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INDENYL AND FLUORENYL TRANSITION METAL COMPLEXES

V. STUDY OF REVERSIBLE ISOMERIZATION OF η^6- AND η^5-FLUORENYLCHROMIUM TRICARBONYL ANIONS BY IR AND PMR SPECTROSCOPY

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Summary

IR and PMR spectroscopy was used to study the reversible isomerization of η^6- and η^5-fluorenylchromium tricarbonyl anions (I and II, respectively) in solutions. Consideration was given to the dependence of the equilibrium position and nature of the resulting particles on the type of cation (Li^+, Na^+, K^+, $Ph_3PCH_3{}^+$, n-Bu_4N^+), the solvent and the presence of solvating cation additives (dicyclohexyl-18-crown-6 (IV), DMSO). The η^5-isomer exists in THF solution as an equilibrium mixture of solvent-separated and contact ion pairs (SSIP and CIP, respectively), the cation in the latter being located near the oxygen atom of one of the carbonyl groups. The existence of such an equilibrium is also shown for the salts of the $C_5H_5(CO)_3Cr^-$ anion. The dependence of the equilibrium constants for I $\rightleftharpoons$ II on the above factors was determined. For the K salt in THF solution at 28°C both IR and PMR spectroscopy gave fairly coincident values of K_{eq} equal to 7.15 and 7.35, respectively. IR spectroscopy was applied to the kinetic studies of the reversible isomerization of K salts of I and II at 0—28°C with and without crown ether IV. The process is shown to be entropy controlled. The equilibrium position is governed by the type of cation, the degree of its solvation and the temperature. The factors promoting the formation of SSIP's lead to the equilibrium being shifted towards I.

The fluorenyl anion forms two isomeric chromium tricarbonyl complex anions, viz., η^6- and η^5-fluorenylchromium tricarbonyl anions (I and II, respectively), which can be mutually and reversibly isomerized and represent conve-

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For part IV see ref. 7.

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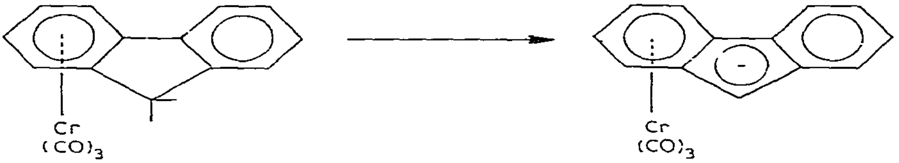
nient models for studying metallotropic rearrangements. The synthesis of I and II and their reactions with some electrophiles have been described earlier by us [1,2]. This work reports on studies of the reversible isomerization I $\rightleftharpoons$ II using IR and PMR spectroscopy.

Salts of η^6-anion I are formed via deprotonation of η^6-fluorenylchromium tricarbonyl (III), (eq. 1) with a variety of agents (t-BuOK and t-BuONa in THF at —70° C, n-BuLi in ether at —30°C, alkali metal solutions in hexamethyltriamidophosphate (HMPA) at 25°C, triphenylmethylenephosphorane * in THF at —70°C). The choice of deprotonating agent is determined by which solvent and counterion are required.



(1)

The reaction course can be conveniently followed by the change of the IR spectrum. The IR spectrum of III contains two ν(CO) bands at 1968 and 1895 cm^{-1} in the region of CO stretching vibrations (ν(CO)), corresponding to symmetric and degenerate vibrations of A_1 and E modes, respectively, with the local symmetry C_{3v} of the Cr(CO)$_3$ moiety. On addition of the deprotonating agents the yellow colour of the solution of starting III changes immediately to dark red, the IR spectrum completely loses the ν(CO) bands, and new bands corresponding to I appear (Fig. 1a).

