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Metal stabilized carbanions

XII *. Intramolecular $Cr(CO)_3$ migration from a phenyl to a cyclopentadienyl ring through a σ-bond

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Abstract

The potassium salts of (η^6-phenyl-TCC)cyclopentadienyl, 3-(η^6-phenyl-TCC)indenyl, and 9-(η^6-phenyl-TCC)fluorenyl, have been prepared in THF solution by metallation of the corresponding neutral complexes with potassium hydride. The anions are fairly stable at room temperature and have been fully characterized by ^1H and ^{13}C NMR spectroscopy. Above 50 °C the $Cr(CO)_3$ group (TCC) migrates irreversibly to the cyclopentadienyl residue. A kinetic study of this process has been carried out, and a mechanistic scheme for the haptotropic shift is proposed.

Introduction

Haptotropic migrations of a tricarbonylchromium unit, TCC, in *ortho*-condensed bicyclic polyene complexes from one ring to the other have been observed for both neutral [1] and anionic [2] systems. Kinetic studies have demonstrated that the migration is intramolecular. Extended Hückel molecular orbital calculations have been used to predict the preferred reaction route for metal migration in several bicyclic organic ligands, and a favoured route involving the periphery of the two coordination sites was indicated [3].

Recently, we described [4] a new kind of intramolecular TCC migration occurring between two coordination sites linked by a σ-bond, namely the $\eta^6 \rightarrow \eta^5$ haptotropic

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* For parts X and XI see refs. 15 and 7, respectively.

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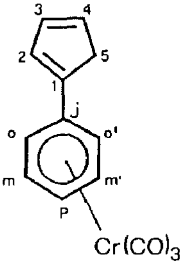
shift from the phenyl to the "*open*" pentadienyl residue in 3-(phenyl)pentadienyl anion. Information on this type of haptotropic rearrangement is very scarce. Metal migration in 9-(η^6-phenyl-TCC)antracene was observed by Öfele et al. [5], but the process was judged to be intermolecular since an intramolecular path seems to be unlikely on steric grounds. More recently, Ustynyuk et al. [6] have briefly reported that TCC migration occurs in 4-bromobiphenyl but not in the more hindered 2-(phenyl)toluene.

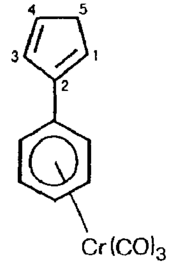
We present here the results of a kinetic study of the haptotropic rearrangement of TCC from the phenyl to the cyclopentadienyl molecular portion in phenylcyclopentadienyl, 3-(phenyl)indenyl, and 9-(phenyl)fluorenyl anions. The results are compared with those for the TCC migration in the "*open*" 3-phenylpentadienide and the "*ortho*-condensed" indenide and fluorenide systems.

Results

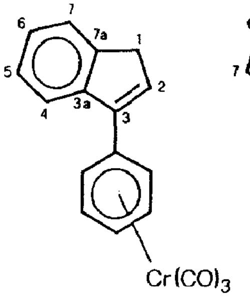
The neutral complexes 1-(η^6-phenyl-TCC)cyclopentadiene (I) and 2-(η^6-phenyl-TCC)cyclopentadiene (I′) (isomeric mixture 85/15), 3-(η^6-phenyl-TCC)indene (II) and 9-(η^6-phenyl-TCC)fluorene (III) were prepared as previously described [7],



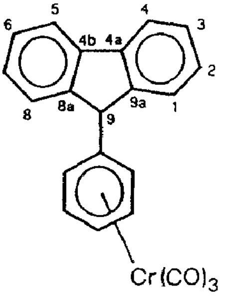
I



I'



II



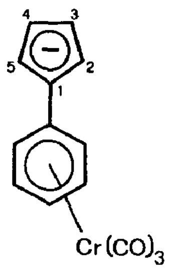
III

and converted into the corresponding anions by treatment of their THF solutions with an excess of KH in the presence of 18-crown-6 ether at 290 K under argon. The initial yellow colour of the solutions of neutral complexes quickly turned to dark green (solution of I + I′ and II) or orange (solution of III), and quantitative evolution of hydrogen gas occurred, in accord with eq. 1:

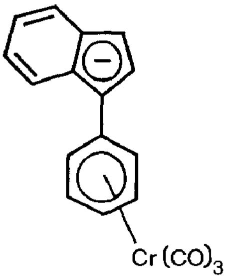
$$RH + KH \xrightarrow{290\text{ K, THF/18-crown-6 ether}} K^+R^- + H_2 \tag{1}$$

Quenching of the reaction mixtures with aqueous oxygen-free THF immediately restored the yellow colour, and the starting neutral complexes could be recovered unchanged in high yield.

