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INDENYL AND FLUORENYL TRANSITION METAL COMPLEXES.

IV *. REACTIONS OF 2- AND 4-AZAFLUORENES ** WITH CHROMIUM HEXACARBONYL

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Summary

Reactions of 2- and 4-azafluorenes (I, II) and their methyl derivatives, 3-methyl-2-azafluorene (III) and 7-methyl-4-azafluorene (IV) with chromium hexacarbonyl in a 1/1 diglyme/heptane mixture at 140°C have been studied. A N-donor complex, $C_{12}H_9NCr(CO)_5$ is formed in the reaction of I with $Cr(CO)_6$. Compounds II—IV react to give arenechromiumtricarbonyl derivatives with benzene rather than pyridine ring bound to the metal. [η^6-(4b,5,6,7,8,9b)-4-Azafluorene]chromiumtricarbonyl (VIII) gives the corresponding hydrochloride under the action of HCl. Methyl iodide decomposes VIII to produce 4-azafluorene iodomethylate. Deprotonation of VIII with BuLi in ether at —20°C followed by dilution with hexane leads to precipitation of the corresponding Li salt (Xb), having η^6-structure. Methylation of Xb with methyl iodide proceeds stereospecifically to yield the *exo*-methyl derivative XII. Treatment of VIII with excess t-BuOK at 25°C in THF results in a mixture of η^6-(Xa) and η^5-anions (XI), the former predominating.

Introduction

Indene and fluorene may react with Group VIB metal carbonyls to give complexes of various types, differing in the mode of coordination of the metalcar-

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* For part III see ref. 3.

** Names recommended by IUPAC are 9H-indeno[2,1-c]pyridine and 5H-indeno[1,2-b]pyridine, respectively. Below we will use the trivial names given in the title.

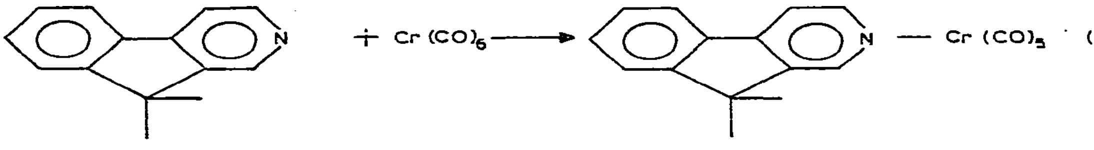
bonyl moieties. The synthesis, structure and some chemical reactions of η^5- and η^6-complexes and their isomeric anions formed by deprotonation of the parent compounds have been described in the preceding communications of this series [1—3].

Reactions of azafluorenes, fluorene heteroanalogues, with metal carbonyls have not been studied thus far. Their products may be N-donor as well as η^5- and η^6-complexes. Such reactions broaden the area of the search for new metallotropic rearrangements. In this work we describe the reactions of 2- and 4-azafluorene, 3-methyl-2-azafluorene (III) and 7-methyl-4-azafluorene (IV) with chromium hexacarbonyl, and the structures and some reactions of the products formed.

Results and discussion

It would seem reasonable to use the literature data on reactions of pyridine and substituted pyridines with chromium carbonyl to predict the outcome of reactions of $Cr(CO)_6$ with I—IV. Pyridine is known to react with $Cr(CO)_6$ under thermal conditions to give a mixture of substitution products, $Py_nCr(CO)_{6-n}$, where n is 1, 2, 3 [4,5]. It is also known that the presence of an o-alkyl substituent strongly reduces the pyridine ring's ability to form N-complexes. Thus, according to Luttringhaus [6], α-picoline does not react with $Cr(CO)_6$ under thermal conditions. Instability of α-picoline-chromiumcarbonyl complexes provides the possibility for the synthesis of η^6-benzenechromiumtricarbonyl by refluxing $Cr(CO)_6$ in a benzene/α-picoline solution [7]. This effect is probably due to screening of the nitrogen lone pair by the neighbouring alkyl group. One might therefore expect that 2-azafluorene (I) having no o-substituent would react with chromium carbonyl similarly to pyridine to give N-complexes. On the other hand, compounds II—IV should show less tendency to form N-adducts, as their nitrogen atoms are screened by o-substituents. They may therefore be expected to give complexes containing coordinated benzene rings.

