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INDENYL AND FLUORENYL TRANSITION METAL COMPLEXES

X *. ANIONIC CHROMIUM TRICARBONYL COMPLEXES OF FLUORADENE, SUBSTITUTED FLUORENES AND INDENE: THE STRUCTURE OF ION PAIRS AND $\eta^6 \rightarrow \eta^5$ REARRANGEMENTS

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Summary

The metallotropic $\eta^6 \rightleftarrows \eta^5$ tautomeric equilibrium in anionic chromium tricarbonyl complexes of fluoradene, substituted fluorenes and indene has been studied. A criterion is proposed for determining the ion-pair type in η^6-anions according to the E-band splitting in the ν(CO) region of their IR spectra. The influence of ligand structure and cation solvation on $K_{eq.}$ is discussed.

Introduction

We have previously described the reversible and equilibrium isomerization of η^6- and η^5-fluorenylchromium tricarbonyl anions (Ia, Ib), which is a novel type of metallotropic tautomerism [1]. Both isomer (Ia, Ib) anions, as well as their interconversion, which consists of the "sliding" of a chromium tricarbonyl group along the plane of the fluorenyl ligand between the five- and six-membered rings, have been studied by IR [2,3], ^{1}H NMR [2,4] and ^{13}C NMR [4,5] spectroscopy. The tautomeric equilibrium for chromium tricarbonyl anions of fluorene and its carbocyclic analogues is primarily governed by the structure of the polynuclear π-ligand, as well as by the cation and its solvation. The latter brings up the necessity to take into account the existence of two kinds of ion pairs — contact (CIP) and solvent-sep-

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* For Part IX see ref 5.

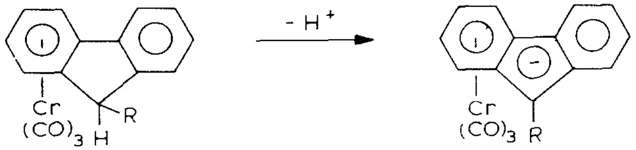
arated (SSIP) — for the salts of both tautomers. The present paper describes the results of a more detailed study of the influence of the polynuclear π-ligand structure and of the type of ion pair on the rearrangement observed.

To this end, we have synthesized η^6-fluoroadenechromium tricarbonyl (II) *, chromium tricarbonyl complexes of 9-substituted fluorenes ((9-$RC_{13}H_9$)$Cr(CO)_3$: III–V, III, R = CH_3; IV, R = t-C_4H_9; V, R = C_6H_5) ** and 3-methylfluorene (VI, VII, VI, (3-methyl-1-4,4a,9a-η^6-fluorene)chromium tricarbonyl; VII, (3-methyl-4b-5-8a,8-η^6-fluorene)chromium tricarbonyl) *** and have studied their deprotonation. We also studied the deprotonation of the previously described [6] (η^6-triphenylmethane)chromium tricarbonyl (VIII), whose anion should possess an η^6-structure.

Results and discussion

Deprotonation of complexes II–VI

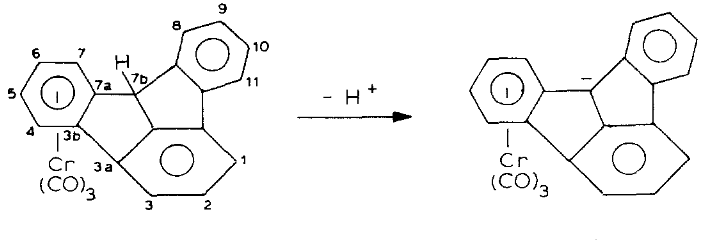
The deprotonation of complexes II–VI was carried out in absolute THF by treating with excess base at −78 °C, as described for fluorenechromium tricarbonyl [2,7]. Tertiary C_4H_9OM (M = Na, K, Rb, Cs), a saturated solution of alkali metals in HMPA, and triphenylmethylenephosphorane were used as bases. Under these conditions, complexes of fluoradene(II) and substituted fluorenes (III–V) are converted into anions with an η^6-structure (IIa) and IIIa–Va quantitatively.



(1)

(III, R = CH_3,
IV, R = t-C_4H_9,
V, R = C_6H_5)

(IIIa, R = CH_3,
IVa, R = t-C_4H_9,
Va, R = C_6H_5)



(2)

(II)

(IIa)

Whilst studying the reaction of VIII with butyllithium in a THF/diethyl ether

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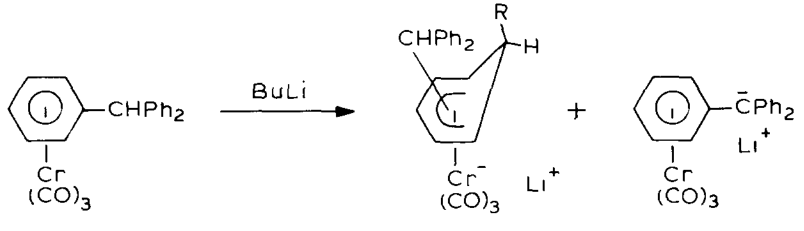
* The name recommended by IUPAC is (3b,4-7,7a-η^6-7b*H*-indeno[1,2,3-*jk*]fluorene)chromium tricarbonyl. The trivial name is used here.

