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INDENYL AND FLUORENYL TRANSITION METAL COMPLEXES

VIII *. SYNTHESIS, STRUCTURE AND PROPERTIES OF METAL CARBONYL DERIVATIVES OF AZAFLUORENES, INDOLE, CARBAZOLE AND THE CORRESPONDING ANIONS

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Summary

The interaction of indole, carbazole and aza-analogues of fluorene, 1-azafluorene (I), 2-azafluorene (II), 3-methyl-II (III), 3-azafluorene (IV), 4-azafluorene (V), 7-methyl-V (VI) and [2,3]benzo-V (VII) with $Cr(CO)_6$ (diglyme/heptane, 140°C), and with $(NH_3)_3Cr(CO)_3$ (boiling dioxan) and of II with $[BrM(CO)_5][NEt_4]$ (M = Cr, Mo, W) has been studied. In all cases II and IV form only N-donor complexes of the $LCr(CO)_5$ type, and the other heterocycles: arenechromium tricarbonyl derivatives coordinated to the benzene, and not the heterocyclic, ring. The interaction of I and III with $(NH_3)_3Cr(CO)_3$ results in the formation of a mixture of both types of complexes, predominantly arene ones. Reactions with $(NH_3)_3Cr(CO)_3$ give appreciably higher yields than similar processes involving $Cr(CO)_6$. Deprotonation of arenechromium tricarbonyl compounds (THF, t-BuOK) leads to η^6-anions which reversibly isomerize in the case of complexes III, V and VI into η^5-anions. These are new examples of metallotropic tautomerism in which the metal "slips" between the rings along

* For part VII see J. Organometal. Chem., 226 (1982) 239.
** Deceased.

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the plane of the aromatic ligand. In the case of η^6-anions of complexes of indole, carbazole, I and VII no such isomerization takes place. Alkylation of η^6-anions yields 9-*exo*-alkyl compounds. These are also the only substances that can be isolated from the alkylation of tautomeric mixtures of anions obtained from XI, XIII and XXIV.

Introduction

Reversible isomerization of η^6- and η^5-fluorenylchromium tricarbonyl anions and their stereospecific alkylation, recently reported by us, constitute a new type of metallotropic rearrangements [1]. Expanding the range of polynuclear aromatic ligands makes it possible to study the influence of ligand structure on such processes and to increase the number of possible structural types of compounds capable of such transformations. In the present work we report on the synthesis of the arenechromium tricarbonyl-type complexes of indole, carbazole and fluorene aza-analogues, i.e., 1-azafluorene (I), 2-azafluorene (II), 3-methyl-2-azafluorene (III), 3-azafluorene (IV), 4-azafluorene (V), 7-methyl-4-azafluorene (VI) and [2,3]benzo-4-azafluorene (VII) *, as well as a number of N-donor complexes of these ligands of the $LCr(CO)_5$ type, on their deprotonation and some reactions. The first results for chromium carbonyl complexes II, III, V and VI have been published [2].

Results and discussion

1. Interaction of $Cr(CO)_6$ with indole, carbazole and azafluorenes

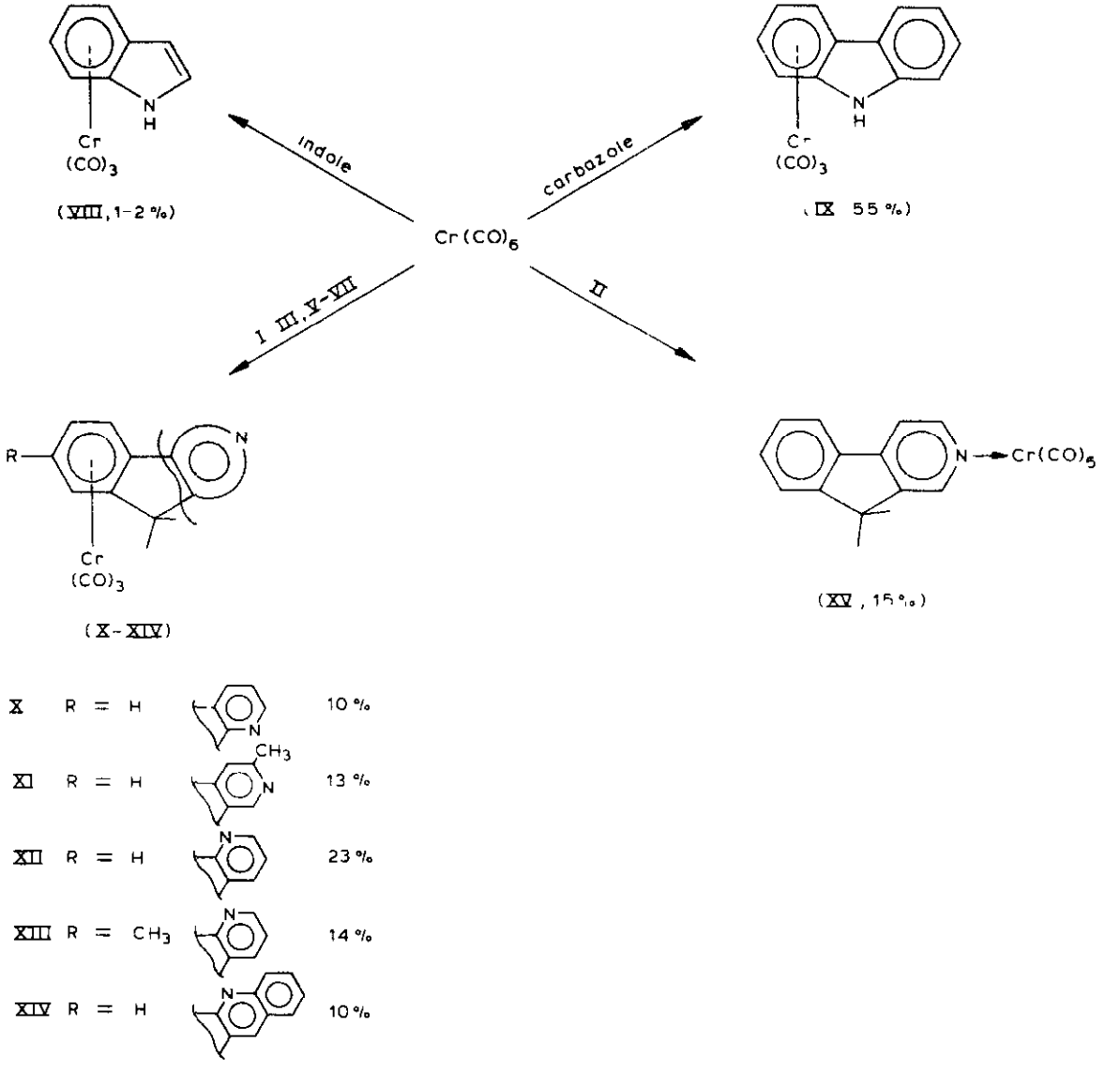
Thermal reaction of chromium carbonyl with aromatic hydrocarbons is one of the principal methods of synthesizing arenechromium tricarbonyl complexes. The best results in these reactions are, as a rule, obtained by an optimal choice of the solvent and the temperature conditions. We have studied the interaction of indole, carbazole and azafluorenes I—III and V—VII with chromium carbonyl in a boiling diglyme/heptane (≈1/1) mixture. Under these conditions a sufficiently high temperature is ensured in the reaction mixture, and it is possible to use Strohmeier's modified head to return the sublimed $Cr(CO)_6$ into the reaction sphere. Results of the reactions are shown in Scheme 1.

Arenechromium tricarbonyl complexes form indole, carbazole and azafluorenes I, III and V—VII in yields of the order of 10—25%. Only carbazole complex IX is obtained with a yield of 55%. The lower yield of VIII and X—XIV is probably caused by too drastic reaction conditions leading to a partial decomposition, as well as by losses in the chromatographic separation. The synthesis of XI—XIII has already been described by us [2]. Derivatives of indole and carbazole VIII and IX were first obtained by Fischer and coworkers [3] from the interaction of free arenes with $Cr(CO)_6$ in dibutyl ether in yields of 80 and 46%,

* In accordance with the nomenclature recommended by IUPAC, the azafluorenes used in this work are designated as: I, 9 H-indeno[2,1-b]pyridine; II, 9 H-indeno[2,1-c]pyridine; IV, 5 H-indeno[1,2-c]pyridine; V, 5 H-indeno[1,2-b]pyridine; VII, 10 H-indeno[1,2-b]quinoline. We use the trivial names to stress the genetic relationship between azafluorene and fluorene systems.

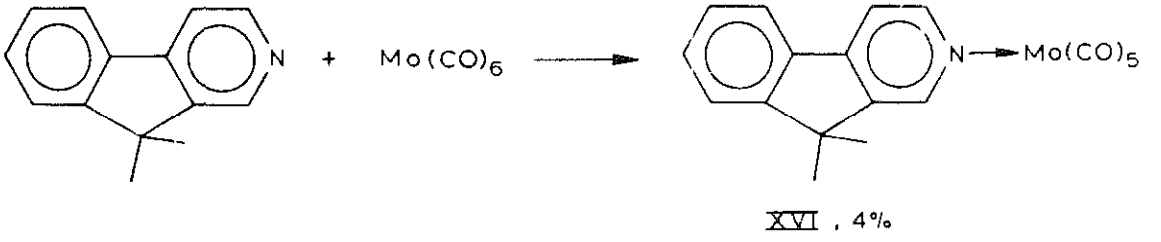
respectively. Our attempts to obtain indole complex VIII by Fischer's procedure failed; the yield did not exceed 1—2%. Complexes VIII and IX obtained in a diglyme/heptane mixture and purified chromatographically melt with decomposition at 155—157 and 180—182°C, respectively, which is much higher than the melting points given in the literature [3], 95 and 110°, respectively.

SCHEME 1



2-Azafluorene (II) with $Cr(CO)_6$ forms the N-donor complex XV. Similar complexes for the other azafluorenes seem to be unstable in the reaction conditions. For I and III they have been obtained under milder conditions (see below).