The ν(CO) frequencies of anion I depend on the type of counter-ion, solvent and solvating additive (dicyclohexyl-18-crown-6 (IV) and are listed in Table 1. In the spectrum of the alkali metal salts of I the degenerate low frequency band of class E is split into two components due to lowering of the local symmetry of the Cr(CO)$_3$ moiety under the effect of the negative charge on the five-membered ring and the positively charged cation. The band frequencies and splitting magnitude (about 20—25 cm^{-1}) are practically independent of the nature of the alkali metal, the solvent (THF, HMPA, dimethoxyethane (DME)) and addition of crown ether IV. However, in the spectrum of the triphenylphosphonium salt of I the low frequency band of the E mode is degenerate, the same effect being attained by adding (n-Bu$_4$N)I to the solutions of alkali metal salts of anion I in THF. Such a degeneration is probably due to a smaller effect of the two factors responsible for the disturbance of the local symmetry C_{3v} of the Cr(CO)$_3$ moiety: first, the action of the negative charge of the five-membered ring is reduced by it being shielded by the large cation and, second, the intrinsic disturbing effect of the cation is small. Establishment of the contribution of the two factors to the splitting of the E band in the salts of I and the nature of the cation—anion interaction therein requires additional study.

The rearrangement of I to II in THF (reaction 2) starts at about —20°C and at a rate convenient for kinetic measurement proceeds in the temperature

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* This agent has been conveniently used by N.N. Zemlyansky to obtain phosphonium salts of a number of substituted fluorenes, cyclopentadienes and some other strong CH acids of this type. We wish to thank him for a supply of pure $(C_6H_5)_3P{=}CH_2$ and provision of the method.

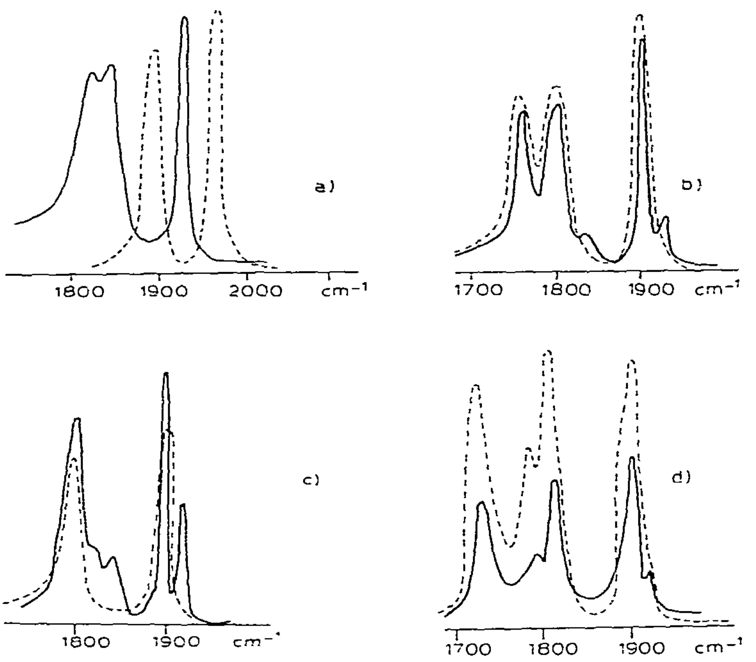
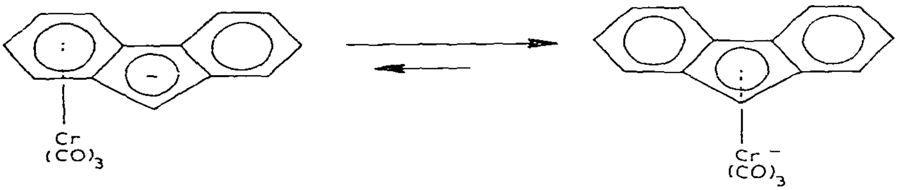


Fig. 1. Absorption IR spectra in the ν(CO) region. (a) ——— η^6-$C_{13}H_9Cr(CO)_3^-K^+$ in THF at −40°C; - - - - - - η^6-fluorenechromium tricarbonyl in THF; (b) ——— equilibrium mixture of the K salts of I and II at 28°C in THF; - - - - - - η^5-$C_5H_5(CO)_3Cr^-K^+$ in THF; (c) ——— equilibrium mixture of the K salts of I and II in the presence of crown ether IV (THF, 28°C); - - - - - - η^5-$C_5H_5(CO)_3Cr^-K^+$ in the presence of IV; (d) ——— η^5-$C_{13}H_9(CO)_3Cr^-Li^+$ in THF; - - - - - - η^5-$C_5H_5(CO)_3Cr^-Li^+$ in THF.

region 0 to 25°C. As this takes place, the IR spectrum shows a gradual decrease of the band of I down to a certain limit and a simultaneous increase of the bands of II. Generally, the appearance of the spectrum of II in the ν(CO) region depends on the type of cation, solvent and solvating additives (Table 1, Figs. 1b—d).