** Complexes III–V were obtained as both *exo*- and *endo*-isomers. Their synthesis will be described elsewhere.

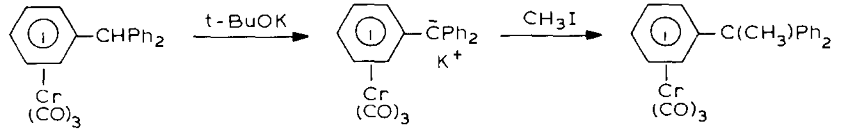
*** Complex VI was isolated in a pure state; VII was obtained with an admixture of VI mixture, Ceccon et al. [6] came to the conclusion that the reaction mainly proceeds through alkylation of the coordinated ring with the formation of the cyclohexadienyl anion (IX), while the Li salt (VIIIa) formed due to deprotonation is only a side-product.



(VIII) (IX) (VIIIa) (3)

During the reaction, bands at 1818 and 1900 cm^{-1} were observed in the IR spectrum of the reaction mixture. For the Li salt of the structurally analogous hexadienylchromium tricarbonyl anion $(PhS)_2CHC_6H_6Cr(CO)_3^-$ Li^+, Semmelhack et al. [8] reported ν(CO) 1712, 1802 and 1901 cm^{-1}, which is plainly contrary to the observations made by Ceccon et al. *.

We have found that the reaction of VIII with tertiary BuOK in THF yields exclusively the VIIIa, K-salt (ν(CO) 1917 and 1829 cm^{-1}). In accordance with this, its methylation with CH_3I results in the formation of complex X:



(VIII) (VIIIa) (X) (4)

The η^6-fluoradenyl anion (IIa) is methylated and acylated in a similar way (cf.

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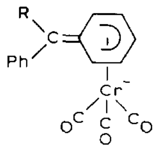
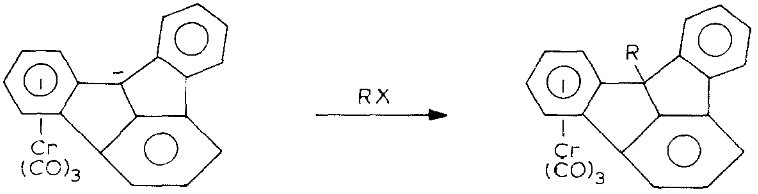
* Whilst this paper was being prepared for publication, Ceccon et al. published a paper [30] which claimed a hexadienyl structure (XVa) for the potassium salt of η^6-diphenylmethanechromium tricarbonyl (XV), based on the fact that the *meta*- and *para*-protons of the coordinated nucleus in the ^{1}H NMR spectrum of XVa are shown to be non-equivalent. Analogously, a similar structure (XVIa) was also claimed for the triphenylmethylchromium tricarbonyl anion. It is our belief, however, that the non-equivalence of these protons can be explained by an increased rotational barrier along the C_r–C_α bond mainly due to an increase in steric hindrance as compared to the non-coordinated diphenylmethyl anion. In our opinion, only an X-ray study can distinguish between the structures of VIIIa and XVIa.



(XVa R = H,
XVIa R = Ph)

Experimental):



(IIa) (XI, R = CH_3, XII, R = CH_3CO) (5)

Nature of the ion pairs in η^6-anions (IIa—VIa)

The determination of the type of ion pairs in the η^6-fluorenylchromium tricarbonyl anion (Ia), the η^6-indenylchromium tricarbonyl anion (XIIIa) and the related η^6-anions IIa–VIIIa poses certain difficulties. UV spectra, which have been used so successfully for non-coordinated fluorenyl anions [9], fail to provide interpretable information for the chromium tricarbonyl complexes, since the spectra in the 250–350 nm region exhibit a broad, unresolved band and are uncharacteristic.

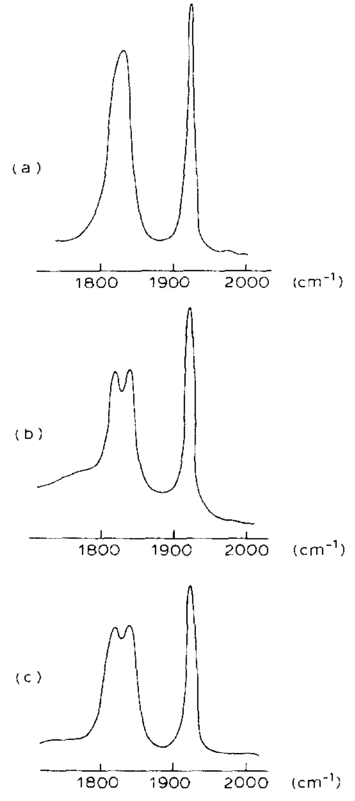


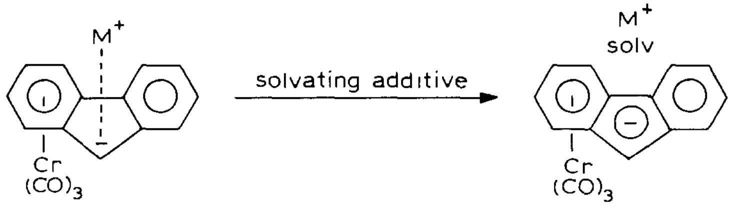
Fig. 1. IR spectra of the η^6-fluorenylchromium tricarbonyl anion (Ia) in the ν(CO) region at −78 °C in THF. (a) Cs-salt; (b) Cs-salt in the presence of HMPA; (c) K-salt.