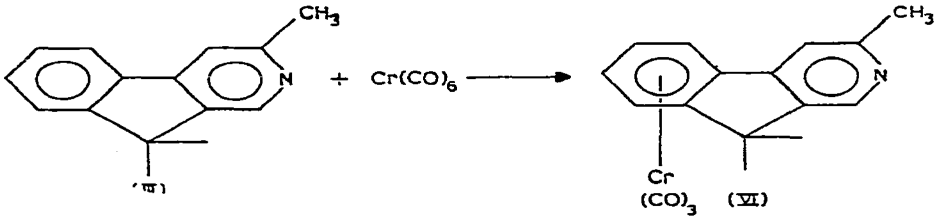
Reactions of I—IV with chromium carbonyl were performed in a 1/1 diglyme/heptane mixture at 140° C. On the whole, the predictions above proved correct. Thus, the pentacarbonyl complex V was the only product isolated from the reaction betweem I and $Cr(CO)_6$:



(I) (V) (1)

Increase of reaction duration did not lead to the formation of other complexes while the yield of V decreased due to decomposition. Compound V proved only very poorly soluble and we could not obtain a satisfactory PMR spectrum of this product. The structure of V was inferred from its IR spectrum in THF: $\nu(C{\equiv}O)$ 1905, 1942, 1983(sh) and 2070 cm^{-1} (practically the same as for $PyCr(CO)_5$ [5]).

Compounds II—IV reacted with $Cr(CO)_6$ to give arenechromiumtricarbonyl complexes with benzene ring coordinated to the metal:



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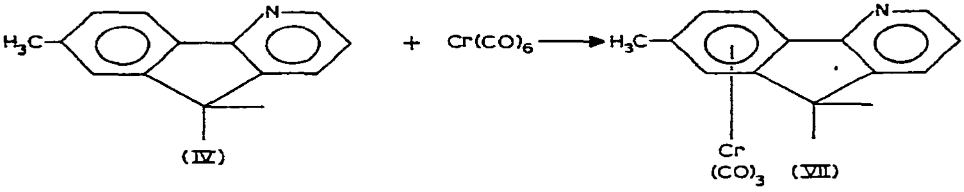

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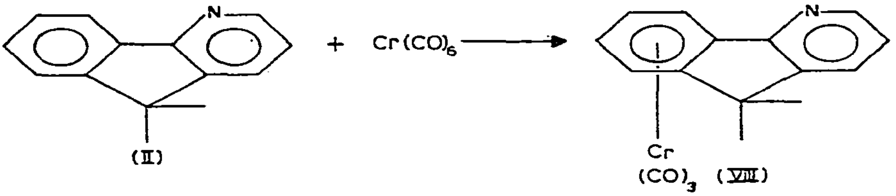
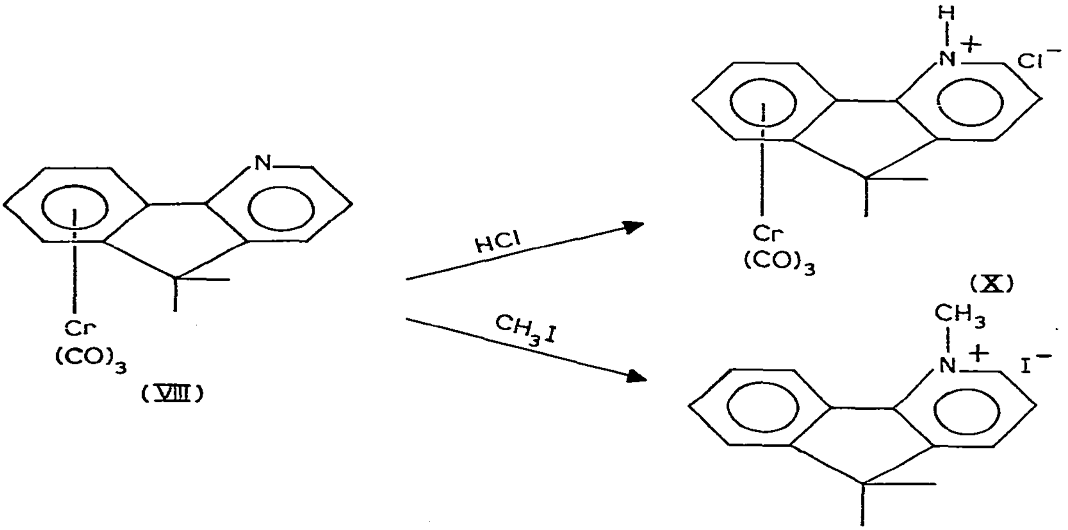