(2)

It can be assumed from the nature of this dependence that a cation—anion interaction exists in solution for II. In HMPA where all the alkali metal cations show good solvation and in THF added with crown ether IV the salts of II exists as SSIP's and the IR spectrum corresponds to a local symmetry C_{3v} for the $Cr(CO)_3$ moiety, i.e. two ν(CO) ($A_1 + E$) bands appear (Table 1). A similar spectrum is also seen for the methylphosphonium salt of II in THF and in this case a fairly strong cation—anion interaction, which would disturb the C_{3v} symmetry, is impossible because of the large size of the cation. For Li, K and Na salts of II in THF in the absence of IV the ion pairs are mostly of the contact

TABLE 1

FREQUENCIES IN THE ν(CO) REGION OF ANIONS I AND II (cm^{-1})

Solvent	Counter-ion	Solvating additive	η^6-$C_{13}H_9Cr(CO)_3^-$		η^5-$C_{13}H_9(CO)_3Cr^-$ [a]	
			ν(CO) (E)	ν(CO) (A)	ν(CO) (E)	ν(CO) (A)
THF	K^+	—	1817 1841	1927	1766 1807	1905
THF	Na^+	—	1812 1835	1925	1762 1811	1907
THF	Li^+	—	1820 1839	1927	1733 1820	1915
THF	K^+	Dicyclohexyl-18-crown-6	1822 1842	1927	1800	1905
THF	Na^+	Dicyclohexyl-18-crown-6	1821 1840	1925	1800	1903
THF	Na^+	DMSO [b]	1821 1841	1927	1797	1903
THF	$Ph_3PCH_3^+$	—	1832	1927	1802	1905
THF	n-Bu_4N^+	—	1829	1924	1778 1798	1903
DME	K^+	—	1816 1840	1927	1768 1806	1907
HMPA	K^+	—	1820 1844	1928	1798	1904
HMPA	Na^+	—	1820 1844	1928	1798	1904
HMPA	Li^+	—	1820 1844	1928	1799	1904

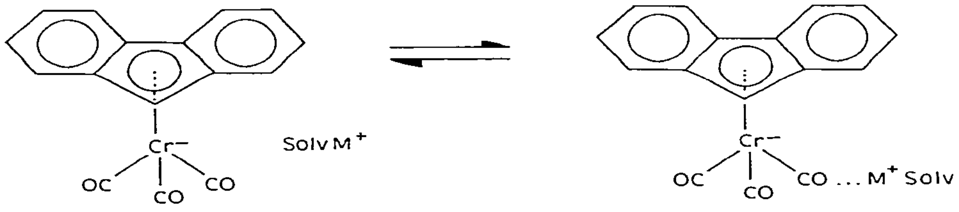
[a] For solutions in THF and DME in the absence of solvating additives frequencies are given for the CIP's predominating in these conditions. [b] THF/DMSO = 5 : 1.

type (Fig. 1b), the symmetry of the metal tricarbonyl moiety is reduced and the low frequency *E* band is split into two components. The amount of splitting for the Li salt of II (89 cm^{-1}) is much larger than that for the Na and K salts (49 and 41 cm^{-1}, respectively) due to the greater effect of the small Li cation. Because of this, the bands belonging to the SSIP's (1798 and 1905 cm^{-1}) and CIP's (1733, 1820 and 1915 cm^{-1}) (Fig. 1d), can be readily distinguished for the Li salt whereas for the K and Na salts of II the band of the SSIP at 1798 cm^{-1} is observed as a shoulder on the 1805 cm^{-1} band belonging to the CIP. Thus for the alkali metal salts of II in THF in the absence of crown ether IV an equilibrium between the SSIP's and CIP's, shifted towards the latter, exists. On passing from the SSIP's to the CIP's the low frequency band shifts regularly towards the long wave region in the series K, Na, Li (1766, 1762 and 1733 cm^{-1}, respectively). The frequencies of the remaining two bands increase in the same series (1807, 1811 and 1820 cm^{-1}, respectively, and 1905, 1907 and 1915 cm^{-1}, respectively). Such a shift is typical for the interaction of a cation with the oxygen atom of one of the carbonyl groups. In the case of localization of the cation near the negatively charged chromium atom one would expect a high frequency shift for all the three ν(CO) bands in this series. Thus the above data indicate that in the CIP of II the alkali metal cation is located in the vicinity of the oxygen atom of one of the CO groups. Previously, similar arguments were used to assign the bands of the salts η^5-$C_5H_5(CO)_2Fe^-M^+$ (M = Li, Na, K) to CIP's and SSIP's [3,4].