^{1}H NMR spectroscopy can hardly be used to solve this problem since it is difficult to separate the two contributions of the counter-ion to the screening of the π-ligand protons: i.e. the influence of the electrostatic field and the redistribution of π-electron density [10]. ^{13}C NMR spectroscopy can be used effectively only to study the salts of small and sufficiently hard cations (Li^+, Na^+), but it is useless for studying K^+, Rb^+ and Cs^+ salts [11]. Therefore, we used the pattern of the IR spectrum in the ν(CO) region in order to determine the type of ion pairs in the solutions of the η^6-salts IIa–VIIIa and XIIIa.

An experimental study of the dependence of the IR spectra of Ia salts on counter-ion and medium has shown that in SSIP the E-band is split, and for pure SSIP the splitting (ΔE) constitutes 20–22 cm^{-1}, whereas in CIP the E-band is degenerate ($\Delta E = 0$), with only a slight broadening of this band being observed.

We believe that in CIP the counter-ion is located over the plane of the five-membered ring close to the carbanion centre (which agrees with the data for non-coordinated fluorenyl and indenyl anions [12]) from the side opposite to the chromium tricarbonyl group.

Now, we can present the following evidence in support of our tentative conclusions. First of all, the IR spectrum of Ia salts in pure THF depends on the nature of the counter-ion, while no dependence was observed in the presence of solvating additives. For bulky and poorly solvating cations (Rb^+, Cs^+, $n\text{-}Bu_4N^+$, $Ph_3PCH_3{}^+$), it is possible to observe a transition of CIP to SSIP in the presence of excess solvating additive (dicyclohexyl-18-crown-6 (DCH-18-C6), HMPA), cf. eq. 6 and Figs. 1(a) and 1(b).

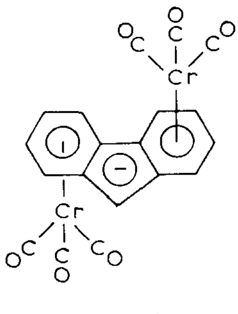


(Ia), CIP   (Ia), SSIP

(6)

Secondly, regardless of the counter-ion, ΔE is 20 cm^{-1} in the IR spectra of (η^6,η^6-fluorene)bis(chromium tricarbonyl) (XIV) salts, because the counter-ion cannot be located over the five-membered ring in XIVa due to steric reasons and therefore XIVa salts exist as SSIP.

(Continued on p. 192)



(XIVa)

TABLE 1

IR SPECTRAL DATA IN THE ν(CO) REGION, TYPES OF ION PAIRS AND TAUTOMERIC EQUILIBRIUM CONSTANTS FOR THE ISOMERIC ANIONS OF THE η^6- AND η^5-SERIES IN THF

Anion	Counter ion	Solvating additive	Anion with η^6-structure				Anion with η^5-structure				Tautomeric equilibrium constant $K_{eq} = 2[\eta^5]/[\eta^6]$ [a]
			ν(CO)			Type of ion pair	ν(CO)			Type of ion pair	
			A_1	E			A_1	E			
(9-t-Butyl)- [b] fluorenylchromium tricarbonyl anions (IVa, IVb)	K^+	–	1925	1832		CIP	1905	1815	1770	CIP	100%
	K^+	DCH-18-C6	1923	1839	1818	SSIP	1902	1797		SSIP	6.0
	Cs^+	–	1925	1832		CIP	1905	1810	1768	CIP	3.0
	Cs^+	cryptand-2,2,2	1922	1843	1821	SSIP	1902	1798		SSIP	6.4
(3-Methylfluorenyl)chromium carbonyl anions (VIa, VIb)	K^+	–	1927	1840	1817	SSIP	1905	1806	1766	CIP	12.0
	K^+	DCH-18-C6	1927	1841	1817	SSIP	1905	1798		SSIP	4.2
(9-Methylfluorenyl)chromium tricarbonyl anions (IIIa, IIIb)	K^+	–	1926	1841	1817	SSIP	1905	1806	1766	CIP	17.1
	K^+	DCH-18-C6	1927	1840	1817	SSIP	1906	1798		SSIP	6.2
(Fluorenyl)chromium tricarbonyl anions (Ia, Ib)	Li^+	–	1927	1839	1820	SSIP	1915	1820	1733	CIP	100% η^5
	Li^+	–	1927	1837 [c]		CIP	1915	1820	1733	CIP	100% η^5
	Na^+	–	1925	1835	1812	SSIP	1907	1811	1762	CIP	13.7
	K^+	–	1927	1841	1817	SSIP	1905	1807	1766	CIP	14.3
	Rb^+	–	1930	1840		CIP	1904	1804	1766	CIP	5.0
	Cs^+	–	1929	1840		CIP	1904	1804	1766	CIP	1.22