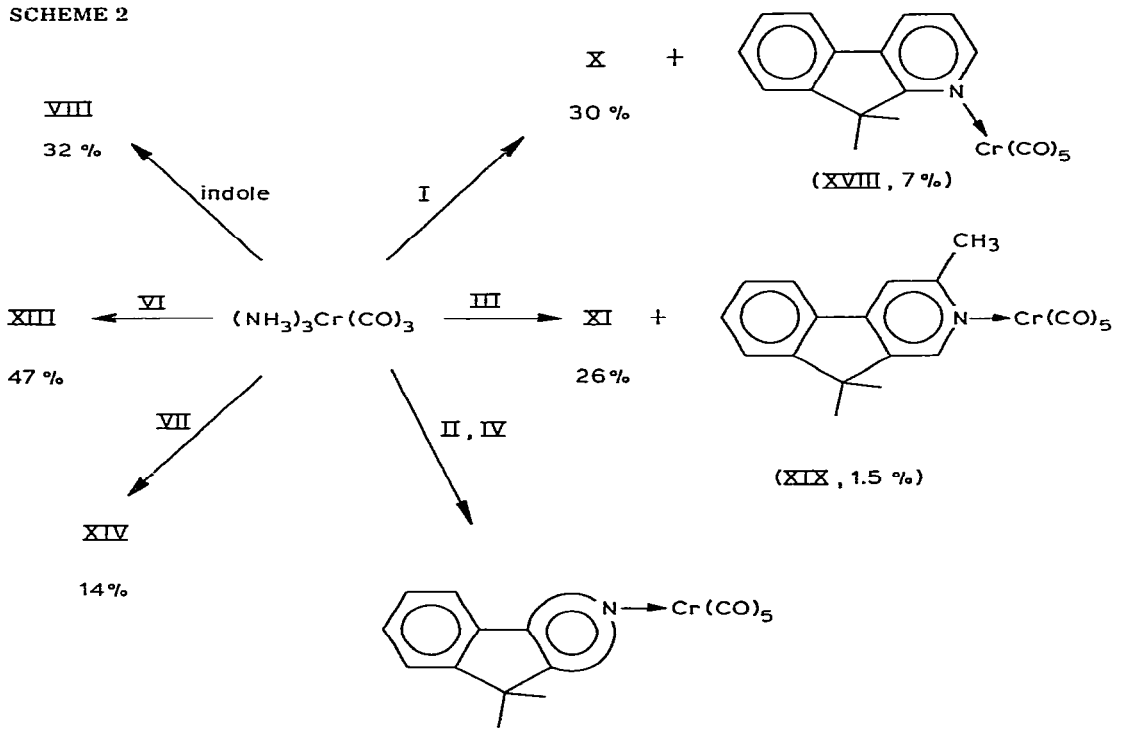
In a similar way II reacts with $Mo(CO)_6$; the yield of the N-donor complex XVI is lower because of low stability of this compound.

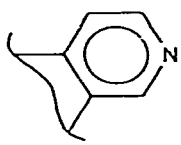


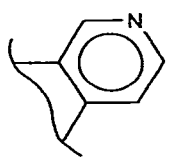
2. Interaction of indole and azafluorenes with $(NH_3)_3Cr(CO)_3$

Thermal interaction of arenes with $(NH_3)_3Cr(CO)_3$ (Rausch's method [4]) proceeds under milder conditions (boiling dioxan) than a similar process with the participation of $Cr(CO)_6$. This is why it usually gives better yields in the synthesis of arenechromium tricarbonyl complexes with limited stability. Results of the reactions of nitrogen-containing arenes with $(NH_3)_3Cr(CO)_3$ in boiling dioxan, studied by us, are shown in Scheme 2.

SCHEME 2



XV  14 %

XVII  5 %

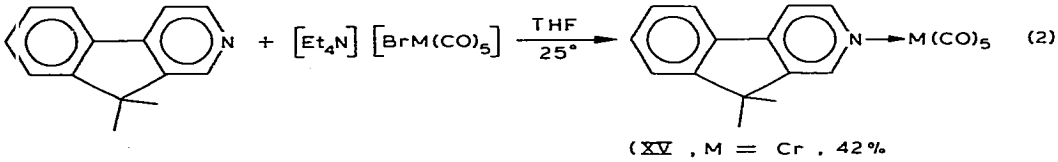
It is clear that for the given set of heterocycles such interactions can have three results: i) formation of exclusively arene complexes VIII, XIII and XIV is observed in the reactions of $(NH_3)_3Cr(CO)_3$ with indole and azafluorenes VI and

VII; ii) N-donor complexes XV and XVII are formed when $(NH_3)_3Cr(CO)_3$ interacts with 2- and 3-azafluorenes; iii) mixtures of arene and N-donor complexes result from the reactions of $(NH_3)_3Cr(CO)_3$ with azafluorenes I and III. Comparing Schemes 1 and 2 one can see that the yield of arenechromium tricarbonyl complexes obtained by Rausch's method is higher than that from reactions with $Cr(CO)_6$, even when a mixture of arene and N-donor complexes is formed. In these cases (i.e., reactions of $(NH_3)_3Cr(CO)_3$ with I and III) the yield of η^6-complexes X and XI is higher than for the $LM(CO)_5$ type of derivatives XVIII and XIX. On the other hand, in this case complexes of the N-donor type are also formed more readily, which is confirmed by the fact that XVIII and XIX are isolated.

The lower yield of 3-azafluorene derivative XVII is, most probably, caused by the instability of the initial IV, which is readily transformed into 3-azafluorenone-9. Addition of the chromium pentacarbonyl group to the nitrogen atom raises the oxidative stability of 3-azafluorene ligand.

3. Reactions of $[Et_4N]$ $[BrM(CO)_5]$ (M = Cr, Mo, W) with 2-azafluorene

The interaction of $[Et_4N]$ $[XM(CO)_5]$ with amines is a convenient method to synthesize N-donor complexes of the carbonyls of Group VIA metals [5]. As applied to 2-azafluorenes, this method makes it possible to obtain N-donor complexes of all the metals of the chromium subgroup:



(XV, M = Cr, 42%
XVI, M = Mo, 18%
XX, M = W, 41%)

In reaction 2 the yield of complexes XV and XVI is higher than in the other methods (cf. Scheme 1 and eq. 1, for XV also Scheme 2). Application of reaction 2 to 4-azafluorene does not lead to complexes of the XV type [2].

All complexes of the arenechromium tricarbonyl type, VII—XIII, are yellow crystalline substances with high melting points and are stable in air over long periods of time. Complex XII is red. Their structure is easily determined from IR and ^1H and ^{13}C NMR spectra. In the IR spectra (Table 1) in the $\nu(CO)$ region they show two intense *A* (1960—1990 cm^{-1}) and *E* (1880—1910 cm^{-1}) bands. In the ^1H NMR spectra proton signals from the metal-coordinated benzene ring are shifted upfield on average by 1.5—2.0 ppm as compared with their position in the spectrum of the free ligand, and lie in the region of 4.5—6.5 ppm. Chemical shifts of the protons of the uncoordinated rings (6.5—8.5 ppm) do not change their position significantly in comparison with their position in the free ligand spectrum. In the ^{13}C NMR spectra (Table 2) the shift of the signals from metal-bonded carbon atoms to high field amounts to 20—40 ppm.

Complexes of the $LM(CO)_5$ type, XV—XX, are yellow high-melting substances, stable in air in the solid state over long periods of time. Chromium derivatives XV, XVI and XVIII are less soluble in organic solvents than the arenechromium-

TABLE 1

VALUES OF ν(CO) FREQUENCIES (cm^{-1}) IN IR SPECTRA OF η^6-π-COMPLEXES OF THE $LCr(CO)_3$ TYPE AND OF THE CORRESPONDING η^5- AND η^6-ANIONS IN THF. EQUILIBRIUM CONSTANTS OF THE METALLOTROPIC REARRANGEMENT ($K_{eq.}^{28°}$) [a]

η^6-Complex			η^6-Anion [b]			η^5-Anion [b]			$K_{eq.}^{28°}$
	A_1	E		A_1	E		A_1	E	
XXI	1968	1895	XXIa	1927	1841 1817	XXIb	1905	1807 1766	14.30 [c]
VIII	1960	1875	VIIIa	1936	1850 1825		—	—	—
IX	1964	1888	IXa	1940	1860 1835		—	—	—
X	1974	1903	Xa	1932	1847		—	—	—
XI	1976	1903	XIa	1932	1851 1828	XIb	1910	1814 1771	6.00
XII	1973	1900	XIIa	1933	1856 1820	XIIb	1911	1810 1774	0.37
XIII	1971	1899	XIIIa	1930	1852 1808	XIIIb	1911	1800 1770	0.15
XIV	1975	1902	XIVa	1934	1858 1813		—	—	—
XXII	1975	1902	XXIIa	1929	1848 1825	XXIIb	1907	1812 1770	8.75
XXIII	1970	1893	XXIIIa	1930	1852 1810	XXIIIb	1907	1800 1772	0.45
XXIV	1970	1895	XXIVa	1930	1850 1805	XXIVb	1905	1795 1770	0.20
XXXI	1970	1892	XXXIa	1930	1845		—	—	—

[a] $K_{eq.}^{28°}$ = [η^5-anion]/[η^6-anion]. [b] Frequencies are given for K salts of these anions. [c] Value corrected for degradation.

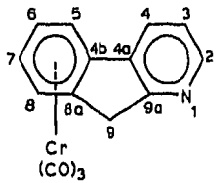
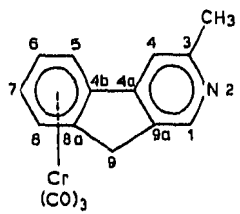
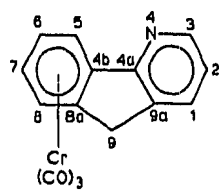
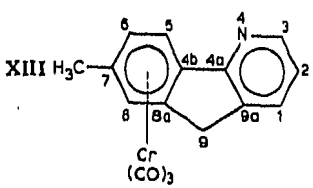
tricarbonyl complexes of the same ligands but have a higher mobility on Al_2O_3 and SiO_2, which seems to be associated with blocking of the nitrogen unshared electron pair. In the IR spectra of these compounds in the ν(CO) region 4 bands are seen with frequencies practically coinciding with those observed in the $PyCr(CO)_5$ spectrum [6], which confirms the structure of these substances.

