermediate σ-benzyl derivative XVII was not seen in the course of reaction process The IR spectrum of XVIII exhibits only ν(C=O) bands typical of arenechromium tricarbonyl complexes (1895 and 1970 cm^{-1}). The ^{1}H NMR spectrum of XVIII (Fig 1) also supports the structure of (1-benzyl-3a,4-7,7a-η^6-indene)chromium tricarbonyl. The signals due to Cr(CO)$_3$-coordinated ring protons are shifted upfield by 1.5—2.0 ppm.

To establish the exact benzyl group position in XVIII unequivocally we carried out its X-ray structure determination Crystals of XVIII are monoclinic, at —120°C a = 12.948(4), b = 13.613(5), c = 13.613(5) Å, β = 113.00(4)°, V = 1556.9(8) Å^3, M = 342.33, d_{calcd} = 1.46 g cm^{-3}, Z = 4, space group $P2_1/a$. Cell parameters and intensities of 1374 independent reflections with $I \geqslant 2\sigma$ were measured with an automated four circle Syntex P2$_1$ diffractometer at —120°C (λ Mo-K_α, graphite monochromator, $\theta/2\theta$ scan, $2 \leqslant 2\theta \leqslant 50°$ absorption corrections neglected, μ (λMo) = 7.8 cm^{-1}) The structure was solved by the heavy atom method and refined by the least squares technique in the full-matrix isotropic (anisotropic for the Cr atom) approximation, R = 0.095, R_w = 0.087. Unfortunately, the structure turned out to be disordered and this naturally affected the accuracy of the molecular geometry determination.

Disorder is caused by the Ph ring occupying two positions. C(11) . . C(16) and C(11*) . . C(16*) as a result of rotation about the C(1)—C(10) bond possibly

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND TEMPERATURE FACTOR ($Å^2$) PARAMETERS ANISOTROPIC TEMPERATURE FACTORS ARE IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{*} + \quad + B_{23}klb^{*}c^{*}]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	2911(1)	131(1)	1531(2)	1 68(7)	1 99(8)	2 02(7)	−0 25(7)	0 81(5)	−0 14(8)
Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
O(1)	1729(7)	−1765(6)	1297(10)	3 9(2)	C(11)	634(17)	−1157(14)	−3921(24)	1 7(4)
O(2)	3287(9)	158(7)	4805(12)	6 0(2)	C(12)	968(19)	−1366(17)	−5067(26)	2,7(5)
O(3)	694(8)	1099(7)	812(11)	5 1(2)	C(13)	356(10)	−2025(9)	−6367(14)	3,4(3)
C(1)	2532(9)	−523(8)	−2065(13)	2 2(2)	C(14)	−694(18)	−2412(15)	−6454(26)	2 1(4)
C(2)	2987(9)	−1574(8)	−1654(13)	2 5(2)	C(15)	−985(11)	−2149(9)	−5227(15)	3 6(3)
C(3)	3774(9)	−1595(8)	−285(13)	2 4(2)	C(16)	−405(18)	−1559(16)	−4065(26)	2 5(4)
C(4)	3936(8)	−616(7)	433(12)	1 7(2)	C(17)	2187(9)	−1022(8)	1371(13)	2 5(2)
C(5)	4670(8)	−272(8)	1841(12)	2 2(2)	C(18)	3134(11)	149(10)	3495(16)	4 2(3)
C(6)	4610(9)	741(8)	2176(13)	2 5(2)	C(19)	1590(11)	733(9)	1128(14)	3 2(3)
C(7)	3858(9)	1378(8)	1117(13)	2 6(2)	C(11*)[a]	874(20)	618(18)	−3340(29)	3 3(5)
C(8)	3127(9)	1022(8)	−296(13)	2 5(2)	C(12*)[a]	−5(21)	−1116(19)	−6939(31)	3 9(6)
C(9)	3165(8)	22(7)	−638(11)	1 9(2)	C(14*)[a]	−124(22)	−2534(19)	−5553(31)	3 5(5)
C(10)	1245(10)	−443(8)	−2741(14)	3 1(2)	C(16*)[a]	−1303(22)	−1201(19)	−5702(32)	4 0(6)