	$Ph_3PCH_3^+$	–	1927	1831		CIP	1905	1802		CIP	3.38
	K^+	DCH-18-C6 [d]	1927	1842	1822	SSIP	1904	1798		SSIP	5.42
(9-Phenylfluorenyl)chromium tricarbonyl anions (Va, Vb)	K^+	–	1926	1840	(1823) [e]	CIP	1905	1810	1767	CIP	0.7
	Rb^+	–	1927	1840		CIP	1905	1810	1767	CIP	0.44
	Cs^+	–	1927	1840		CIP	1905	1810	1767	CIP	0.30
	K^+	DCH-18-C6	1927	1842	1822	SSIP	1905	1808		SSIP	0.2
(Indenyl)chromium tricarbonyl anions (XIIIa, XIIIb)	K^+	–	1927	1833		CIP	1908	1806	1767	CIP	100% η^5
	K^+	HMPA	1928	1842	1820	SSIP	1900	1792		SSIP	100% η^5
(Fluoradenyl)-chromium tricarbonyl anion (IIa)	K^+	–	1937	1859	1842	SSIP	–		–	–	100% η^6
	Rb^+	–	1932	1858	(1835sh) [e]	CIP	–		–	–	100% η^6
	Cs^+	–	1931	1852		CIP	–	–	–		100% η^6
	Cs^+	HMPA	1931	1859	1835	SSIP	–	–	–		100% η^6
	K^+	DCH-18-C6	1927	1840	1820	SSIP	–	–	–		100% η^6
(Triphenylmethyl)-chromium tricarbonyl anion (VIIIa)	K^+	–	1916	1829		CIP	–	–	–		100% η^6
	K^+	HMPA	1917	1829	1809	SSIP	–	–	–		100% η^6

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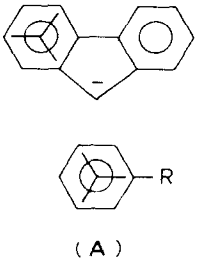
[a] For isomer anions of the $[9\text{-}RC_{13}H_8Cr(CO)_3]^-$ type, the equilibrium constant was determined according to the formula $K_{eq} = 2[\eta^5]/[\eta^6]$, taking into account that the rearrangement of $\eta^5 \rightarrow \eta^6$ is degenerated twice. In the case of VIa, VIb, for which the $\eta^5 \rightarrow \eta^6$ transformation is not degenerate, K_{eq} was determined according to the same formula. [b] The form and location of the ν(CO) bands of the tautomer anions and $K_{eq.}$ do not depend on the type of configuration (*endo-* or *exo-*) of the starting neutral complex $(\eta^6\text{-}9\text{-}RC_{13}H_9)Cr(CO)_3$. [c] In 2,5-dimethyltetrahydrofuran. [d] The IR spectra in the ν(CO) region and $K_{eq.}$ for Ia, Ib salts with other cations (Na^+, Rb^+, Cs^+, $PH_3PCH_3^+$) in the presence of solvating additives are identical to the IR spectra and K_{eq} of Ia,Ib, K-salts in the presence of DCH-18-C6. [e] For salts of the η^6-series Va and IIa, a small amount of SSIP was observed in the mixture where CIP predominated.

The conclusion concerning the existence of the Ia,K-salt in THF mainly in the form of SSIP (Fig. 1(c)), based on the IR spectrum, is confirmed by the $\Delta S^{\neq}$ values found during the study of the kinetics of $\eta^6 \rightarrow \eta^5$ isomerization of this salt [2,4].

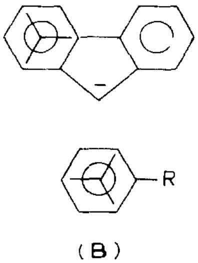
The appearance of the E-band in the ν(CO) region in IR spectra of the η^6-anion salts IIa–VIa and Xa can serve as a criterion for determining ion-pair types in solution (Table 1).

To elaborate on the above, let us consider in a more detailed manner the η^6-triphenylmethylchromium tricarbonyl anion (VIIIa). The IR spectra of solutions of VIIIa salts with the alkali cations Na^+, K^+, Rb^+ and Cs^+, as well as that of a solution of the triphenylmethylphosphonium salt, contain only two bands in the ν(CO) region. The E-band is not split, which indicates the predominance of CIP. Adding DCH-18-C6 or HMPA to the solution destroys CIP, which leads to E-band splitting, $\Delta E = 20$ cm^{-1} (Table 1). The effect of counter-ions and solvating additives on the E-band in the IR spectra of the η^6-anion VIIIa, which cannot rearrange into an η^5-isomer by the migration of the $Cr(CO)_3$ group to another nucleus, by and large resembles the effect observed previously for Ia salts, which serves to confirm the conclusions regarding the structure of VIIIa salts [5].

The problem of the causes of E-band splitting in SSIP is rather complicated and demands inspection of the conformational effects in chromium tricarbonyl complexes of the fluorenyl anion and its analogues. We believe that the splitting of the E-band in the IR spectra of SSIP of the anion systems studied and of the neutral arenechromium tricarbonyl complexes is explained by the predominance of one of the conformers, notably the eclipsed conformer **A** over the *anti*-eclipsed and staggered conformers **B** and **C** for anion complexes. The presence of the preferred conformation leads to lowering of the local C_{3v} symmetry of the $Cr(CO)_3$ fragment while the antisymmetric vibration of class E becomes non-degenerate.