The result of reactions of nitrogen-containing heterocycles with different chromium carbonyl derivatives is thus determined by the nature of the heterocycle and the carbonyl and by temperature conditions. To obtain η^6-complexes VIII—XIV, the best results are produced by Rausch's method, and for the synthesis of N-donor compounds XV—XX it is more convenient to use the interaction of heterocycles with $[M(CO)_5Br]NEt_4$ (eq. 2). For the arene derivatives there was not a single case of π-complexing on the pyridine moiety.

The ease of formation of N-donor complexes is mainly determined by the nitrogen atom environment. In those cases when there is an alkyl group in the *ortho* position to the nitrogen or a neighbouring "key" carbon atom the stability of derivatives of the pyridinechromium pentacarbonyl type decreases,

TABLE 2

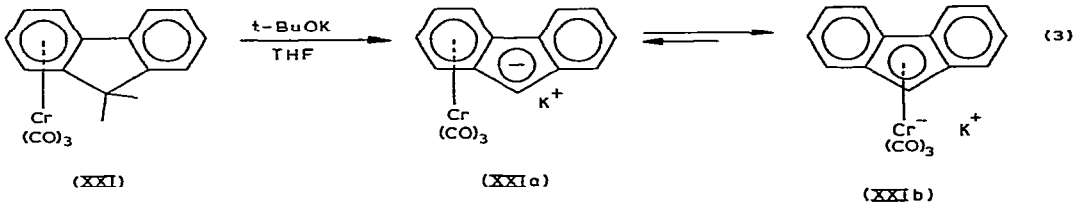
PARAMETERS OF ^{13}C NMR SPECTRA FOR η^6-π-COMPLEXES OF THE $LCr(CO)_3$ TYPE IN $CDCl_3$, δ (ppm) RELATIVE TO TMS (δ = 0.00 ppm)

	π-Complex	Chemical shifts of the ring C_n atoms. Pyridine ring (benzene ring)						Chemical shifts of other hydrocarbons		
		1 (8)	2 (7)	3 (6)	4 (5)	4a (4b)	9a (8a)	C(9)	CH_3	CO
X		— (89.67)	148.91 (91.61)	121.91 (90.21)	127.07 (86.40)	132.51 (107.21)	162.64 (110.46)	38.41	—	232.34
XI		145.00 (88.99)	— (92.81)	157.22 (89.46)	113.66 (87.44)	147.41 (105.65)	133.20 (113.79)	34.53	24.33	231.94
XII		32.19 (89.02)	122.26 (92.82)	148.58 (89.92)	— (87.44)	157.82 (107.41)	135.31 (112.84)	34.27	—	232.31
XIII		132.12 (89.75)	121.98 (105.21)	148.46 (90.57)	— (88.19)	157.84 (109.30)	135.21 (114.10)	34.24	20.76	232.57

and in the reactions of indole, carbazole, azafluorenes V—VII with $Cr(CO)_6$ or with $(NH_3)_3Cr(CO)_3$ they are not formed at all. On the contrary, in II and IV there exist no such complicating factors, and they form only complexes of the pyridine type, XV and XVII. In distinction to pyridine, which is capable of substituting up to three carbonyl groups in $M(CO)_6$ (M = Cr, Mo, W), azafluorenes do not form N-donor complexes containing more than one heterocyclic ligand at the central atom, which seems to be a result of their greater steric requirements.

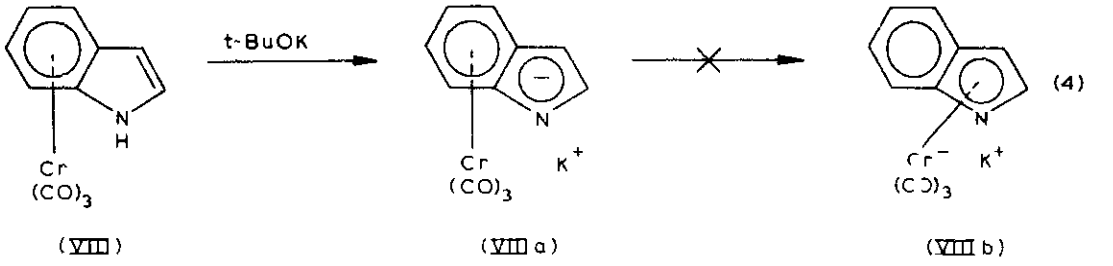
4. Deprotonation of η^6-complexes

In the present series of investigations it was previously shown [7] that deprotonation of η^6-fluorenechromium tricarbonyl (XXI) with an excess of t-BuOK in THF solution at —70°C results in the formation of the η^6-fluorenylchromium tricarbonyl anion (XXIa) which is capable of reversible isomerization into the η^5-form (XXIb) at temperatures higher than —20°C.

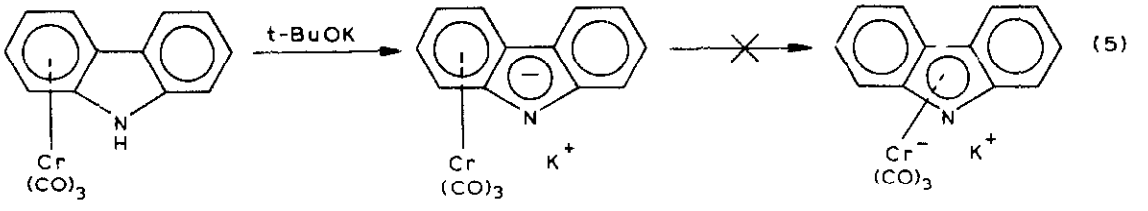


It is convenient to observe this process by means of IR spectra in the ν(CO) region. Assignment of the bands in the XXIa ⇌ XXIb mixture has already been made. The constant of this metallotropic equilibrium, $K_e = [\eta^5]/[\eta^6]$ is significantly dependent on the medium, solvating additives and temperature [7]. For solutions of potassium salts in THF at 28°C it is 7.15. When comparing this value with the equilibrium constants of similar systems it is necessary to take into account that for XXI rearrangement can take place into any of the two equivalent benzene rings with equal probability. With this degeneration taken into account, the corrected value of $K_e = 2[\eta^5]/[\eta^6] = 14.3$ will be used by us subsequently.

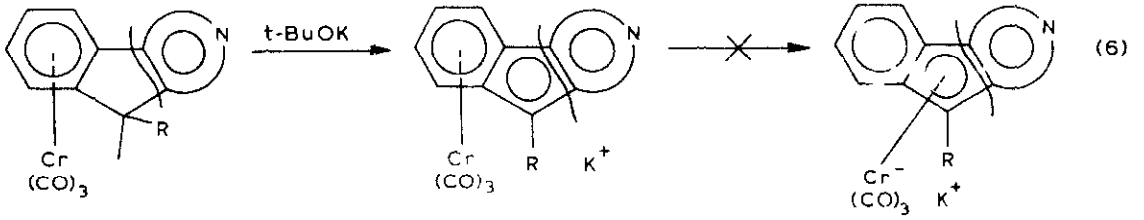
Under the same conditions (THF, t-BuOK excess, —70°C) complexes of the arene type, VIII—XIV, and 9-CH_3 derivatives of some of them, XXII—XXIV, XXXI (synthesis of the latter compounds is described below), are deprotonated with the formation of the η^6-anions VIIIa—XIVa, XXIIa—XXIVa and XXXIa (eq. 4—6), whose IR spectra practically coincide with the spectrum of XXIa (Table 1). The presence of a negative charge on the η^6-anions results in the ν(CO) bands being shifted to a lower frequency and the *E* band being split into two (the latter is not true for the η^6-anion of 1-azafluorene complex Xa). The further course of the reaction depends on the structure of the heterocyclic ligand. In complex η^6-anions of indole and carbazole, VIIIa and IXa, no isomerisation into the η^5-form is observed, as is the case for anions Xa, XXXIa and XIVa. Anions XIa—XIIIa, as well as their 9-methyl derivatives XXIIa—XXIVa, are reversibly converted into the η^5-isomers. The process takes place with a significant rate in THF at temperatures above 0°C (eq. 7). The ν(CO) frequencies of the η^5-anions and the isomerization equilibrium constants (K_{eq}) for η^5- and



(VIII) (VIII a) (VIII b) (4)



(IX) (IX a) (IX b) (5)

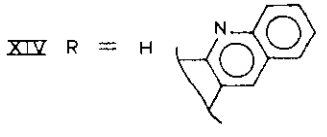


X R = H
XXXI R = CH_3

Xa
XXXIa
XIVa

Xb
XXXIb
XIVb

(6)



XIV R = H

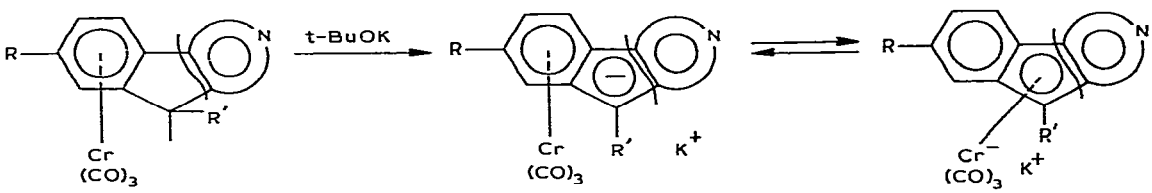
η^6-anions, determined from the optical densities of the *A* bands, are listed in Table 1.

It is seen from these data that placing the CH_3 group in position 9 somewhat increases the relative stability of the η^5-isomers, but that the methyl group in position 7 stabilizes the initial η^6-tautomer. The data for XXIII and XXIV are not very accurate because the deprotonation of these compounds does not go to completion. Equilibria 7 are thus new examples of tautomeric equilibria in which the metal migrates between the rings along the π-electron system plane.