The structure of anion II and the suggested assignment of the bands were confirmed by studies on the known model salts η^5-$C_5H_5(CO)_3Cr^-M^+$(V), where M = Li, Na, K, for which η^5-coordination has been firmly established as the only possible. The salts of V were obtained by us by reducing $[\eta^5$-$C_5H_5(CO)_3$-$Cr]_2Hg$ (VI) with alkali metal amalgams or K/Na alloy in THF and also by splitting VI with alkali metal solutions in HMPA. Although the salts of anion V have been studied fairly extensively, the problem concerning the type of ion pairs had not received systematic consideration. In HMPA and THF with added IV, alkali metal salts of V exists as SSIP's (Fig. 1c), and in THF there is an equilibrium between the SSIP's and CIP's (Fig. 1b). Thus all the observations for II are equally valid for V.

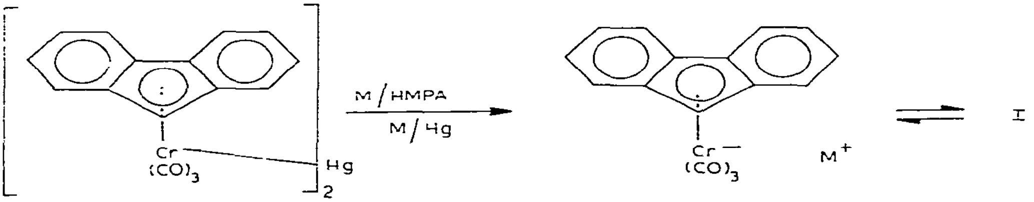
As the temperature of the Li salt of V in THF decreases to —70° C, the intensities of the 1788 and 1899 cm^{-1} bands belonging to the SSIP's increase. Such a behaviour is typical of carbanion salts [5].

The above data prove conclusively that in solutions of salts of II and their cyclopentadienyl analogues V in ether solvents of THF type equilibria between the SSIP's and CIP's (IIa and IIb, respectively) exist.



(IIa) (IIb) (3)

That the isomerization I → II is reversible is suggested by the following data. First, after about 1 h at 25°C and 7.5 h at 0°C the IR spectrum of the reaction mixture ceases to change, the bands of both I and II being observed, which can be clearly seen in Fig. 1b. The spectra of the equilibrium mixture I ⇌ II of the K salts of V shown in this figure, differ in that the spectrum of the mixture contains bands at 1841 and 1927 cm^{-1} belonging to I (the spectra of II and V, as stated above, are practically the same). Second, addition of crown ether IV leads to an increase in the relative intensity of the bands of I as compared with that of II, i.e. a shift of the equilibrium position (Fig. 1c). Third, the same equilibrium position is attained if one starts from the isomeric η^5-anion II, obtained by reducing the η^5-mercury compound (VII) with a K/Na alloy in THF, an alkali metal amalgam or with alkali metal solutions in HMPA.



(4)

Irrespective of the fact which isomeric anion, I or II, is initially generated, an equilibrium mixture of I and II will be formed in the long run, $K_{eq.}$ = [II]/[I] being independent of the method employed to obtain the mixture but being dependent of the type of cation, solvent and the temperature. The K_{eq} values determined from the IR spectra are listed in Table 2. The relative concentrations of isomers I and II were determined from the optical densities of the ν(CO) bands of the A_1 mode, assumpting equal extinction coefficients. This assumption is justified by the fact that in the course of reaction 2 the sum of the optical densities of these bands remains practically the same. For II, the intensity of the ν(CO) (A_1) band gives the total content of both the CIP's and SSIP's.