(4)

Arenechromiumtricarbonyl complexes VI—VIII, the products from reactions 2—4, were isolated as yellow crystalline substances stable in air as solids. Their structures follow unambiguously from their PMR spectra, which contain benzene ring proton signals shifted to higher field by ca. 2 ppm compared with those of uncoordinated azafluorenes, and from the IR data. We failed to detect



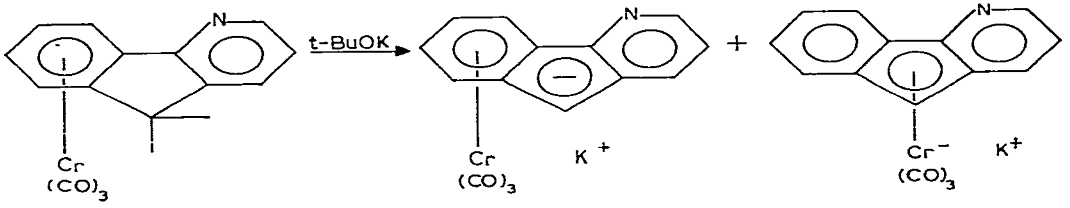
(5)

N-bonded intermediates in reactions 2—4. An attempt was made to synthesize a pyridine type chromium carbonyl complex with 4-azafluorene (II).

Pyridine is known to react with (THF)$M(CO)_5$ or $[XM(CO)_5]^-$ under mild conditions to give high yields of pentacarbonyl complexes [8—10]. The application of this technique with II as N-donor, however, failed to produce pentacarbonyl complexes.

Chemical transformations of VIII have been studied in more detail. Protonation of the nitrogen occurs when dry HCl is bubbled through an ether solution of VIII to give a near quantitative yield of the corresponding hydrochloride. Elimination of the $Cr(CO)_3$ group and formation of 4-azafluorene iodomethylate, however, takes place under the action of methyl iodide in absolute ethanol at 60° C (Scheme 5).

Deprotonation of VIII with excess t-BuOK in THF at 25° C results in a mixture of isomeric η^6- (Xa) and η^5-anions (XI), as indicated by disappearance of the ν(C≡O) bands of VIII at 1910 and 1980 cm^{-1} in the IR spectrum and appearance of the bands of Xa at 1820, 1855 and 1935 cm^{-1} and of XI at 1775 and 1912 cm^{-1} (one more band which should be present in the spectrum of XI at 1815 cm^{-1} is probably obscured by the 1820 cm^{-1} band of Xa).