5. Reactions of η^6-anions and η^6,η^5-tautomeric mixtures with electrophiles

Reactions of complex anions of indole (VIIIa) and carbazole (IXa) incapable of isomerization into the η^5-forms with electrophiles (CH_3I, CH_3COCl and p-$CH_3C_6H_4SO_2N(NO)CH_3$) proceed with the addition of the electrophile onto the nitrogen atom (Scheme 3)

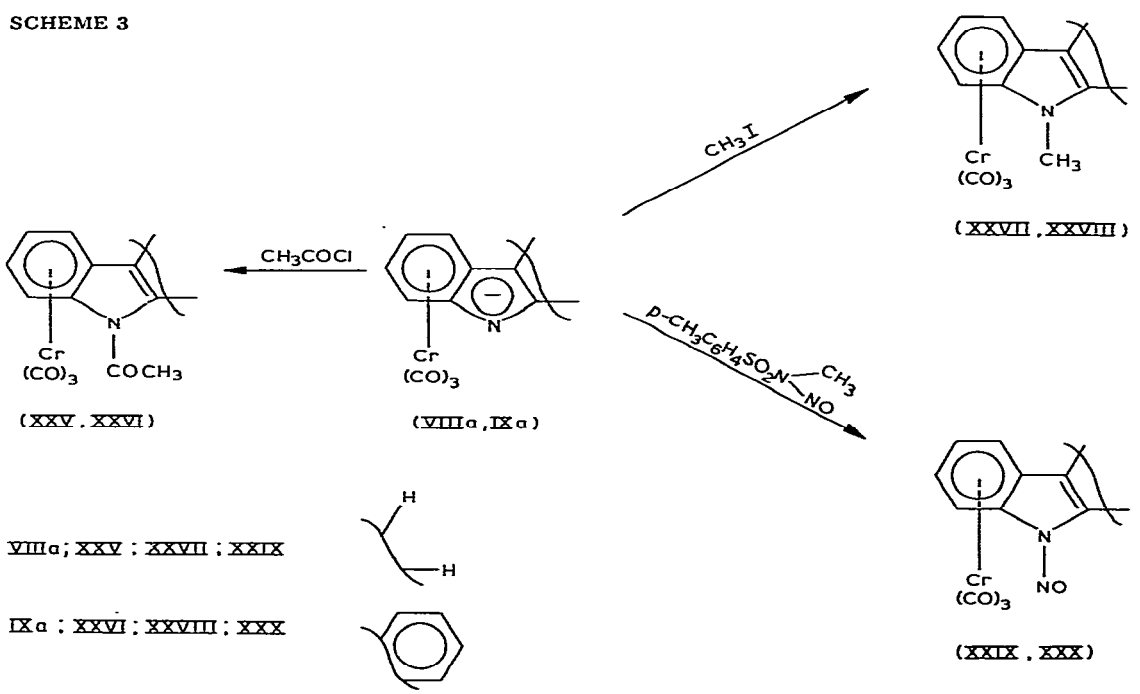
The neutral complexes XXV—XXX could not be thermally rearranged into η^5-isomers.



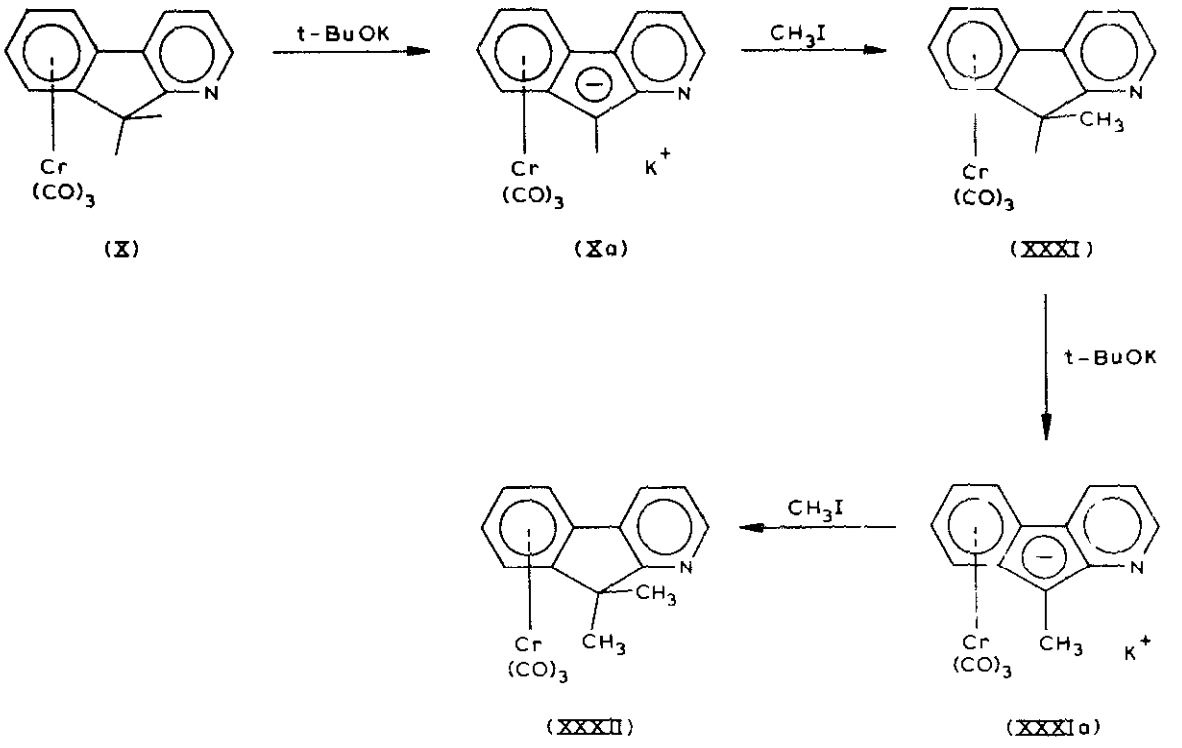
XI	R = R′ = H	XIa	XIb
XXII	R′ = CH3, R = H	XXIIa	XXIIb
XII	R = R′ = H	XIIa	XIIb
XXIII	R′ = CH3, R = H	XXIIIa	XXIIIb
XIII	R′ = H, R = CH3	XIIIa	XIIIb
XXIV	R = R′ = CH3	XXIVa	XXIVb

Methylation of the η^6-anion Xa follows the same route as methylation of η^6-fluorenyl analogue XXIa [8]. The *exo*-methyl compound XXXI is formed if Xa contains no excess of deprotonating base, and the product of exhaustive methylation XXXII if the interaction takes place in the presence of excess t-BuOK (Scheme 4). Formation of an *exo*-methyl derivative in the methylation of XIIa has already been described by us [2]. To obtain pure salts of the η^6-anions, n-butyllithium in ether is used as the base. Lithium salts of η^6-anions are in this case precipitated with hexane, and the excess of butyllithium remaining in solution is removed by decantation.

SCHEME 3



SCHEME 4

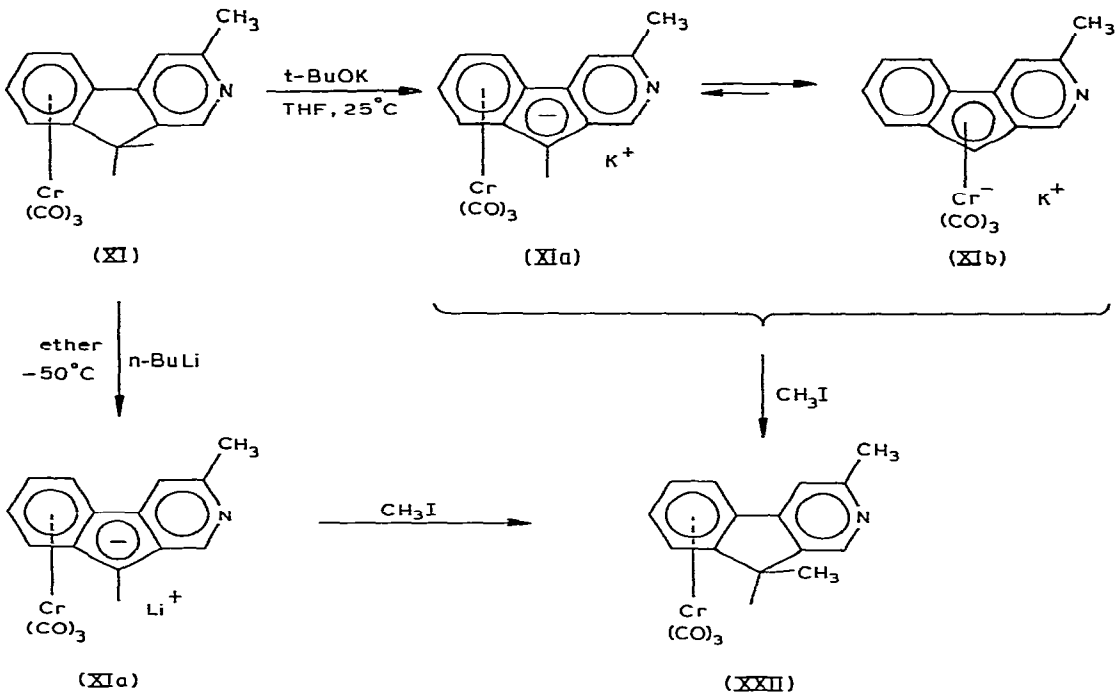


If the η^6-anion is capable of conversion into the η^5-isomer, these operations must be performed at temperatures below —20°C. The stereochemistry of the methylation reactions has been determined with the help of ^{1}H NMR spectroscopy. In the spectrum of XXXII two signals are seen from the protons of the methyl groups at δ1.54 (*exo*) and 1.74 (*endo*) ppm, and in the spectrum of the *exo*-methyl complex XXXI a doublet of methyl protons is observed at δ 1.59 ppm and a quadruplet of H(9) at δ 4.02 ppm. Therefore, in the spectra of other 9-methylated azafluorene complexes the appearance of a doublet in the 1.5—1.6 ppm region indicates an *exo*-position for the methyl group, location of the doublet in the 1.7—1.8 ppm region with the same value of $J(H(9),CH_3)$ is indicative of an *endo* configuration for the methyl substituent. Manifestation of signals from the *exo*-methyl protons at higher field, as compared with the signals from the *endo*-isomers, and the addition to η^6-anions XXIa and XIIa of one alkyl group in the *exo*-position has already been noted by us in this series of investigations [8], as well as by other authors [9,10]. Since the correctness of this assignment has been confirmed by an X-ray study [9], determination of the stereochemistry of methylation reactions from ^{1}H NMR spectra is quite reliable.