[a] * Carbon atoms in the other Ph ring orientation

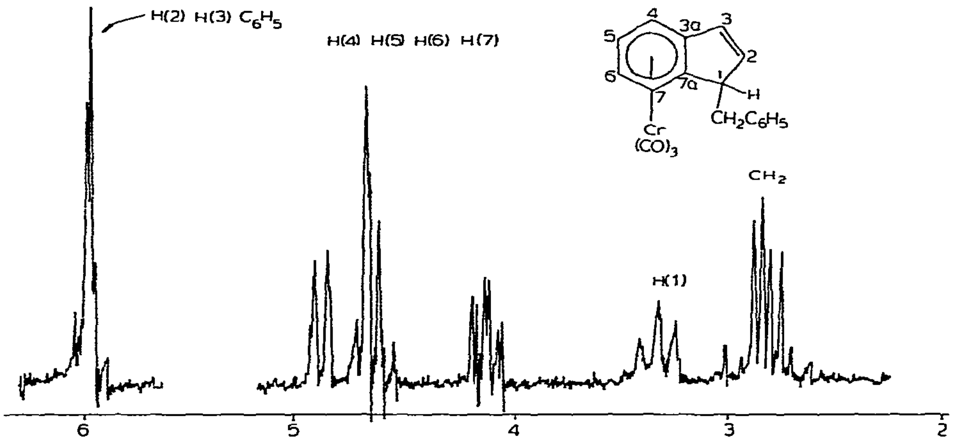


Fig 1 The ^{1}H NMR spectrum of (1-benzyl-3a,4-7,7a-η^6-indene)chromium tricarbonyl (XVIII) in C_6D_6

a smaller rotation about the C(10)—C(11) bond However, the pattern is still more complicated due to almost complete overlapping of C(13), C(15) in one Ph ring position and C(13*), C(15*) in its other position on C(13*), C(15*) and C(13), C(15), respectively, in the molecule related to the reference one by an inversion centre in [(0, 0 — 1/2)] As a result, the C(13), C(13*), C(15) and C(15*) atoms have an effective occupancy $g = 1$, while all the remaining atoms of the Ph ring have $g = 1/2$.

Atomic coordinates and temperature factor parameters are given in Table 1, main bond lengths and angles are shown in Figures 2 and 3 *, respectively In molecule XVIII the Cr atom is bonded to six carbons of the benzene ring in the indenyl ligand and three carbonyl groups. Thus the metal atom acquires a pseudooctahedral coordination typical of (η^6-arene)$Cr(CO)_3$ complexes, and bond angles (O)C—Cr—C(O) are only decreased slightly compared to the ideal value of 90°.

Average distances Cr—C(cycle) of 2.23(1) Å and C—C(cycle) of 1.41(2 (Å)) are close to those found in similar complexes [25]. The metal carbonyl group geometry is also unexceptional with the average bond lengths Cr—C(O) and C—O being 1.80 and 1.18 Å, respectively. As a rule, tricarbonylchromium complexes with fused polycyclic aromatic ligands, where the Cr atom interacts with one benzene ring, show a staggered mutual orientation of a coordinated benzene cycle and the $Cr(CO)_3$ group. However, the complex studied has an almost eclipsed conformation (Fig. 3). The indene system is planar (maximum deviations of carbon atoms from a mean square plane is less than 0.03 Å), both Cr and methylene C(10) atoms are situated at one side of this plane at distances of 1.732(2) and 1.01(1) Å, respectively, confirming the *endo* orientation of the benzyl substituent relative to the $Cr(CO)_3$ fragment

Isolation of the intermediate σ-methyl derivative (XIV) on methylation of the η^5-indenylchromium tricarbonyl anion (Xa) with further rearrangement of XIV to give a mixture of XV and XVI, and the benzylation stereochemistry

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* Only one of two orientations of the Ph ring is presented in the figures