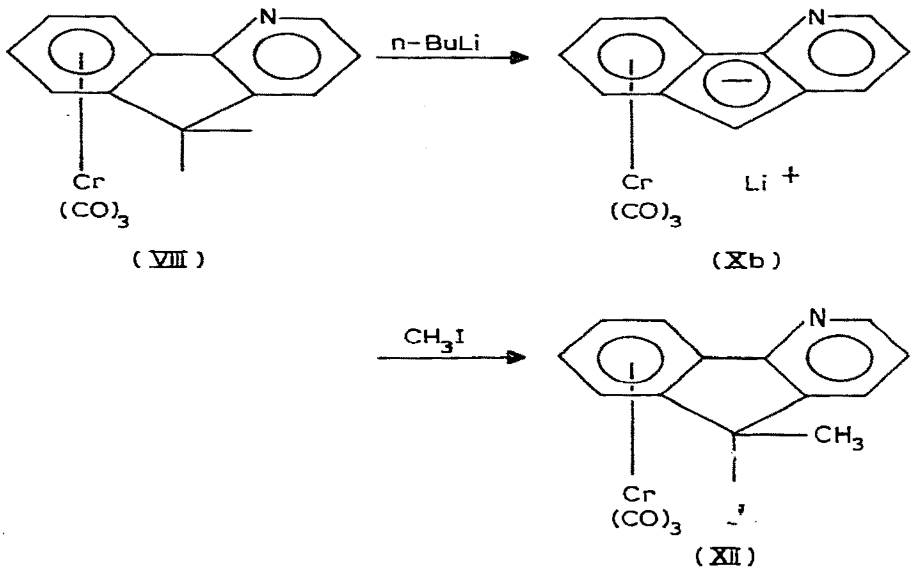


(6)

(VIII) (Xa) (XI)

Frequency assignment for Xa and XI was carried out by analogy with related anions of η^6-fluorenechromiumtricarbonyl [1,3]. Deprotonation of VIII however differs from deprotonation of η^6-fluorenechromiumtricarbonyl carried out under the same conditions in that the amount of the η^5-anion XI present in the reaction mixture is always lower than that of Xa. It may be argued that relative instability of η^5-anion XI and the absence of pyridine ring π-complexes is due to the effect of the electron withdrawing nitrogen atom which decreases electron density in both pyridine and five-membered rings.

We have shown previously that the isomeric species $[\eta^6\text{-}C_{13}H_9Cr(CO)_3]^-K^+$ and $\eta^5\text{-}C_{13}H_9(CO)_3Cr^-K^+$ react with methyl iodide to give stereochemically different products: the first compound gives (η^6-9-*exo*-methylfluorene)chromiumtricarbonyl and the second one the corresponding *endo*-isomer. The methyl proton signals of the *exo*-compound (δ = 1 ppm) are shifted to higher field from those of the *endo*-isomer (δ = 1.3 ppm) [3]. Deprotonation of VIII with n-BuLi in ether at —20° C followed by precipitation of the lithium salt Xb with petroleum ether, removal of excess n-BuLi by decantation and treatment of Xb with methyl iodide in THF at —10° C leads to [η^6-(4b,5,6,7,8,9b)-9-*exo*-methyl-4-azafluorene]chromiumtricarbonyl (XII) containing an *exo*-methyl substituent (reaction 7):



(7)

The PMR spectrum of XII in C_6D_6 contains, along with all the principal features, a CH_3 group doublet at 0.88 ppm having integral intensity equal to three and $J(H_9, CH_3)$ of 7.4 Hz. It should be noted that the spectrum also contains a doublet at 1.16 ppm whose intensity amounts to 5% of that of the 0.88 ppm signal. It seems very likely that the weak signal corresponds to the *endo*-isomer, possibly formed during methylation of a small admixture of η^5-anion XI.

At present we are carrying out investigations on the synthesis of metal carbonyl π-complexes with fluorene heteroanalogues, their metalation, metallotropic rearrangements in and reactions of anions formed in the course of metalation with electrophiles.