We have shown [1] that methylation of the tautomeric mixture XXIa ⇌ XXIb results in a mixture of *exo*- and *endo*-η^6-9-methylfluorenechromium tricarbonyls. The first is formed from XXIa and the second from the η^5-anion XXIb. Upon alkylation of a tautomeric mixture of azafluorenyl anions XIa ⇌ XIb we isolated only the *exo*-alkyl derivative (Scheme 5), as when methylating the pure η^6-isomer

It also proved impossible to isolate isomers with an *endo*-9-methyl group from the alkylation of XIIIa ⇌ XIIIb (Scheme 6). Under equilibrium conditions the fraction of the η^5-form XIIIb in this system is considerably lower (Table 1) than in the XIa ⇌ XIb system. Under the conditions of exhaustive methylation at position 9 (XIII, THF, excess of t-BuOK and CH_3I), the 9,9-dimethyl derivative

SCHEME 5



XXXIII is formed, and benzylation of tautomeric mixture XXIVa ⇌ XXIVb leads to the *exo*-benzyl complex XXXIV. The arrangement of the alkyl groups in XXII, XXIV and XXXIV follows from the positions of the corresponding signals in the ^{1}H NMR spectra. Doublets of methyl protons for XXII and XXIV at δ 1.6 and 1.5 ppm, respectively, indicate its *exo*-position ($J(CH_3, H(9)) = 7.2$ Hz), whereas for XXXIV a singlet at 1.76 ppm indicates the endo-position for the CH_3 group and, therefore, an *exo*-configuration of benzyl radical.

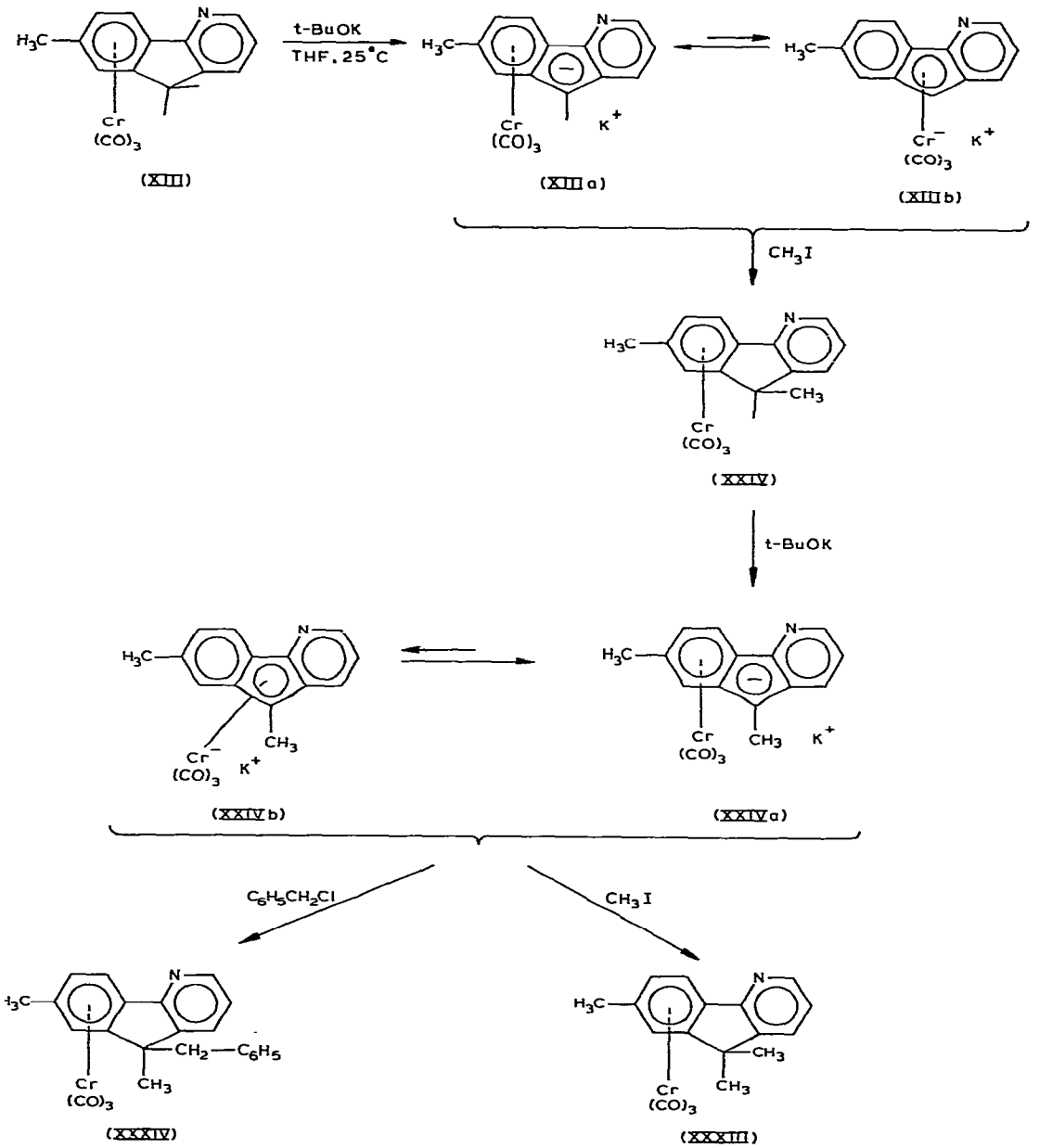
In all probability, the absence of *endo*-isomers in the reactions presented in Schemes 5 and 6 is caused by the instability of the intermediate σ-compounds formed upon alkylation at the metal.

6. Deprotonation of N-donor complexes

Deprotonation of N-donor complexes XV and XX proceeds under the usual conditions (THF, t-BuOK, 25°C), and is accompanied by the deepening of colour, from yellow to reddish-brown. The IR spectrum in the ν(CO) region practically does not change, i.e., the means of coordination of the 2-azafluorenyl ligand remains constant. Acylation of the XVa and XXa anions formed with acetyl chloride gave the enolacetates XXXV and XXXVI (Scheme 7). In the spectra of XXXV and XXXVI in KBr discs there is a band at 1768 cm^{-1} resulting from stretching vibrations of the carbonyl moiety of ester groups.

The data presented show that the direction of reactions between carbonyl compounds of Group VIA metals and azafluorenes, indole and carbazole, as well as the structure and the properties of anions resulting from the deprotonation of

SCHEME 6

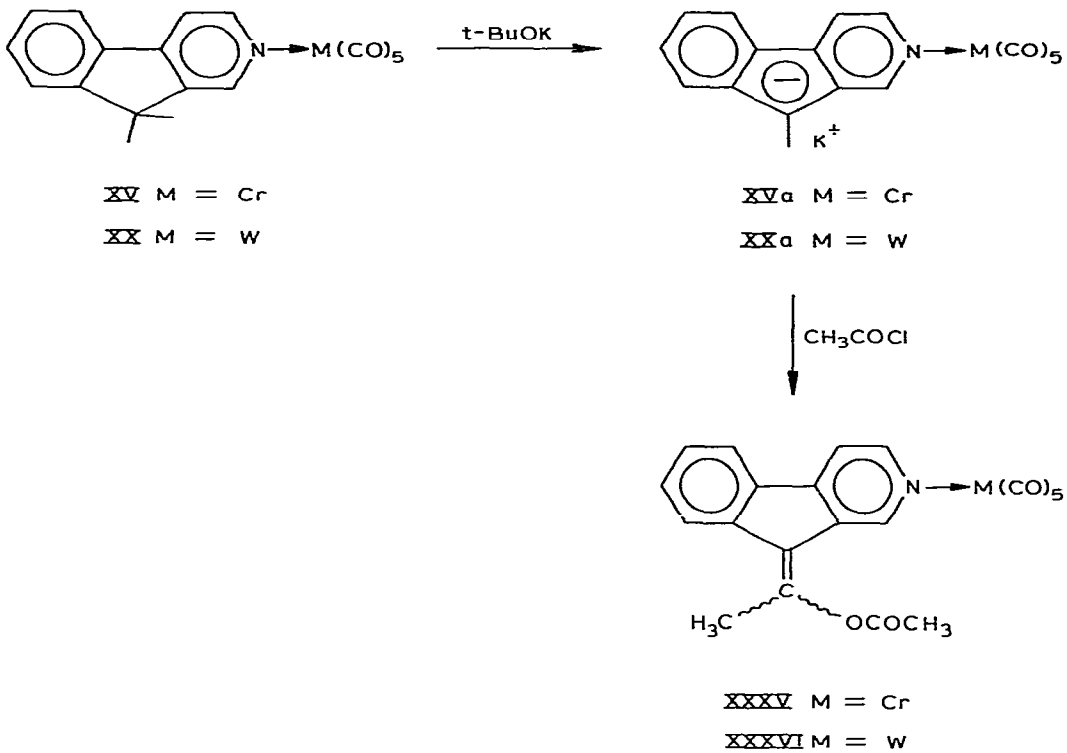


the complexes formed is primarily determined by the structure of heterocyclic ligand.

Experimental

All operations, except preparative TLC, were carried out under an atmosphere of argon. ^{1}H NMR spectra were recorded on a 'Varian XL 100' instrument. Chemical shifts are given in the δ scale in ppm.

SCHEME 7



XV M = Cr
XX M = W

XVa M = Cr
XXa M = W

XXXV M = Cr
XXXVI M = W

1. Reactions of $M(CO)_6$ (M = Cr, Mo) with azafluorenes, indole and carbazole in a mixture of diglyme and heptane

The general procedure for the interaction of azafluorenes II, III, V and VI with $Cr(CO)_6$ and the characteristics of the complexes XV and XI—XIII obtained have already been published [2]. Reactions of azafluorenes I and VII, indole and carbazole with $Cr(CO)_6$, as well as of 2-azafluorene (II) with $Mo(CO)_6$, were conducted in a similar way.