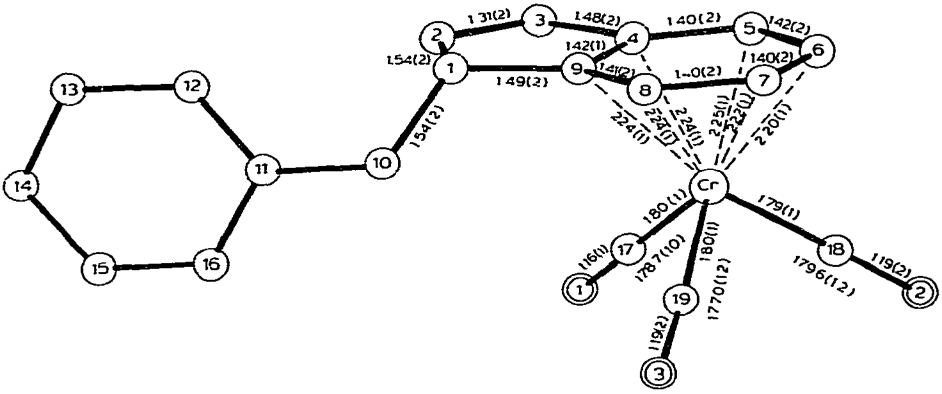


Fig 2 Molecular geometry of XVIII with atom numbering and relevant bond lengths

determined by an X-ray analysis of XVIII, fully prove the "ricochet" mechanism of the reaction. This conclusion gives grounds for interpreting the results alkylation of the tautomeric mixture of η^5- and η^6-fluorenylchromium tricarbonyl anions (XIa and XIb). The XIa/XIb ratio at ambient temperature is $\approx 7/1$. Both anions react independently, as their interconversion rate, found by us from rearrangement kinetics studies [24], is considerably lower than the rate of reaction with CH_3I. The η^6-isomer (XIb) is present in smaller amounts and being more nucleophilic, reacts with CH_3I through a direct attack of the ring with *exo*-isomer formation (XXI) (Scheme 6). The same stereochemical result is observed during reaction of pure XIb generated at low temperature [23] The η^6-anion XIb in this respect behaves as the similar iron [26] and manganese [27] complexes

Methylation of XIa first yields the σ-methyl derivative (XIX) which cannot be isolated, but may be identified in the IR spectrum by the presence of the typical $\nu(CO) = 2007$ cm^{-1} band As a result of ricochet rearrangement, XIX

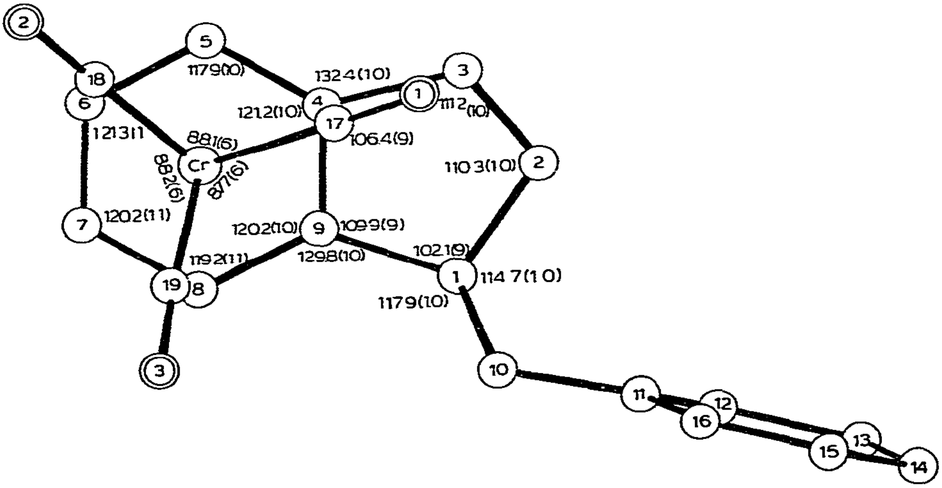
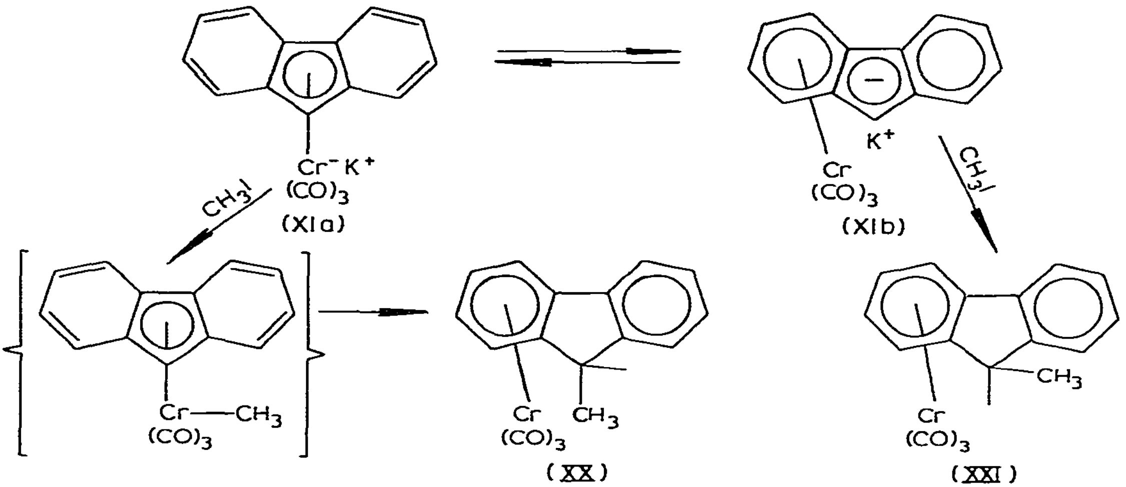