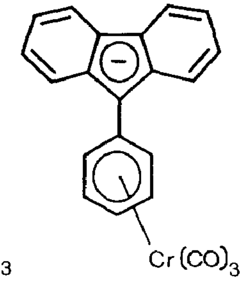
The ^{1}H NMR spectra of the anionic solutions were consistent with the formation of the species (η^6-phenyl-TCC)cyclopentadienyl (Ia), 3-(η^6-phenyl-TCC)indenyl (IIa) and 9-(η^6-phenyl-TCC)fluorenyl (IIIa) anions:



Ia



IIa



IIIa

The spectra consist of two distinct resonance patterns: one at high field ($\delta < 5.29$ ppm), an AA′BB′C system arising from the complexed phenyl ring protons common for the three substrates, and the other at low field, arising from the protons of the uncomplexed portion of the ligands. Ia exhibits an AA′BB′ pattern for the cyclopentadienyl protons, IIIa a unique ABCD spectrum for the fluorenyl moiety, and the signals from indenyl residue of IIa give rise to ABCD and XY patterns due to the benzo and cyclopentadienyl ring protons, respectively.

Table 1

^{1}H NMR parameters for I, I′, Ia, and Ib

H_i	I [a]	I′ [a]	Ia [b]	Ib [b]
	Chemical shifts, δ_i (ppm)			
$o = o'$	5.976	6.003	5.713	7.298
$m = m'$	5.760	5.760	5.622	7.043
p	5.557	5.608	4.916	6.863
1	–	6.854	–	–
2	7.055	–	6.270	4.835
3	6.560	6.846	5.860	4.342
4	6.531	6.596	5.860	4.342
5	3.362	3.232	6.270	4.835
i,j	Coupling constants, $J_{i,j}$ (Hz)			
$o,m = o',m'$	6.72 ± 0.03	6.72 [c]	7.17 ± 0.04	7.76 ± 0.04
$o,p = o',p$	1.03 ± 0.02	1.03 [c]	1.10 ± 0.03	1.21 ± 0.04
$o,m' = o',m$	0.37 ± 0.03	0.37 [c]	0.06 ± 0.04	0.51 ± 0.04
o,o'	1.69 ± 0.04	1.69 [c]	1.76 ± 0.07	1.96 ± 0.06
$m,p = m',p$	6.36 ± 0.02	6.35 [c]	5.99 ± 0.03	7.34 ± 0.03
m,m'	1.38 ± 0.04	1.38 [c]	1.70 ± 0.05	1.50 ± 0.06
1,3	–	1.43 ± 0.07	–	–
1,4	–	1.94 ± 0.07	–	–
1,5	–	1.74 ± 0.06	–	–
2,3	2.24 ± 0.04	–	3.89 ± 0.07	2.19 ± 0.06
2,4	1.21 ± 0.04	–	1.80 ± 0.07	2.19 ± 0.06
2,5	-1.28 ± 0.03	–	3.77 ± 0.13	2.14 ± 0.04
3,4	5.35 ± 0.03	4.84 ± 0.07	4.35 ± 0.13	2.15 ± 0.03
3,5	-1.61 ± 0.04	-1.66 ± 0.06	1.80 ± 0.07	2.19 ± 0.06
4,5	1.61 ± 0.04	1.27 ± 0.05	3.89 ± 0.07	2.19 ± 0.06

[a] 10^{-2} *M* in acetone-d_6; *T* 300 K. [b] 10^{-2} *M* in THF-d_8/18-crown-6 ether, counter-ion K^+; *T* 300 K.
[c] Not refined by iteration.

Table 2

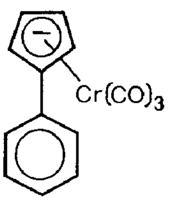
^{1}H NMR parameters for II, IIa, and IIb