It was not possible to determine K_{eq} values for the Li salts of I and II in THF as the Li salt of I, as distinct from the similar Na and K salts, decomposes rapidly in THF solution to give η^6-fluorenechromium tricarbonyl.

TABLE 2

EQUILIBRIUM POSITIONS IN THE SYSTEM I ⇌ II

Cation	Solvent	Temperature (°C)	K_{eq} = [II]/[I]
K$^+$	THF	28	7.15
K$^+$	THF	0	5.57
K$^+$	THF + crown ether IV	28	2.71
K$^+$	HMPA	28	2.50
Na$^+$	THF	28	6.85
Na$^+$	THF + crown ether IV	28	2.85
Na$^+$	HMPA	28	2.50
$Ph_3PCH_3^+$	THF	28	1.69
Li$^+$	HMPA	28	2.70

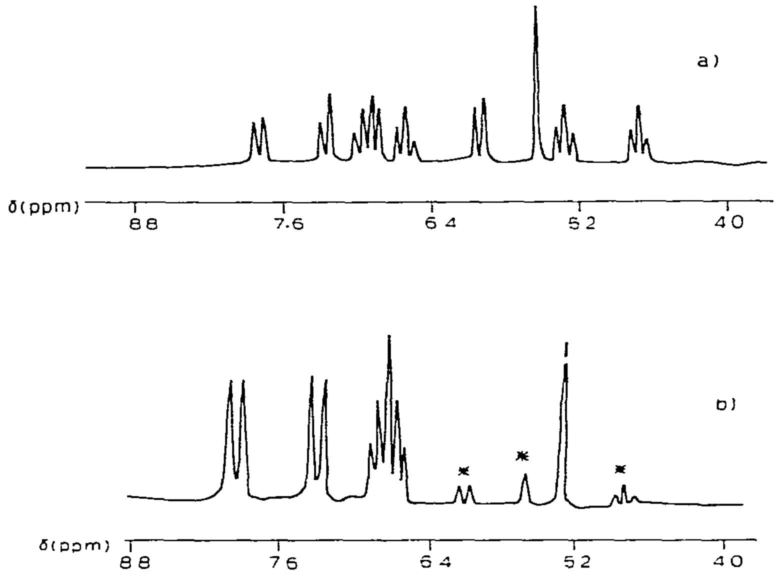


Fig. 2. (a) PMR spectrum of the K salt of I in THF-d_8 at —40°C. The multiplet centred at 6.9 ppm is a superposition of the doublet H(4) and triplet H(7), which is demonstrated with the aid of double resonance and integration. In the spectrum of the K salt of I at 28°C the difference in the chemical shifts δ_1 and δ_7 increases and there are undisturbed doublet H(4) and triplet H(7); (b) PMR spectrum of the equilibrium mixture of the K salts of I and II in THF-d_8 at 28°C. $K_{eq.}$ = 7.35 from the ratio between the intensities of the singlets at 5.40 and 5.53 ppm, considering that the singlet at 5.40 ppm from the H(9) proton of anion II coincides with the triplet at 5.32 ppm of the H(2) proton of anion I. The asterisk indicates the signals of anion I, part of these signals being hidden by those of anion II.

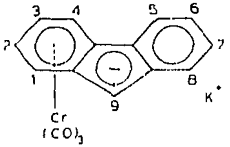
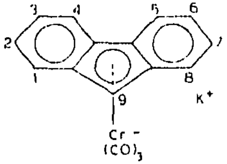
It can be seen from the K_{eq} values that in all cases the η^5-form of II predominates in the mixture. The addition of crown ether IV to the THF solution shifts the equilibrium towards I. A similar effect is produced by HMPA or by replacement of an alkali metal by $Ph_3PCH_3^+$.