Fig 3 Projection of the molecule XVIII on the benzene ring plane with relevant bond angles

SCHEME 6

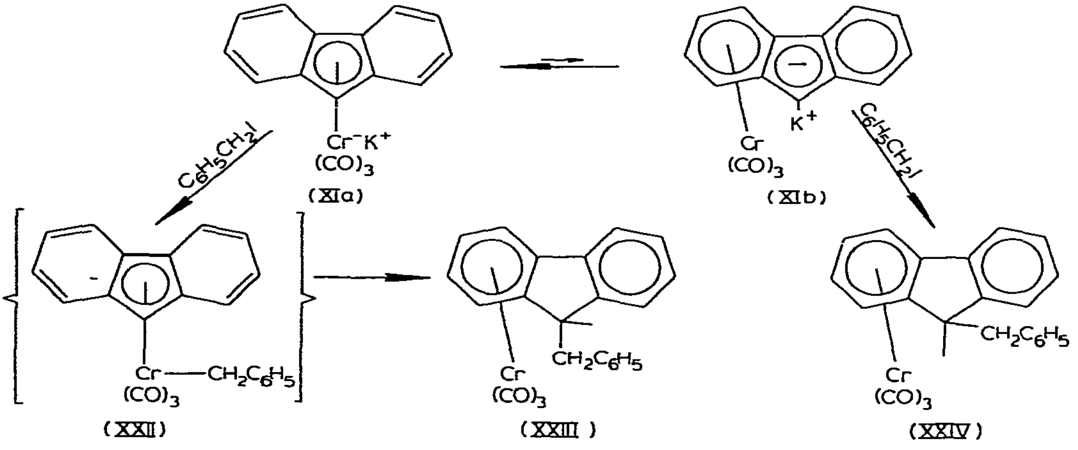


converts to (9-*endo*-methyl-1-4,4a,9a-η^6-fluorene)chromium tricarbonyl (XX)

Isomers XX and XXI are not completely separated chromatographically Their 3 : 1 ratio was found by integration of methyl group signals in the ^{1}H NMR spectrum This ratio is much lower than that of the starting anions XIa and XIb (7 1), and most probably this may be explained by low thermal stability of the intermediate XIX, the bulk of which decomposes without rearrangement

Benzyl bromide benzylation of the XIa $\rightleftharpoons$ XIb mixture in THF at 40—45°C does not yield crystalline product (Scheme 7) With benzyl iodide the reaction takes place at temperatures below 0°C. In the IR spectrum of the reaction mixture, one can see, as in the case of reaction with CH_3I, intermediate formation of a σ-benzyl derivative (XXII), characterized by a 2004 cm^{-1} band which quickly disappears during isomerisation of XXII Chromatographically isolated fractions failed to produce crystals suitable for X-ray analysis Elemental analysis, and IR, ^{1}H NMR spectra showed the substance to be a single isomer, i.e. (9-*endo*-benzyl-1—4,4a,9a-η^6-fluorene)chromium tricarbonyl (XXIII) The *exo* isomer XXIV was not isolated; this may be due to loss from the mother liquor during crystallization