(A)



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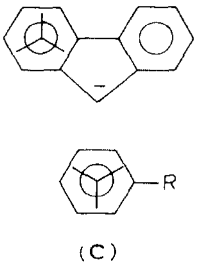

(C)

It is known that for chromium tricarbonyl complexes of substituted benzenes the eclipsed conformer **A** predominates if the substituent is an electron-releasing group which does not produce strong steric effects (CH_3, C_2H_5, OCH_3, etc.) [13]. This is just what happens in the case of Ia, as the carbanion centre in the α-position is a very strong donor, while the planar fluorenyl ligand does not introduce steric hindrance. The donating effect of the carbanion centre is greatly reduced in the case of CIP due to interaction with the cation. In this case, the difference in conformer energy is small, and in the IR spectrum the E-band is a superposition of their adjacent E-bands. The total local C_{3v} symmetry of the $Cr(CO)_3$ group is only slightly lowered; the E-band is therefore only broadened. In the case of SSIP, the donating influence of the carbanion centre is greater, the difference in conformer energy increases, and one of the conformations becomes predominant, leading to splitting of the *E*-band.

Thus, the determination of the preferred conformation in Ia and other η^6-anions becomes very important for the determination of the ion-pairs therein. An unambiguous definition of the conformation for the complexes under discussion using X-rays is possible only for solids [13]. When determining the preferred conformation in solutions using ^{1}H NMR [14] and ^{13}C NMR [15] spectroscopy, a number of suggestions have to be made. We are primarily interested in cases where the conclusions drawn on the basis of NMR spectroscopy can be compared with X-ray studies, and the *E*-band in the IR spectrum is split. Regretably, all these data are known only for chromium tricarbonyl complexes of methylbenzoate and acetophenone. For the former, the **B**-conformation is realized in a crystal [16], predominates (63%) in solution [15], while the splitting of the *E*-band (ΔE) amounts to 7 cm^{-1} at $-65\,^\circ$C [17]. For the second complex, the **A**-conformation exists in a crystal [18], predominates in solution (80%) [19], while the splitting of the *E*-band amounts to 10 cm^{-1} [20].

It is characteristic that fulvenechromium tricarbonyl complexes, whose rotational barrier around the metal-π-ligand axis is higher than that for arenechromium tricarbonyls [21], usually exhibit a more substantial splitting of the *E*-band in the IR spectrum, reaching 20 cm^{-1} [22].

These examples confirm the splitting of the *E*-band as a criterion for the existence of a preferred conformation for an arenemetal tricarbonyl complex in solution. This conclusion is supported by data known for fluorenyl anion complexes. Thus, the zwitter-ion η^6-fluorenylmanganesetricarbonyl has the **A** * conformation in crystal form: this conformation is also predominant in solution **, while the *E*-band is split (ΔE 19 cm^{-1}) [25]. Finally, for η^6-$C_{13}H_9Cr(CO)_3^-$ K^+ (Ia), according to ^{13}C NMR spectral data [4,24] and to an analysis of ^{1}H NMR data [24] in accordance with the approach described in ref. 14, the eclipsed **A**-conformation should dominate in solution, and ΔE 19 cm^{-1} (THF).

Thus, the proposed method for the determination of ion pairs in Ia and in its analogues leads to conclusions which are compatible with both data on the equilibrium of ion pairs in non-coordinated alkali salts of fluorene, and with the facts known about the conformations of arenechromium tricarbonyl complexes ***. At present, the approach is only qualitative. Quantitative determination of the proportion of a certain type of ion pair can be carried out on the basis of separating IR spectral bands of CIP and SSIP mixtures, which includes determination of extinction coefficients for the corresponding pure form bands. This approach may also help us to study the dependence of the type of ion pair in Ia–VIIIa, XIIIa on the solvent,

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* Conformation **A** for the $Mn(CO)_3$ group was calculated from the complete atomic coordinates cited in [23].

** This conclusion was drawn by us on the basis of the analysis [24] of this compound's ^{13}C NMR spectrum [25].

*** The presence of a predominating conformation in chromium tricarbonyl complexes of substituted arenes should lead to three CO-group signals in the ^{13}C NMR spectrum, and not one, as observed for all neutral arenechromium tricarbonyl complexes that have the preferred conformation, as well as for Ia. This is probably explained by the redistribution of CO groups ("scrambling"), which is faster than the rotation around the arene-metal axis. The possibility of scrambling as regards AreneCr(CO)_3 was discussed in ref. 26.