The K salts of the isomeric η^6- and η^5-anions (I and II, respectively) were studied by the PMR method. Figure 2a shows the PMR spectrum of the K salt of I in THF-d_8 at —40°C. One can readily identify the H(9) signals at δ = 5.53 ppm and two AMPX patterns from the coordinated and noncoordinated benzene rings, respectively. The chemical shifts and spin-spin coupling constants can be readily determined by the rules for first-order spectra (see Table 3). The assignment of the signals is based on the assumption that the doublets from the H(4) and H(5) protons should be located at a lower field than those from the H(1) and H(8) ones because of a substantially larger contribution from the ring current of the second benzene ring. The same order of chemical shifts has been found for 9-fluorenylsodium [6]. The triplet signals were assigned to H(2) and H(3) (H(6) and H(7), respectively) with the aid of double resonance spectra. It should be noted that the chemical shifts of the protons of the K salt of I are temperature dependent, which may be due to the equilibrium between the two types of the ion pairs.

At a gradual increase of temperature the isomerization I → II becomes more pronounced. At 28°C the process proceeds readily and equilibrium is established after about 1 h. The equilibrium constant was determined from the ratio

TABLE 3

PMR SPECTRAL PARAMETERS FOR ANIONS I AND II [a]

Anion	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7	δ_8	δ_9	J_{12}	J_{23}	J_{34}	J_{56}	J_{67}	J_{78}
 [b]	6.00d	5.32t	4.70t	6.89d	7.78d	6.60t	6.94t	7.24d	5.53s	6.4	5.6	6.7	7.9	6.2	7.2
 [c]	7.32d	6.72 [d]	6.62 [d]	8.00d	8.00d	6.62 [d]	6.72 [d]	7.32d	5.40s	7.8	7.2	7.6	7.6	7.2	7.8
9-fluorenylsodium [e]	7.38	6.86	6.51	7.97	7.97	6.51	6.86	7.88	5.99	8.2	6.7	8.0	8.0	6.7	8.2

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[a] Chemical shifts are given in ppm, coupling constants in Hz. [b] At −40°C in THF-d_8. [c] At +28°C in THF-d_8. [d] The signals of the H(2), H(3) and H(6), H(7) protons represent the AB pattern of the ABMX system. [e] According to ref. 6.

between the intensities of the singlet signals from H(9) in I and II and equals 7.35, which agrees well with K_{eq} = 7.15 obtained by IR spectroscopy at the same temperature.

The spectrum of the η^5-anion II, containing an equilibrium amount of the η^6-form of I, is shown in Fig. 2b. The two benzene rings in II are equivalent and give a spectrum of the ABMX type.

In order to gain a better insight into the isomerization mechanism of I $\rightleftharpoons$ II, we studied the kinetics of reaction 2 for the K salts in THF at 0, 7, 15,5, 25 and 28°C, with and without crown ether IV. The kinetic data were treated by eq. 5 for the first order reversible reaction for each of the isomers:

$$\ln \frac{D_{eq.} - D_1}{D_{eq.} - D_2} = (k_1 + k_2)(t_2 - t_1) \qquad (5)$$

where D_{eq}, D_1 and D_2 are the optical densities of the bands at 1927 and 1905 cm^{-1} in the equilibrium position and at times t_1 and t_2, respectively. The calculation of $(k_1 + k_2)$ by an increase of the content of isomer II or decrease of I gives converging results, which points to the correct choice of eq. 5.

The kinetic and thermodynamic parameters for the isomerization I $\rightleftharpoons$ II are listed in Tables 4 and 5. It can be seen from Table 4 that with decreasing temperature K_{eq} = [II]/[I] decreases both in the presence and in the absence of crown ether IV. The type of dependence of K_{eq} on temperature and on the relation between the values of $\Delta H^{\neq}_{\mathrm{I}\to\mathrm{II}}$ and $\Delta H^{\neq}_{\mathrm{II}\to\mathrm{I}}$ suggests that from the viewpoint of enthalpy I is more favourable. At the same time in the equilibrium state II predominates due to the contribution of the entropy term, as the process I → II is characterized by a positive value of ΔS. It is possible to estimate the increase in entropy in reaction 2, equal to about 10 e.u., from the values of $\Delta S^{\neq}_{\mathrm{I}\to\mathrm{II}}$ and $\Delta S^{\neq}_{\mathrm{II}\to\mathrm{I}}$. In addition, large absolute values of the negative activation entropies for processes I → II and II → I, especially in the absence of IV, should be noted. In the presence of IV the absolute values of $\Delta S^{\neq}_{\mathrm{I}\to\mathrm{II}}$ and $\Delta S^{\neq}_{\mathrm{II}\to\mathrm{I}}$ are smaller, probably due to substantial solvation of the potassium cation in I and II.