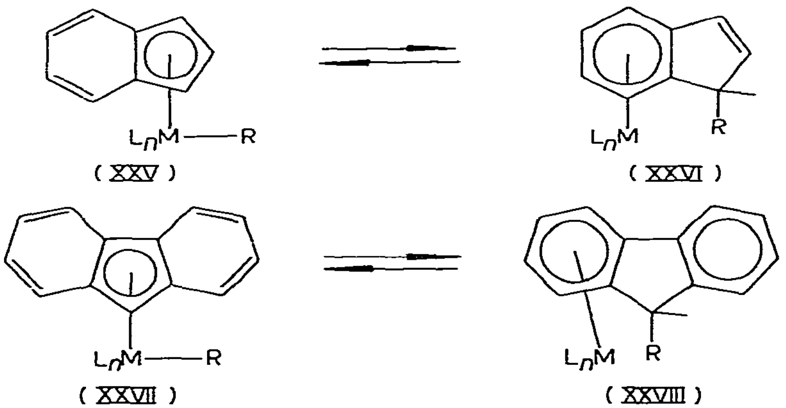
SCHEME 7



Thus η^5-anions Xa and XIa react with alkyl halides by a ricochet rearrangement (Scheme 3) If such processes are conducted in THF, without intermediate isolation of σ-alkyl derivatives, the yields are as low as 10—40% and it is not possible to evaluate the losses due to instability of the σ-alkyl intermediate. It is preferable to use alkyl iodides, as the reaction proceeds under milder conditions, and the initially formed σ-derivatives may either be isolated (reaction of Xa with methyl iodide) or identified in the IR spectrum. Reaction of Xa with benzyl bromide proceeds only at 40°C. At this temperature the rates of σ-benzyl complex XVII isomerization and formation are comparable. For this reason the complex is not seen in the IR spectra Alkyl halides with branched radicals were not used in the reactions, as it is known that metalcarbonyl anions do not produce corresponding σ-derivatives in reasonable amount with these [28].

At present it is not clear whether the transfers of alkyl and $Cr(CO)_3$ groups is synchronous or sequential It may be assumed that rearrangements shown in Scheme 8 will be equilibrium and reversible processes, provided the pairs of η^5- and η^6-isomers have similar thermodynamic stabilities In principle, this can be achieved by varying the ligands (alterations of R and L, introduction of substituents into indenyl and fluorenyl ligands, selection of metal M etc.) Of major importance is probably the ratio of energies of the C—R and M—R bonds. In our work "ricochet" isomerization is irreversible, the "hard" alkyl, bonded to the "soft" metal migrates to a ligand carbon atom. Extra energy released due to formation of a strong carbon—carbon bond is the driving force of the rearrangement. On the contrary, if "soft" alkyl-tin or -germanium halogenides (R = $SnMe_3$, $GeEt_3$) are used as electrophiles, the first complexes formed having element—transition metal bonds are, as we have shown [23], quite stable. For intermediate types of electrophiles there may be found agents for which the innersphere ricochet rearrangements are reversible Further results will be presented in our future publications.

SCHEME 8



(XXV) (XXVI)

(XXVII) (XXVIII)

Experimental

All operations, except thin-layer chromatography, were carried out under argon. THF was purified by boiling over K/Na alloy and distillation immediately before use. Silica gel L 40/100 μ (Chemapol, Czechoslovakia) was used for chromatography. ^{1}H NMR spectra were determined on a Varian XL-100 instrument. Starting mercury derivatives with η^5-structures (XII and XIII) were made according to previously described techniques [23]