Experimental

All the operations except for preparative thin-layer chromatography and synthesis of compound IX were carried our under dry pure argon. The solvents were refluxed over K/Na alloy (tetrahydrofuran) or Na (diglyme, ether) and distilled under nitrogen flow immediately before use. Azafluorenes were synthesized as recommended in the literature (II and IV, ref. 11; I and III, ref. 12), purified from diphenyl admixtures by chromatographing on columns packed with silica gel, and recrystallized from hexane prior to use. Materials for chromatography were silica gel L 100/160 (Chemapol, CSSR) and water free Al_2O_3. PMR spectra were recorded on an XL-100-15 Varian instrument operated at 100 MHz. IR spectra were obtained with an UR-20 spectrophotometer.

Reactions of azafluorenes I—IV with chromium carbonyl

General procedure

An equimolar mixture of an azafluorene and $Cr(CO)_6$ was refluxed in a 1/1 diglyme/heptane mixture at 140°C using a modified Strohmeier head in order to return sublimed chromium carbonyl to the reaction mixture. The process was monitored by IR spectroscopy. After removal of the solvent under vacuum, the residue was chromatographed on silica gel in ether. Complexes V—VIII were isolated by elution of yellow bands with ether and reprecipitated from THF or chloroform with heptane. The crystals obtained were washed with small quantitaties of ether to remove small admixtures of unreacted initial azafluorenes.

2-azafluorenechromiumpentacarbonyl (V)

I (0.50 g, 3 mmol) was refluxed together with $Cr(CO)_6$ (0.66 g, 3 mmol) in a mixture of diglyme (30 ml) and heptane (30 ml) for 2,5 h to give V in a yield of 0.15 g (15%). M.p. (THF-heptane) 185—187°C (decomp.). ν(C≡O) (THF) 1905, 1942, 1983, 2070 cm^{-1}. Found: C, 56.17; H, 2.72; N, 3.90; Cr, 14.42. $C_{17}H_9O_5NCr$ Calcd.: C, 56.83; H, 2.52; N, 3.90; Cr, 14.48%.

[η^6-(4b,5,6,7,8,9b)-3-methyl-2-azafluorene]chromiumtricarbonyl

III (0.54 g, 3 mmol) and $Cr(CO)_6$ (0.66 g, 3 mmol) were refluxed in a mixture of 30 ml diglyme and 30 ml heptane for 14 h. The mixture was treated as described above. 0.14 g of VI were obtained (13% yield). M.p. ($CHCl_3$-heptane) 144—146°C. ν(C≡O) (diglyme/heptane 1/1) 1902, 1973 cm^{-1}. PMR ($CDCl_3$) (δ, ppm): singlets at 8.6, 7.36, 3.96, 2.66 (H_1, H_4, H_9, CH_3); doublets at 6.1, 5.82 (H_5, H_8); multiplet at 5.42 (H_6, H_7). Found: C, 58.61, H, 3.55; N, 4.41; Cr, 16.63. $C_{16}H_{11}O_3NCr$ Calcd.: C, 60.57; H, 3.50; N, 4.41; Cr, 16.39%.

[η^6-(4b,5,6,7,8,9b)-7-methyl-4-azafluorene]chromiumtricarbonyl (VII)

IV (1.32 g, 7.1 mmol) was refluxed together with $Cr(CO)_6$ (1.55 g, 7.1 mmol) in 30 ml diglyme and 30 ml heptane for 10 h. The reaction mixture was treated as before to give VII (0.34 g, 14%). M.p. ($CHCl_3$-heptane) 162—164°C. ν(C≡O) (heptane): 1910, 1980 cm^{-1}. PMR ($CDCl_3$), (δ, ppm): singlets at 5.64, 3.92, 2.28 (H_8, H_9, CH_3); doublets at 8.46, 7.68, 6.46, 5.2 (H_3, H_1, H_5, H_6); multiplet at 7.2 (H_2). Found: C, 60.29; H, 3.41; N, 4.47; Cr, 16.29. $C_{16}H_{11}O_3NCr$ Calcd.: C, 60.57; H, 3.50; N, 4.41; Cr, 16.39%.