Reaction of 1-azafluorene (I) with $Cr(CO)_6$. Yellow crystals of η^6-(4b,5,6,7,8,8a)-1-azafluorenechromium tricarbonyl (X) (0.1 g; 10%) were obtained from 0.76 g (3.46 mmol) $Cr(CO)_6$ and 0.55 g (3.3 mmol) I, after 6 h of boiling in a mixture of 25 ml diglyme and 25 ml heptane, solvent evaporation in vacuo and chromatographic separation of the residue on a column with silica gel (30 × 2.5 cm) in ether. M.p. 156—158°C (chloroform/heptane). Found: C, 59.18; H, 3.01; N, 4.59; Cr, 17.09. $C_{15}H_9O_3NCr$ calcd.: C, 59.41; H, 2.99; N, 4.62; Cr, 17.15%. ν(CO) (THF) 1903, 1974 cm^{-1}. ^1H NMR ($CDCl_3$): 4.06 (singlet (s), 2 H(9)), 5.40 (multiplet (m), H(6), H(7)), 5.86 (doublet (d), H(8); $J_{8,7}$ = 5.2 Hz), 6.04 (d, H(5); $J_{5,6}$ = 5.6 Hz), 7.30 (m, H_3), 7.84 (d, H(4); $J_{4,3}$ = 7.6 Hz), 8.50 (d, H(2); $J_{2,3}$ = 4.4 Hz).

Reaction of [2,3]-benzo-4-azafluorene (VII) with $Cr(CO)_6$. Red crystals of [η^6-(4b,5,6,7,8,8a)-[2,3]-benzo-4-azafluorene]chromium tricarbonyl (XIV) (0.1 g; 10%) were obtained from 0.6 g (2.73 mmol) $Cr(CO)_6$ and 0.6 g (2.76 mmol) VII, after 12 h of boiling in a mixture of diglyme and heptane (30 ml

each) and chromatographic separation of the products on a silica gel column (30 × 2 cm) with ether as eluent. M.p. 185—187°C (chloroform/heptane). Found: C, 64.56; H, 3.28; N, 3.93; Cr, 14.49. $C_{19}H_{11}O_3NCr$ calcd.: C, 64.59; H, 3.14; N, 3.96; Cr, 14.72%. ν(CO) (THF) 1902, 1975 cm^{-1}. ^1H NMR (acetone-d_6): CH_2 group protons give an AB spectrum (δ(AB) = 4.18; δ(A) = 4.30; δ(B) = 4.06; J(AB) = 22 Hz), 5.68 (triplet (t), H(6), 5.88 (t, H(7)), 6.10 (d, H(8); $J_{8,7}$ = 6.8 Hz), 6.66 (d, H(5), $J_{5,6}$ = 7.2 Hz), 7.30—8.14 (m, 4 H of carboxylic ring of quinoline moiety), 8.26 (s, H(1)).

Reaction of 2-azafluorene (II) with Mo(CO)$_6$. Light-yellow crystals of 2-azafluorenemolybdenum pentacarbonyl (XVI) (53 mg; 4.4%) were obtained from 0.79 g (3.09 mmol) $Mo(CO)_6$ and 0.5 g (2.68 mmol) II, after 4 h of boiling in a mixture of diglyme with heptane (30 ml each) and chromatographic separation of the residue on a column with silica gel in ether. M.p 189—191°C (with decomposition). Found: C, 51.08; H, 2.13; N, 3.56; Mo, 23.28. $C_{17}H_9O_5NMo$ calcd.: C, 50.77; H, 2.01; N, 3.48; Mo, 23.85%. ν(CO) (CH_2Cl_2) 1902, 1947, 1982(sh), 2080 cm^{-1}.

Reaction of indole with Cr(CO)$_6$. (3a,4-7,7a-η^6-Indole)chromium tricarbonyl (VIII) (0.3 g; 9%) was obtained from 1.5 g (12.5 mmol) indole and 4 g (18 mmol) $Cr(CO)_6$ after 5 h of heating in a mixture of 65 ml diglyme and 30 ml heptane, solvent evaporation in vacuo and chromatography of the residue on a column with silica gel in benzene. M.p. 155—157°C (benzene/heptane). Lit. data decomp. temp. 95°C [3]. ν(CO) (THF) 1875, 1960 cm^{-1}. ^1H NMR (acetone-d_6) 10.46 (broad singlet, H(1)), 7.53 (t, H(2)), 6.46—6.55 (m, H(3) and H(4)), 5.33 (t, H(5)), 5.61 (t, H(6)) and 6.64 (d, H(7), $J_{7,6}$ = 7 Hz).

Reaction of carbazole with Cr(CO)$_6$. (1-4,4a,9a-η^6-Carbazole)chromium tricarbonyl (IX) (2.95 g; 55%) was obtained from 3 g (18 mmol) carbazole and 10 g (45 mmol) $Cr(CO)_6$, after 3.5 h of heating in a mixture of 150 ml diglyme and 100 ml heptane, solvent evaporation in vacuo and chromatography on silica gel M.p. 170—172°C (decomp., from benzene). Lit. data m.p. 110°C (decomp.) [3] ν(CO) (THF (1888, 1964 cm^{-1}. ^1H NMR (acetone-d_6) (δ, ppm) 6.3 (d, H(1)), 6.9 (d, H(4)), 8.08 (d, H(5)), J = 7 Hz; 5.30 (t, H(3)), 5.80 (t, H(2)), 10.32 (broad singlet, N—H), 7.18—7.46 (3 H, m, uncoordinated ring).

General procedure for reactions of $(NH_3)_3Cr(CO)_3$ with indole and azafluorene

A mixture of $(NH_3)_3Cr(CO)_3$ and the heterocyclic compound is boiled in dioxan for several hours, the solvent is removed in vacuo, and the residue chromatographed on silica gel. As a rule, the following order of elution of complexes is observed: the most mobile N-donor complexes $LCr(CO)_5$ (L = azafluorene) and $NH_3Cr(CO)_5$ *. They are readily eluted with petroleum ether, benzene or a mixture of these solvents (1/1). The unreacted azafluorene ** was eluted with ether and the less mobile π-complexes, π-$LCr(CO)_3$, with ether or chloroform. One should take care there are no benzene impurities in the dioxan used, otherwise π-$C_6H_6Cr(CO)_3$ is readily formed.

Below, in describing the experiments, only those reaction products are

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* Formation of $NH_3Cr(CO)_5$ as a by-product was not observed in all cases

** Indole mobility coincides with that for $(NH_3)Cr(CO)_5$

characterized (in the order of elution, with the solvent and eluent indicated in brackets) which have not been previously described.

Interaction of indole with $(NH_3)_3Cr(CO)_3$. 3a,4-7,7a,η^6-Indolechromium tricarbonyl (0.17 g, 32%) was obtained from 0.25 g (2.1 mmol) indole and 0.4 g (2.1 mmol) $(NH_3)_3Cr(CO)_3$, after 4 h of boiling in 20 ml dioxane and chromatography on a column with silica gel.

Interaction of 1-azafluorene (I) with $(NH_3)_3Cr(CO)_3$. Yellow crystals of 1-azafluorenechromium pentacarbonyl (XVIII) (0.29 g; 6.6%) (petroleum ether) were obtained from 2.28 g (12.2 mmol) $(NH_3)_3Cr(CO)_3$ and 2.38 g (14.25 mmol) I, after 4 h of boiling in 50 ml dioxane and chromatographic separation of products on a silica gel column (35 × 2 cm). M.p. 139—141°C (with decomposition). Found: C, 56.10; H, 2.20; N, 3.78; Cr, 14.49. $C_{17}H_9O_5NCr$ calcd.: C, 56.83; H, 2.53; N, 3.90; Cr, 14.48%. ν(CO) (CH_2Cl_2): 1905, 1942, 1974, 2077 cm^{-1}. 1.12 g (30%) X (chloroform) was also obtained.

Interaction of 2-azafluorene (II) with $(NH_3)_3Cr(CO)_3$. 0.02 g $NH_3Cr(CO)_5$ and 0.2 g (14%) XV were obtained from 0.7 g (3.74 mmol) $(NH_3)_3Cr(CO)_3$ and 0.7 g (4.18 mmol) II, after 3.5 h of boiling in 40 ml dioxane and chromatographic separation of the residue on a silica gel column (40 × 1.5 cm) (benzene).

Interaction of 3-azafluorene (IV) with $(NH_3)_3Cr(CO)_3$. Yellow crystals of 3-azafluorenechromium pentacarbonyl (XVII) (0.027 g; 4.2%) were obtained from 0.5 g (2.68 mmol) $(NH_3)_3Cr(CO)_3$ and 0.3 g (1.8 mmol) IV, after 3.5 h of boiling in 25 ml dioxan and chromatographic separation of the residue on silica gel (40 × 2 cm) (petroleum ether and benzene (1/1)). M.p. 169—171°C (with decomposition). Found: C, 56.77; H, 2.62; N, 3.72; Cr, 14.33. $C_{17}H_9O_5NCr$ calcd.: C, 56.83; H, 2.53; N, 3.90; Cr, 14.50%. ν(CO) (CH_2Cl_2): 1908, 1945, 1990, 2080 cm^{-1}.

Interaction of 3-methyl-2-azafluorene (III) with $(NH_3)_3Cr(CO)_3$. Yellow crystals of 3-methyl-2-azafluorenechromium pentacarbonyl (XIX) (petroleum ether) (0.050 g; 1.5%) were obtained from 1.7 g (9.1 mmol) $(NH_3)_3Cr(CO)_3$ and 1.7 g (9.4 mmol) III, after 3.5 h of boiling in 50 ml dioxane and chromatographic separation of the products on silica gel (35 × 2 cm). M.p. 140—142°C (with decomposition). Found: C, 57.68; H, 2.58; N, 3.87; Cr, 13.98. $C_{18}H_{11}O_5NCr$ calcd.: C, 57.91; H, 2.57; N, 3.75; Cr, 13.93%. ν(CO) (CH_2Cl_2): 1895, 1945, 1973, 2070 cm^{-1}. Also obtained was 0.73 g (25.5%) of XI (chloroform).