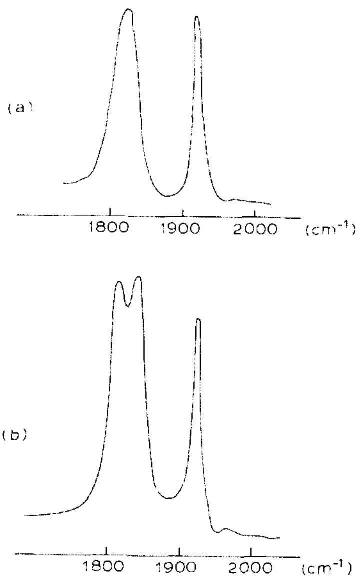


Fig. 2. IR spectra of the η^6-indenylchromium tricarbonyl anion (XIIIa) in the ν(CO) region at −78 °C in THF. (a) K-salt; (b) K-salt in the presence of HMPA.

the presence of solvating additive, counter-ion, and π-ligand structure (cf. Table 1).

The nature of the solvent has a considerable effect on the type of ion pairs. For instance, in HMPA, which strongly solvates alkali cations, Ia–VIIIa and XIIIa salts exist in the form of SSIP (Fig. 2(b)). In 2,5-dimethyltetrahydrofuran, on the other hand, all these salts exist as CIP, including the Ia, Li salt. In THF, which occupies an intermediate position regarding its solvating ability, the type of ion pairs depends on the nature of the counter-ion (cf. Table 1).

The π-ligand structure also has a considerable influence on the type of ion pairs in Ia–VIIIa and XIIIa. The higher the degree of delocalization of the charge along the entire ligand, the smaller the portion of the charge for the five-membered ring, and the more probable the formation of SSIP. Accordingly, in the process of transition from η^6-indenyl (XIIIa) to η^6-fluorenyl (Ia) and η^6-fluoradenyl (IIa) anions, the amount of SSIP grows. Thus, the XIIIa K-salt exists as CIP (Fig. 2(a)), and the Ia, K- and IIa, K-salts (Fig. 3(c)) as SSIP. At the same time, the Ia, Rb-salt exists as CIP, while the IIa, Rb-salt (Fig. 3(d)) is probably a mixture of CIP and SSIP, with the latter predominating.

The influence of the $Cr(CO)_3$ group on the structures of the ion pairs is less direct. Its electron-withdrawing effect leads to delocalization of the charge from the π-ligand, thereby promoting, as compared to non-coordinated carbanions, SSIP formation. For instance, in THF, potassium fluorenyl exists as CIP [9], while the Ia, K-salt exists as SSIP.

It is not yet clear why the amount of CIP grows during the transition from Ia to IIIa–Va η^6-anions that have substituents in the 9-position.

Nature of the ion pairs in η^5-anions

At temperatures above 0 °C, the η^6-anions IIIa–VIIa and XIIIa, like Ia [2],

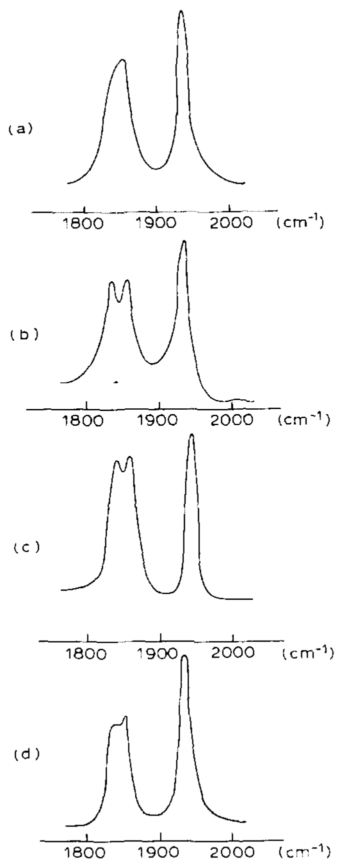
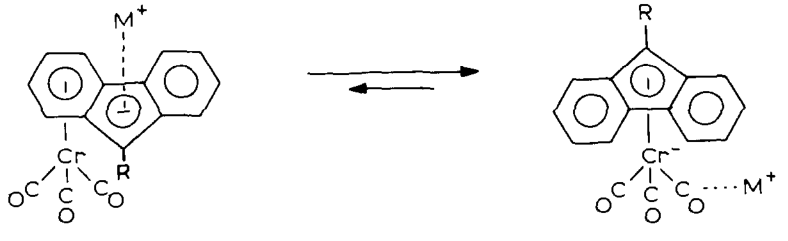
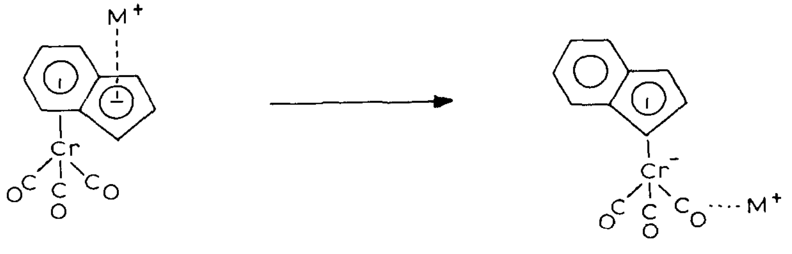


Fig. 3. IR spectra of η^6-fluoradenylchromium tricarbonyl anion (IIa) in the ν(CO) region at 25 °C in THF. (a) Cs-salt; (b) Cs-salt in the presence of HMPA; (c) K-salt; (d) Rb-salt.

isomerize into the η^5-forms IIIb–VIIb and XIIIb. Cf. Table 1 for ν(CO) frequencies of the η^5-anions, and data on the tautomeric equilibrium of systems 7 and 8.)