The equilibrium in the system I $\rightleftharpoons$ II shifts towards I on addition of crown ether IV or use of HMPA as solvent, but the most pronounced shift of equilibrium towards I is observed case when the large cation $Ph_3PCH_3^+$ is used (see

TABLE 4

KINETIC ISOMERIZATION DATA FOR THE K SALTS OF ANIONS I AND II

Isomerization conditions	T (°K)	$k_{\mathrm{I}\to\mathrm{II}} \times 10^4$ (s^{-1})	$k_{\mathrm{II}\to\mathrm{I}} \times 10^4$ (s^{-1})	K_{eq}
In THF absence of IV	273	1.11	0.2	5.57
	280	1.22	0.21	5.96
	288.5	4.0	0.63	6.37
	298	8.9	1.23	6.95
	301	17.1	2.4	7.15
In THF, in the presence of IV	273	0.62	0.4	1.57
	285.5	2.75	1.12	2.46
	298	18.5	6.86	2.71

TABLE 5

THERMODYNAMIC ACTIVATION PARAMETERS FOR ISOMERIZATION I $\rightleftharpoons$ II

Parameters	In the absence of IV		In the presence of IV	
	I → II	II → I	I → II	II → I
E_A (kcal/mol)	16.3 ± 2.18	14.39 ± 2.37	21.9 ± 2.13	18.4 ± 3.36
$\Delta H^{\neq}$ (kcal/mol)	15.7 ± 2.04	13.8 ± 2.2	21.3 ± 2.10	17.8 ± 3.20
log A	8.95 ± 1.16	6.69 ± 1.07	13.27 ± 1.33	10.23 ± 1.9
$\Delta S^{\neq}$ (e.u.)	—19.6 ± 2.55	—29.9 ± 4.8	0.2 ± 0.02	—13.7 ± 2.5

Errors in the calculation of rate constants are less than 5%. Accuracy of measuring K_{eq} is 5%.

Table 2). Thus factors reducing the cation—anion interaction shift the equilibrium towards the η^6-form.

In the case of the equilibrium in THF or similar solvents, where the content of CIP's is sufficiently large without any solvating additives, one of the principal factors determining the equilibrium position will be represented by the susceptibility of the cation to solvation.

A more detailed study of the effect of cations, solvents and solvating additives on the process of metallotropic rearrangements in system 2 and in related systems is being conducted by the authors, and its results will be published separately.

Experimental

Complexes III and VII, used for the generation of the starting anions, were synthesized by previously described methods [1,2]. DME and THF were purified by refluxing over a K/Na alloy and were distilled in an argon atmosphere before use. HMPA was distilled in argon over calcium hydride. Solutions of I and II were prepared and cuvettes for measuring the IR spectra (CaF_2, a layer thickness of 0.1 mm) were filled in argon atmosphere. Temperature measurements were made by using a Zeiss cryostat. IR spectra were measured on a Zeiss UR-20 spectrometer equipped with a B 102a logarithmic recorder for intensity measurements.

The salts of the η^5-anion I in THF or DME were generated by treatment of 2 mg of fluorenechromium tricarbonyl in 1 ml of solvent at —40°C with a threefold excess of t-BuOK or an equimolecular amount of triphenylmethylenephosphorane. Alkali metal salts in HMPA were obtained by adding to a solution of III in HMPA of the above concentration several drops of a concentrated solution of Li, Na or K in the same solvent. The salts of η^5-anion II and its cyclopentadienyl analogue V in THF were produced by reducing the mercury derivatives of VI and VII with alkali metal amalgams, and in HMPA with alkali metal solutions in the same solvent. For the determination of the PMR spectra the K salt of I in THF-d_8 was generated as shown above for preparing solutions for the determination of the IR spectra.

The PMR spectra were recorded on a JEOL FX-100 spectrometer in the FT mode. The spectrum of anion I was recorded at —40° C and that of the equilibrium mixture of anions I and II at 28°C.

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