K[η^5-$C_9H_7(CO)_3Cr$] (Xa) interaction with benzyl bromide

0.5 g (0.003 mol) of benzyl bromide was added at once to a tetrahydrofuran solution of K[η^5-$C_9H_7(CO)_3Cr$] derived from 1.0 g (0 0014 mol) of [η^5-$C_9H_7(CO)_3Cr$]$_2$Hg. The compound was stirred for 15—20 minutes at 30—35°C Then the solvent was removed in vacuo, the residue was treated with hexane and the extract was concentrated to 1/2 of the volume and cooled to —70°C The residue precipitated was separated from the mother liquor and chromatographed on a thin layer of silica gel in 1/1 benzene/petroleum ether mixture The main yellow band with R_f 0 48 to 0 6 was collected After solvent removal and recrystallization from benzene/heptane mixture, 0 14 g (15%) of XVIII was obtained M.p 99—100°C (decomposition) ν(C≡O) (CH_2Cl_2) 1895, 1970 cm^{-1} ^{1}H NMR (C_6D_6, δ, ppm) see Fig 1, CH_2-group AB-part of ABX spectrum at 2.76 (2 H), five-membered ring (H(1)-X part of ABX spectrum at 3 26 (1 H) H(2) and H(3) multiplet at 6 0 (2 H), coordinated six-membered ring 4 62 (2 H), 4.88 (1 H), 4 1 (1 H) The proton signal of the benzyl group six-membered ring coincides with the solvent signal

Reaction of tautomeric anion mixture (XIa $\rightleftharpoons$ XIb) with methyl iodide

0 16 ml (0 0025 mol) of freshly distilled CH_3I was added at —70°C while stirring to the equilibrium anion mixture XIa $\rightleftharpoons$ XIb in THF, prepared from 0.5 g (0.00062 mol) [η^5-$C_{13}H_9(CO)_3Cr$]$_2$Hg (XIII) 15—20 minutes after CH_3I addition the temperature of the reaction mixture was gradually raised to room temperature. At 0°C the IR spectrum of the reaction mixture did not show any starting anions XIa and XIb (ν(C═O) see ref 22), while absorption bands with ν(C═O) 1897, 1932, 1970 and 2007 cm^{-1} appeared. At room temperature, the high frequency band ν(C═O) 2007 cm^{-1} had completely disappeared, and the band intensity at 1932 had decreased THF was removed in vacuo, the residue was benzene treated, and the extract was chromatographed on a thin layer of silica gel in 1/1 benzene/petroleum ether mixture. The main yellow band (R 0.36 to 0.6) was collected. 0.12 g (54%) of compounds XX and XXI was obtained after the solvent was removed in vacuo The ^{1}H NMR spectrum of the product appeared as a superposition of those described earlier for XX and XXI separately [23]

The XX/XXI ratio in the mixture was equal to 3/1 as estimated from relative intensities of methyl group signals.

Interaction of tautomeric anion mixture XIa $\rightleftharpoons$ XIb with benzyl iodide

A solution of 0.2 g (0.0009 mol) of benzyl iodide in 5—8 ml of THF was added to the anion mixture, generated from 0 47 g (0.0017 mol) [η^5-$C_{13}H_9$-$(CO)_3Cr$]$_2$Hg (XIII), and cooled to —70°C. Then the temperature of the reaction was raised to ambient At 0°C the IR spectrum contained bands at 1930 and 2004 cm^{-1}, assigned to XXIII. Above 0°C the latter band disappeared completely during the rearrangment and the former decreased to a certain extent

After removal of THF in vacuo, the residue was treated with benzene, the extract was filtered, and chromatographed on a thin layer of silica gel in 1/1 benzene/petroleum ether The wide yellow band (R_f 0.47 to 0 63) was collected. After reprecipitation from benzene/heptane, the yellow amorphous substance was chromatographed on a thin layer of silica gel in 1/2 benzene/petroleum ether with double plate exposure in chromatographic chamber. The main yellow band (R_f 0 12 to 0.45) was collected Reprecipitation from benzene/heptane mixture yielded 0.15 g (11 25%) of (9-*endo*-benzyl-1-4,4a,9a-η^6-fluorene)-chromium tricarbonyl (XXIII), with m p 153—155°C (dec).

ν(C=O) ($CHCl_3$) 1908, 1977 cm^{-1} (C_6D_6, δ. ppm)· (CH_2, AB part of ABC spectrum at 3 15 (2 H). (H(1), C part of ABC spectrum 3.21 (1 H): coordinated six-membered ring 5 1 (1 H) 4.96 (1 H), 4 8 (1 H), 4 2 (1 H), non-coordinated six-membered ring and benzyl group aromatic ring protons as overlapping multiplets with centre of gravity at 6 94. Found. C, 69.57, H, 4.01; Cr, 13.20. Calcd. for $C_{23}H_{16}O_3$: C, 70 4: H, 4 08, Cr, 13.30%.

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