(7)



(8)

The main trends of CIP or SSIP formation (Table 1) in IIIb–VIIb and XIIIb salts depending on counter-ion, solvent and solvating additives fully correspond to those previously described for Ib [2] and the model anion η^5-$C_5H_5(CO)_3Cr^-$ [2,27], and are not discussed in detail here.

Dependence of the tautomeric equilibrium on the π-ligand nature

The data given in Table 1, which also cites the constants of metallotropic equilibrium, allow us to obtain a clear notion of the effect that the ligand nature and substituents have on these constants. An increase in the degree of charge delocalization in the indenyl, fluorenyl and fluoradenyl ligand series leads to a sharp decline in the relative stability of the η^5-form. That is why η^6-indenylchromium tricarbonyl (VIIIa) is quickly and completely rearranged into the η^5-isomer. The stability of the η^5- and η^6-tautomers for fluorenylchromium tricarbonyl anion is comparable, whereas the η^6-fluoradenylchromium tricarbonyl anion does not rearrange into the η^5-isomer in any noticeable way. The effect of the donor methyl substituent in the 9-position increases the stability of the η^5-isomer somewhat, and the equilibrium constant increases, but this effect is not nearly as strong as in the case of azafluorene complexes [28].

On the contrary, the introduction of a phenyl group into the 9-position leads to poorer stability of the η^5-isomer (Vb) and lowers the metallotropic tautomeric equilibrium constant.

Experimental

All manipulations except preparative TLC were conducted in an argon atmosphere. THF and dioxane were purified by prolonged refluxing over a K/Na alloy, 2,5-dimethyl-THF (EGA-Chemie), and HMPA, over calcium hydride. Diethyl ether was purified over sodium benzophenoneketyl. Solvents were distilled in an argon atmosphere directly before use. IR spectra were recorded with a UR-20 spectrophotometer. ^{1}H NMR spectra were measured on XL-100 Varian (100 MHz) and VP 200 Bruker (200 MHz) spectrometers.

Fluoradene was obtained according to [29].

The deprotonation of the neutral complexes II–VIII and XIII, and the analysis of tautomeric mixtures formed in the process with IR spectroscopy were carried out as described previously [2,5].

Synthesis of (η^6-triphenylmethane)chromium tricarbonyl (VIII)

2.9 g (20 mmol) of $BF_3 \cdot O(C_2H_5)_2$ was added to a mixture of 1.52 g (6.24 mmol) of triphenylmethane and 2 g (4.82 mmol) of $(4\text{-}CH_3C_5H_4N)_3Cr(CO)_3$ in 150 ml of ether. The mixture was stirred at room temperature for 40 min. The solution was filtered, washed with water, and the ether layer was dried over $MgSO_4$. After ether evaporation in vacuo, the residue was subjected to chromatography on a column of silica gel, eluting VIII with petroleum ether/benzene (2/1). Yield 0.66 g (36%). M.p. 164–165 °C (benzene/hexane). Found: C, 70.23; H, 4.16; Cr, 13.56. $C_{22}H_{16}CrO_3$ calcd.: C, 69.47; H, 4.24; Cr, 13.67%. ν(CO) (THF) 1900, 1975 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 5.13 (singlet (s), 1H, 5.05–5.40 (multiplet (m), 5H, coordinated ring), 7.08–7.42 (m, 10H, non-coordinated benzene rings).

Complex VIII was also obtained in 14% yield after refluxing $Cr(CO)_6$ and triphenylmethane in a diglyme/heptane mixture for 16 h, solvent distillation in vacuo, and chromatography.

Methylation of the (η^6-triphenylmethyl)chromium tricarbonyl anion (VIIIa)

To a solution of VIIIa obtained by treating 0.19 g (0.5 mmol) of VIII with 0.22 g (2 mmol) of t-BuOK in 15 ml of THF at 0 °C, was added 0.28 g (2 mmol) of CH_3I. The mixture was gradually heated to room temperature, the solvent was evaporated in vacuo, and the residue recrystallized from a benzene/heptane mixture. Yield 0.13 g (66%) of (η^6-methyltriphenylmethane)chromium tricarbonyl (X), m.p. 187–191 °C. Found: C, 69.66; H, 4.69; Cr, 13.34. $C_{23}H_{18}CrO_3$ calcd.: C, 70.07; H, 4.57; Cr, 13.19%. ν(CO) (THF) 1900, 1975 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.25 (s, 3H, CH_3), coordinated phenyl ring: 5.12 (triplet (t), 2H, *meta*-), 5.38 (doublet (d), 2H, *ortho*-), 5.6 (t, 1H, *para*-); 7.10–7.48 (m, 10H, non-coordinated phenyl rings).