Interaction of 7-methyl-4-azafluorene (VI) with $(NH_3)_3Cr(CO)_3$. 0.48 g (47.2%) of π-complex XIII (chloroform) was obtained from 0.6 g (3.21 mmol) $(NH_3)_3Cr(CO)_3$ and 0.6 g (3.31 mmol) VI, after 3.5 h of boiling in 30 ml dioxan and chromatographic separation of the residue on silica gel (40 × 1.5 cm).

Interaction of [2,3]-benzo-4-azafluorene (VII) with $(NH_3)_3Cr(CO)_3$. From 1 g (5.35 mmol) $(NH_3)_3Cr(CO)_3$ and 1.1 g (5.07 mmol) VII, after 6 h of boiling in 25 ml dioxan and chromatographic separation of the residue on silica gel (30 × 2 cm), was obtained 0.25 g (14%) of the π-complex XIV (chloroform).

General procedure for reactions of $[Et_4N][BrM(CO)_5]$ (M = Cr, Mo, W) with 2-azafluorene (II)

A mixture of $[Et_4N][BrM(CO)_5]$ with II in THF is stirred for several hours at room temperature or upon slight heating, the solvent is removed in vacuo,

and the residue is chromatographically separated on a column with silica gel (80 X 2.8 cm) (the eluent is benzene). N-donor complexes $LM(CO)_5$ (L = 2-azafluorene, M = Cr, Mo, W) are reprecipitated from a chloroform/heptane mixture.

Reaction of II with $[Et_4N][BrCr(CO)_5]$. 0.37 g (42%) of 2-azafluorene-chromium pentacarbonyl XV was obtained from 0.46 g (2.48 mmol) $[Et_4N][BrCr(CO)_5]$ and 0.41 g (2.46 mmol) II in 30 ml THF, after 4 h of stirring (3 h at room temperature and 1 h at 40°C) and chromatography.

Reaction of II with $[Et_4N][BrMo(CO)_5]$. 90 mg (18%) of 2-azafluorene-molybdenum pentacarbonyl XVI was obtained from 0.56 g (1.26 mmol) $[Et_4N][BrMo(CO)_5]$ and 0.21 g (1.26 mmol) II in 30 ml THF, after 2.5 h of stirring at 25°C and chromatography.

Reaction of II with $[Et_4N][BrW(CO)_5]$. Yellow crystals of 2-azafluorene-tungsten pentacarbonyl (XX) (1.55 g; 41%) were obtained from 5 g (9.4 mmol) $[Et_4N][BrW(CO)_5]$ and 1.09 g (6.52 mmol) II in 30 ml THF, after 8 h of stirring and chromatography. M.p. 205—207°C (with decomposition). Found: C, 40.56; H, 1.78; N, 2.57; W, 37.20. $C_{17}H_9O_5NW$ calcd.: C, 41.57; H, 1.85; N, 2.85; W, 37.44%. ν(CO) (CH_2Cl_2); 1902, 1938, 1972(sh), 2080 cm^{-1}.

Preparation of (3a,4-7,7a-η^6-indolyl-1)chromium tricarbonyl anion (VIIIa) and (1-4,4a,9a-η^6-carbazolyl-9)chromium tricarbonyl anion (IXa)

Solutions of VIIIa and IXa in THF were obtained by stirring a mixture of 1—2 mmoles of VIII or IX with a not less than 10% excess of t-BuOK in 15—20 ml of THF for 5—7 min. The yellow colour of the solution is only slightly intensified, but IR spectra are indicative of the completeness of deprotonation.

Reactions of VIIIa and IXa with electrophiles

To solutions of η^6-anions VIIIa and IXa in THF at 0°C (if not specified otherwise) was added an equimolar amount to t-BuOK of electrophile in THF solution (methyl iodide, acetyl chloride) or in solid form (*N*-nitroso-*N*-methyl-tosyl amide). On completion of the reaction (control by IR spectra), THF was removed in vacuo and the residue subjected to recrystallization or chromatography.

VIIIa + CH_3I. Yellow crystals (0.38 g) were obtained from VIIIa (0.38 g, 1.5 mmol VIII), 0.19 g (1.7 mmol) t-BuOK, in 40 ml THF) and 0.24 g (1.7 mmol) CH_3I, after the removal of THF in vacuo and the extraction of the residue with benzene. M.p. 139—141°C (benzene/heptane) (1-methyl-3a,4-7,7a-η^6-indole)chromium tricarbonyl XXVII. ν(CO) (THF): 1878, 1960 cm^{-1}. ^1H NMR (acetone-d_6): 7.44 (d, H(2)) J = 3.5 Hz, 6.42—6.54 (m, H(3) and H(4)), 5.33 and 5.65 (t, H(5) and H(6)), 6.63 (d, H(7)) J = 7 Hz, 3.82 (s, CH_3). Found: C, 54.38; H, 3.44; Cr, 18.71; N, 4.95. $C_{12}H_9CrNO_3$ calcd.: C, 53.95; H, 3.40; Cr, 19.45; N, 5.24%.

IXa + CH_3I. The experiment was conducted similarly to the previous one. 0.56 g (88%) of (9-methyl-1-4,4a,9a-η^6-carbazole)chromium tricarbonyl (XXVIII) was obtained from IXa (0.6 g; 2 mmol IX), 0.24 g (2.1 mmol) t-BuOK, 30 ml THF and 0.3 g (2.1 mmol) CH_3I. M.p. 160—163°C (benzene/heptane). ν(CO) (THF) 1886, 1962 cm^{-1}. ^1H NMR (acetone-d_6): doublets: 6.39 (H(1)), 7.02 (H(4)) and 8.16 (H(5)), J = 7 Hz, triplets: 5.34 (H(3)) and 5.90 (H(2)); 3.75

(s, CH_3); 7.2—7.5 (3 H, multiplet from the coordinated ring protons). Found: C, 61.36; H, 3.43; Cr, 15.67; N, 4.24. $C_{16}H_{11}CrNO_3$ calcd.: C, 60.57; H, 3.47; Cr, 16.39; N, 4.41%.

VIIIa + CH_3COCl. To solution of VIIIa (0.42 g, 1.66 mmol VIII), 0.22 g (2 mmol) t-BuOK in 30 ml THF was added at —10°C and 0.16 g (2 mmol) CH_3COCl in 5 ml THF. The mixture was stirred until it reached the temperature of 10°C and then evaporated to dryness in vacuum. Indole was extracted with heptane and discarded, and the acylation product was extracted with benzene. From the benzene extract was obtained 0.35 g (72%) of (1-acetyl-3a,4-7,7a-η^6-indole)chromium tricarbonyl (XXV). M.p. 170—172°C (toluene/heptane). ν(CO) (THF): 1731, 1890, 1970 cm^{-1}. ^1H NMR (acetone-d_6): doublets: 7.92 (H(2), J = 3.5 Hz), 6.73 (H(3), J = 3.5 Hz), 6.56 (H(4), J = 7 Hz), 7.24 (H(7), J = 7 Hz); triplets: 5.50 and 5.74 (H(5) and H(6)); singlet 2.72 (CH_3CO). Found: C, 53.49; H, 3.36; Cr, 17.37; N, 4.36. $C_{13}H_9CrNO_4$ calcd.: C, 52.89; H, 3.07; Cr, 17.61; N, 4.74%.

VIIIa + p-$CH_3C_6H_4SO_2N(NO)CH_3$. (1-Nitroso-3a,4-7,7a-η^6-indole)chromium-tricarbonyl (XXIX) (0.3 g, 62%) was obtained from VIIIa (0.43 g, 1.7 mmol VIII), 0.21 g (1.9 mmol) t-BuOK, 30 ml THF and 0.41 g (1.9 mmol) *N*-nitroso-*N*-methyltosyl chloride, after 30 min of stirring at 10°C, THF distillation in vacuo and treatment of the residue as in the previous experiment. ν(CO) (THF) 1890, 1970 cm^{-1}. ^1H NMR (acetone-d_6): 7.82 (d, H(2)), J = 3.5 Hz; 6.75 (d, H(3), J = 3.5 Hz); 6.44 (d, H(4), J = 7 Hz); 5.43 and 5.65 (t, H(5) and H(6)); 6.90 (d, H(7) J = 7 Hz). The PMR spectrum showed that substance XXIX contained an *N*-methyltosyl amide impurity.

IXa + p-$CH_3C_6H_4SO_2N(NO)CH_3$. (9-Nitroso-1-4,4a,9a-η^6-carbazole)chromium tricarbonyl (XXX) (0.22 g; 50%) was obtained from IXa (0.41 g, 1.35 mmol IX), 0.17 (1.5 mmol) t-BuOK and 25 ml THF and 0.32 (1.50 mmol) *N*-nitroso-*N*-methyltosyl amide, after 3 h of stirring at 25°C, THF distillation and chromatography of the residue on a column with silica gel in benzene/petroleum ether mixture (3/1). ν(CO) (THF) 1900; 1975 cm^{-1}. ^1H NMR (acetone-d_6): doublets: 8.18 (H(5)), 7.03 (H(4)), 6.75 (H(1)), 5.78 (H(2)) and 5.50 (H(3)), J = 7 Hz; multiplet 7.30—7.61 (uncoordinated ring). The spectrum also showed the presence of *N*-methyltosyl amide as impurity in XXX.

General procedure of deprotonation reactions for $LCr(CO)_3$ π-complexes and $LM(CO)_5$ (L = azafluorenes) N-donor complexes and of the interaction of their anions with electrophiles

A mixture of π-$LCr(CO)_3$ or $LM(CO)_5$ and the deprotonating agent (t-BuOK or n-BuLi) in THF or ether is stirred during 45—90 min. Solution of the excess of electrophilic agent is poured into the formed solution of anions, the solvent is removed in vacuo, and reaction products are separated by means of column or preparative thin-layer chromatography.