[η^6-(4b,5,6,7,8,9b)-4-azafluorene]chromiumtricarbonyl (VIII)

II (5.65 g, 33.8 mmol) reacted with $Cr(CO)_6$ (7.45 g, 33.8 mmol) under reflux in a 40 ml diglyme/40 ml heptane mixture for 35 h to give VIII (2.34 g, 23%). M.p. (THF-heptane) 171—173°C. ν(C≡O) ($CHCl_3$): 1910, 1978 cm^{-1}. PMR (C_6D_6), (δ, ppm): doublets at 8.36, 6.96, 6.16, 4.9 (H_3, H_1, H_5, H_8); quartet 6.58 (H_2); multiplet 4.56 (H_6, H_7); CH_2-group protons gave an AB spectrum: δ(AB) 3.17, δ(A) 3.33, δ(B) 3.01. Found: C, 59.44; H, 3.03; N, 4.47; Cr, 17.03. $C_{15}H_9O_3NCr$ Calcd.: C, 59.41; H, 2.99; N, 4.62; Cr, 17.15%.

Interaction of VIII with HCl

Dry HCl was bubbled through a solution of VIII (0.15 g) in 40 ml ether. The red precipitate formed was repeatedly washed with ether and dried in a vacuum desiccator over KOH to give IX (0.167 g), m.p. 138—139°C. Found: C, 53.10; H, 3.23; N, 4.39; Cl, 10.47; Cr, 15.10. $C_{15}H_{10}O_3NClCr$ Calcd.: C, 53.04; H, 2.97; N, 4.14; Cl, 10.48; Cr, 15.30%.

Interaction of VIII with CH_3I

Excess methyl iodide was added to a solution of VIII (0.27 g) in 10 ml absolute ethanol. The mixture was heated in a vessel equipped with a reflux condenser at 60° C for 8 h. The precipitate formed was isolated by decantation and washed with several portions of benzene until the benzene washes became colourless. A white crystalline solid identical to 4-azafluorene iodomethylate was obtained (0.27 g, 98%).

Preparation of the lithium salt Xb and its reaction with methyl iodide

A hexane solution of n-C_4H_9Li (1.35 ml titre 70.4 mg/ml) was added at once to a solution of VIII (0.45 g, 1.5 mmol) in 100 ml ether at —20° C. More n-C_4H_9Li solution (1.35 ml) was added after stirring the mixture at that temperature for 0.5 h. The mixture was then diluted with 75 ml hexane. Xb was formed as suspended crystals. To ensure complete precipitation of Xb, the mixture was kept at —70° C. The solvent was then removed through a tube, the residue was washed three times with petroleum ether and dissolved in 30 ml THF. CH_3I (0.4 ml) was added to the solution at —10° C. The mixture was warmed to 25° C, THF was removed under vacuum, and the product was chromatographed on silica gel in ether. The compound was eluted with ether from a yellow band, the ether solution was concentrated, and XII was precipitated with heptane. The yield of XII was 0.1 g (21%), m.p. 109—111° C. $\nu(C\equiv O)$ (petroleum ether) 1918, 1983 cm^{-1}. PMR (C_6D_6) (δ, ppm): doublets 8.36, 7.00, 6.2, 4.98, 1.16, 0.88 (H_3, H_1, H_5, H_8, *endo*-CH_3, *exo*-CH_3, $J(CH_3, H_9)$ 7.4 Hz); quartet 6.62 (H_2); multiplet 4.62 (H_6, H_7); quartet 3.62 (H_9, $J(H_9, CH_3)$ 7.4 Hz). Found: C, 60.46; H, 3.60; N, 4.27; Cr, 16.35; $C_{16}H_{11}O_3NCr$ Calcd.: C, 60.57; H, 3.49; N, 4.41; Cr, 16.39%.

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