Synthesis of (η^6-fluoradene)chromium tricarbonyl (II)

A mixture of 0.48 g (2 mmol) of fluoradene and 0.37 g (2 mmol) of $(NH_3)_3Cr(CO)_3$ was refluxed in 20 ml of dioxane for 3 h. After filtering, dioxane was removed in vacuo, and the residue subjected to chromatography on silica gel L 40/100μ. Fluoradene not consumed in the reaction (0.19 g) was eluted with a petroleum ether/benzene mixture (4/1). Then three yellow bands were washed out. The contents of the first band, 0.07 g (eluant: petroleum ether/benzene, 2/1) were discarded.

The second fraction (eluant: petroleum ether/benzene mixture, 1/1), after crystallization from a toluene/heptane mixture, yielded 0.35 g (46%) of II. M.p. 168–170 °C (dec.). Found: C, 70.53; H, 3.16; Cr, 13.54. $C_{22}H_{12}CrO_3$ calcd.: C, 70.21; H, 3.21; Cr 13.81%. ν(CO) (THF) 1909, 1975 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.22 (t, 1H, H(6)), 5.43 (t, 1H, H(5)), 5.98 (d, 1H, H(4)), 6.02 (d, 1H, H(7)) (coordinated ring); 7.30–7.90 (A_2B + ABC-multiplets, 7H) – non-coordinated rings; 5.40 ppm (s, 1H, H(7b)). The contents of the third fraction (0.04 g; eluant: mixture of petroleum ether/benzene, 1/2) was discarded.

Complex II was also obtained in 44% yield after heating fluoradene with chromium hexacarbonyl in a diglyme/heptane mixture (1/1) and chromatographic separation, as described above.

Methylation of the (η^6-fluoradenyl)chromium tricarbonyl anion (IIa)

A solution of IIa was obtained by stirring 0.1 g (0.26 mmol) of II and 0.1 g (0.89 mmol) of t-BuOK in 12 ml of THF at room temperature for 10 min; it was then cooled to 0 °C and 0.12 g of methyl iodide was added. The solution instantly turned yellow. The temperature of the mixture was gradually raised to 20 °C, THF was evaporated in vacuo, and the residue was recrystallized from a benzene/heptane mixture. Yield 0.07 g (70%) of (η^6-7b-methylfluoradene)chromium tricarbonyl (XI) in the form of yellow crystals, m.p. 177–180 °C. Found: C, 70.10; H, 3.59; Cr, 12.69. $C_{23}H_{14}CrO_3$ calcd.: C, 70.77; H, 3.61; Cr, 13.32%. ν(CO) (THF) 1905, 1977 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 1.76 (s, 3H, CH_3), 5.18 (m, 1H, H(6)), 5.4 (m, 1H, H(5)), 5.86 (d, 2H, H(4)) – coordinated ring, 7.24–7.74 (A_2B + ABC-multiplets, 7H) – non-coordinated rings.

Acylation of IIa

In a similar way to the above-described experiment, from 0.23 g (0.61 mmol) of II, 0.23 g (2.1 mmol) of t-BuOK and 0.16 g (2.1 mmol) of acetyl chloride, 0.22 g (88%) of (η^6-7c-acetylfluoradene)chromium tricarbonyl (XII) was obtained. M.p. 197–198 °C. Found: C, 68.50; H, 3.09; Cr, 12.35. $C_{24}H_{14}CrO_4$ calcd.: C, 68.91; H, 3.37; Cr, 12.43%. ν(CO) (THF) 1906, 1977 cm^{-1}. ν(C=O) 1820 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 1.86 (s, 3H, CH_3CO), 5.26 (m, 1H), 5.48 (m, 1H), 5.86 (d, 1H) and 6.28 (d, 1H) – coordinated ring; 7.26–7.84 (A_2B + ABC-multiplets, 7H, non-coordinated rings).

Mixture of VI and VII

A mixture of 2.6 g (14 mmol) of 3-methylfluorene and 2.7 g (14 mmol) of $(NH_3)_3Cr(CO)_3$ in 50 ml of dioxane was refluxed for 6 h. After filtering, the solvent was distilled off in vacuo, and the residue was subjected to chromatography on silica gel L 100/160μ plates in a petroleum ether/benzene mixture (1/1) and recrystallized from a CH_2Cl_2/heptane mixture. 2.4 g (52%) of a mixture of chromium tricarbonyl complexes VI and VII was obtained in a ratio of 45/55 (according to ^1H NMR).

Synthesis of VI

A mixture of VI and VII in an amount of 1 g was subjected to repeated chromatography on silica gel L 5/40 plates with a petroleum ether/benzene mixture (2/1), with the eluant passing each plate twice. The upper third of the wide yellow band was collected separately and after extraction with methylene chloride and precipitation with hexane, 0.28 g of pure VI was obtained. Found: C, 64.90; H, 3.85; Cr, 16.63. $C_{17}H_{12}CrO_3$ calcd.: C, 64.97; H, 3.82; Cr, 16.56. ν(CO) ($CHCl_3$) 1890, 1973 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.30 (s, 3H, CH_3), 3.86 (s, 2H, H(0)), 5.20 (d, 1H, H(2)), 5.92 (s, 1H, H(4)), 5.95 (d, 1H, H(1)), 7.30–7.90 (ABC-multiplet, 4H, H(5)–H(8)).

A mixture of VI and VII was obtained from the lower third of the chromatographic band in a ratio of 16/84 (according to integration of the methyl signals).

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