Xa + CH_3I. Yellow crystals of (9-(*exo*)-methyl-4b,5-8,8a-η^6-1-azafluorene)-chromium tricarbonyl (XXXI) (0.06 g; 19%) was obtained from Xa (0.303 g, 1 mmol) X, 0.14 g (1.25 mmol) t-BuOK, 20 ml THF, after adding 0.25 ml CH_3I and stirring at 25°C, followed by preparative TLC on silica gel in ether. M.p. 136—138°C (heptane/chloroform). Found: C, 60.27; H, 3.58; N, 4.19; Cr, 16.02. $C_{16}H_{11}O_3NCr$ calcd.: C, 60.57; H, 3.50; N, 4.41; Cr, 16.39%. ν(CO) (THF): 1892,

1970 cm^{-1}. ^1H NMR ($CDCl_3$): 1.59 (d, 9-*exo*-CH_3), 4.02 (quadruplet (q), H(9)), 5.40 (m, H(6), H(7)), 5.84 (d, H(8)), 6.00 (d, H(5)), 7.27 (m, H(3)), 7.83 (d, H(4)), 8.50 (d, H(2)).

Exhaustive methylation of Xa

Yellow crystals of (9,9-dimethyl-4b,5-8,8a-η^6-1-azafluorene)chromium tricarbonyl (XXXII) (0.193 g; 39%) were obtained from 0.455 g (1.5 mmol) X, 1 g (8.93 mmol) t-BuOK and 0.8 ml CH_3I in 30 ml THF, after chromatographic separation of the residue. M.p. 201—204° (heptane/chloroform). Found: C, 59.95; H, 4.09; N, 4.09; Cr, 15.63. $C_{17}H_{13}O_3NCr$ calcd.: C, 61.63; H, 3.95; N, 4.23; Cr, 15.70%. ν(CO) ($CHCl_3$): 1905, 1978 cm^{-1}. ^1H NMR ($CDCl_3$): 1.54 (s, 9-*exo*-CH_3), 1.74 (s, 9-*endo*-CH_3), 5.20 (m, H(6)), 5.59 (d, H(8); $J_{8,7}$ = 5.7 Hz), 5.76 (t, H(7)), 5.94 (d, H(5); $J_{5,6}$ = 5.6 Hz), 7.30 (m, H(3)), 7.83 (d, H(4), $J_{4,5}$ = 7.6 Hz), 8.54 (d, H(2); $J_{2,3}$ = 4.4 Hz).

XIa + CH_3I. (a) Yellow crystals of (3.9-(*exo*)-dimethyl-4b,5-8,8a-η^6-2-azafluorene)chromium tricarbonyl XXII (0.045 g; 13.5%) were obtained from 0.317 g (1 mmol) XI, 0.224 g (2 mmol) t-BuOK and 0.2 ml CH_3I in 30 ml THF, after chromatographic separation of the residue. M.p. 135—138°C (heptane/chloroform). Found: C, 60.01; H, 4.15; N, 3.81; Cr, 15.34. $C_{17}H_{13}O_3NCr$ calcd.: C, 61.63; H, 3.95; N, 4.23; Cr, 15.70%. ν(CO) (THF). 1902, 1975 cm^{-1}. ^1H NMR ($CDCl_3$): 1.60 (d, 9-*exo*-CH_3; J(H(9), CH_3) = 7.2 Hz), 2.70 (s, 3-CH_3), 4.13 (q, H(9)), 5.35 (t, H(6)), 5.58 (t, H(7)), 5.82 (d, H(8); $J_{8,7}$ = 6 Hz), 6.06 (d, H(5); $J_{5,6}$ = 6 Hz), 7.30 (s, H(4)), 8.56 (s, H(1)).

(b) 60 mg (12.2%) of substance identical to XXII was obtained from 450 mg (1.42 mmol) XI, 20 ml hexane solution of n-BuLi (titre 9 6 mg/ml) and 0 4 ml CH_3I in 100 ml absolute ether, with the reaction conducted according to the procedure previously described for methylation of Li salt of the (4b,5-8,8a-η^6-4-azafluorenyl-9)-chromium tricarbonyl anion [2], after chromatographic separation of the residue

XIIIa + CH_3I. Yellow crystals of XXIV (7,9-(*exo*)-dimethyl-4b,5-8,8a-η^6-4-azafluorene)chromium tricarbonyl (176 mg, 38.5%) were obtained from 0.280 g (0.884 mmol) XIII, 0.112 g (1 mmol) t-BuOK and 0.4 ml CH_3I in 25 ml THF, after chromatographic separation of the residue on a column with silica gel (30 × 2.5 cm) in ether. M.p. 154—157°C (heptane/chloroform).

Found: C, 61.61; H, 3.84; N, 4.20; Cr, 15.55. $C_{17}H_{13}O_3NCr$ calcd.. C, 61.63; H, 3.95; N, 4.23; Cr, 15.70%. ν(CO) (THF): 1895, 1970 cm^{-1}. ^1H NMR ($CDCl_3$) 1.50 (d, 9-*exo*-CH_3; J(H(9), CH_3) = 7.2 Hz), 2.29 (s, 7-CH_3), 4.04 (q, H(9)), 5.18 (d, H(6)), 5.59 (s, H(8)), 6.41 (d, H(5), $J_{5,6}$ - 6.6 Hz), 7.16 (m, H(2)), 7.62 (d, H(1); $J_{1,2}$ = 7.6 Hz), 8.43 (d, H(3), $J_{3,2}$ = 4.6 Hz).

Exhaustive methylation of XIIIa

205 mg of yellow crystals consisting, according to their PMR spectrum, a mixture of XXIV and XXXIII (1/1) was obtained from 317 mg (1 mmol) XIII, 336 mg (3 mmol) t-BuOK and 0.5 ml CH_3I in 20 ml THF. 150 mg of this mixture, 150 mg t-BuOK and 0.1 ml CH_3I in 10 ml THF were used to obtain yellow crystals of (7,9,9-trimethyl-4b,5-8,8a-η^6-4-azafluorene)chromium tricarbonyl XXXIII (95 mg). M.p. 96—98°C (heptane/chloroform). Found: C, 61.94; H, 4.05; N, 3.81; Cr, 14.70. $C_{18}H_{15}O_3NCr$ calcd.: C, 62 50; H, 4.34, N, 4.06; Cr,

15.10%. ν(CO) ($CHCl_3$): 1903, 1971 cm^{-1}. ^1H NMR ($CDCl_3$): 1.50 (s, 9-*exo*-CH_3), 1.72 (s, 9-*endo*-CH_3), 2.30 (s, 7-CH_3), 5.44 (d, H(6)), 5.74 (s, H(8)), 6.15 (d, H(5)); $J_{5,6}$ = 6.6 Hz), 7.20 (m, H(2)), 7.62 (d, H(1); $J_{1,2}$ = 7.6 Hz), 8.50 (d, H(3); $J_{3,2}$ = 4.6 Hz).

XXIVa + $C_6H_5CH_2Cl$. Yellow crystals of (7,9(*endo*)-dimethyl-9(*exo*)-benzyl-4b,5-8,8a-η^6-4-azafluorene)chromium tricarbonyl XXXIV (87 mg; 68.4%) were obtained from 100 mg (0.32 mmol) XXIV, 300 mg (2.68 mmol) t-BuOK and 1 ml benzyl chloride in 20 ml THF, after chromatographic separation of the residue on a column with silica gel (20 × 2 cm) in ether. M.p. 197—198°C (heptane/chloroform). Found: C, 68.64; H, 4.40; N, 2.84; Cr, 12.38. $C_{24}H_{19}O_3NCr$ calcd.: C, 68.40; H, 4.54; N, 3.33; Cr, 12.34%. ν(CO) ($CHCl_3$): 1905, 1972 cm^{-1}. ^1H NMR ($CDCl_3$): 1.76 (s, 9-*endo*-CH_3), 2.24 (s, 7-CH_3), 3.02 (s, CH_2), 5.42 (d, H(6)), 5.58 (s, H(8)), 6.05 (d, H(5); $J_{5,6}$ = 6.6 Hz), 6.71 (d of 2 *ortho*-H-benzyl group; $J_{ortho,\ meta}$ = 4 Hz), 7.18 (m of 2 *meta*- and 1 *para*-H of benzyl group), 7.47 (d, H(1); $J_{1,2}$ = 7.6 Hz), 8.50 (d, H(3); $J_{3,2}$ = 4.6 Hz).

Acetate of the enol form of 9-acetyl-2-azafluorenechromium pentacarbonyl (XXXV)

Yellow crystals of XXXV (71 mg; 10.2%) were obtained from 0.45 g XV, 0.45 g (4 mmol) t-BuOK and 0.3 g (4.2 mmol) CH_3COCl in 100 ml absolute ether after chromatographic separation of the residue on silica gel plates with benzene. M.p. 151—153°C (with decomposition). Found: C, 56.43; H, 3.13; N, 3.08; Cr, 11.42. $C_{21}H_{13}O_7NCr$ calcd.: C, 56.89; H, 2.96; N, 3.16; Cr, 11.73%. IR spectrum ν(CO) (CH_2Cl_2): 1910, 1940, 2073 cm^{-1}; 1768 cm^{-1} (carbonyl of the ester group in complete IR spectrum in KBr).

Acetate of the enol form of 9-acetyl-2-azafluorenetungsten pentacarbonyl (XXXVI)

Yellow crystals of XXXVI (44 mg; 7.4%) were obtained from 0.5 g (1.02 mmol) XX, 0.25 g (2.2 mmol) t-BuOK and 0.4 g (5.6 mmol) CH_3COCl in 100 ml absolute ether. M.p. 128—130°C (with decomposition). Found: C, 44.90; H, 2.50; N, 2.03; W, 29.91. $C_{21}H_{13}O_7NW$ calcd.: C, 43.85; H, 2.28; N, 2.44; W, 31.96%. IR spectrum ν(CO) (CH_2Cl_2): 1905, 1938, 1975(sh), 2080 cm^{-1}; 1768 cm^{-1} (carbonyl of the ester group in complete IR spectrum in KBr).

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