H_i	II [a]	IIa [b]	IIb [b]	IIa [c]	IIb [c]
	Chemical shifts, δ_i (ppm)				
$o = o'$	6.021	5.860	7.689	5.703	7.697
$m = m'$	5.826	5.727	7.212	5.497	7.190
p	5.709	4.931	7.035	4.722	6.996
1	3.565	6.085	4.916	5.997	4.850
2	6.977	6.959	5.203	6.866	5.147
4	7.734	7.725	7.690	7.580	7.661
5	7.368	6.736	6.689	6.599	6.644
6	7.285	6.618	6.633	6.476	6.587
7	7.554	7.305	7.304	7.156	7.284
i,j	Coupling constants, $J_{i,j}$ (Hz)				
$o,m = o',m'$	6.66 ± 0.03	7.11 ± 0.02	7.89 ± 0.03	7.14 ± 0.02	7.89 ± 0.03
$o,p = o',p$	1.03 ± 0.02	1.11 ± 0.02	1.26 ± 0.03	1.10 ± 0.02	1.28 ± 0.03
$o,m' = o',m$	0.34 ± 0.03	0.26 ± 0.02	0.50 ± 0.03	0.21 ± 0.02	0.51 ± 0.03
o,o'	1.75 ± 0.05	2.07 ± 0.03	1.83 ± 0.05	2.04 ± 0.03	1.99 ± 0.04
$m,p = m',p$	6.37 ± 0.02	6.16 ± 0.01	7.39 ± 0.03	6.03 ± 0.02	7.41 ± 0.02
m,m'	1.24 ± 0.04	1.45 ± 0.02	1.63 ± 0.04	1.49 ± 0.03	1.62 ± 0.05
1,2	2.28 ± 0.02	4.23 ± 0.01	2.99 ± 0.01	4.36 ± 0.01	2.97 ± 0.02
1,4	0.20 ± 0.04	0.80 ± 0.01	0.77 ± 0.01	0.75 ± 0.01	0.79 ± 0.02
1,5	0.68 ± 0.01	–	–	–	–
1,6	0.20 ± 0.04	–	–	–	–
1,7	0.78 ± 0.01	–	–	–	–
2,4	0.15 ± 0.03	–	–	–	–
2,5	0.20 [d]	–	–	–	–
2,6	0.44 ± 0.02	–	–	–	–
2,7	0.00 ± 0.01	–	–	–	–
4,5	7.77 ± 0.01	8.19 ± 0.01	8.72 ± 0.02	8.07 ± 0.01	8.77 ± 0.02
4,6	1.04 ± 0.01	1.00 ± 0.01	1.05 ± 0.02	1.05 ± 0.01	0.97 ± 0.02
4,7	0.78 ± 0.01	0.81 ± 0.01	0.86 ± 0.01	0.74 ± 0.01	0.91 ± 0.02
5,6	7.48 ± 0.01	6.73 ± 0.01	6.48 ± 0.02	6.75 ± 0.01	6.47 ± 0.02
5,7	1.16 ± 0.01	1.23 ± 0.01	1.08 ± 0.02	1.21 ± 0.01	1.00 ± 0.02
6,7	7.52 ± 0.01	7.88 ± 0.01	8.55 ± 0.02	7.76 ± 0.01	8.56 ± 0.02

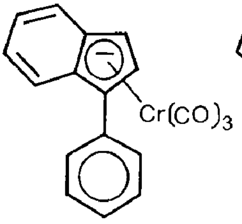
[a] 10^{-2} M in acetone-d_6; T 300 K. [b] 10^{-2} M in THF-d_8, counter-ion K^+; T 300 K. [c] 10^{-2} M in THF-d_8/18-crown-6 ether, counter-ion K^+, T 300 K. [d] Not refined by iteration.

The spectra were analyzed by computer simulation and the parameters obtained are listed in Tables 1, 2 and 3, together with data for the neutral complexes taken from ref. 7. The proton assignments were confirmed by ^{1}H-{^{1}H} NOE measurements.

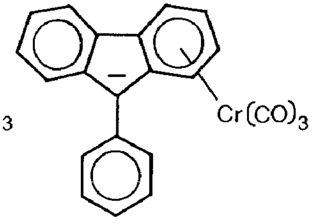
Above 50 °C the isomers Ia, IIa, and IIIa are unstable, and the TCC group irreversibly migrates from the phenyl to the cyclopentadienyl ring as indicated by the ^{1}H NMR spectra of the solutions after heating. The spectra showed unambiguously that only one species was present in each case, namely the η^5-(phenyl)cyclopentadienyl-TCC (Ib), η^5-3-(phenyl)indenyl-TCC (IIb) or η^6-9-(phenyl)fluorenyl TCC (IIIc) anion:



Ib



IIb



IIIc

In the final hapto-isomers the absence of metal coordination to the phenyl ring is shown by the large downfield shift experienced by the corresponding AA′BB′C proton resonance pattern which now appears at $\delta > 6.8$ ppm. On the other hand, coordinative interaction with the metal of the five-membered ring is demonstrated by the large upfield shift displayed by the cyclopentadienyl proton resonances in Ib and IIb. The quantitative formation of IIIc from IIIa is indicated by the signals from the protons of the fluorenyl residue, which give rise to two independent ABCD patterns in the ranges δ 4.8–6.8 and 6.7–7.8 ppm relating to the complexed and uncomplexed benzo rings, respectively. In the case of IIb and IIIc the low field portion of the spectrum is complicated by considerable overlap of resonances belonging to different spin systems, i.e., the uncomplexed phenyl and the benzo fragments. However, the ^{1}H resonance patterns could be analysed by computer simulation and the calculated parameters are listed in Tables 1, 2 and 3. The proton signals were unambiguously assigned by NOE studies.

Both neutral and anionic systems were also studied by ^{13}C NMR spectroscopy, and the spectra obtained are in agreement with the molecular structures deduced from the proton spectral analysis. Carbon signal assignments were made by selective proton decoupling experiments, and the chemical shifts are shown in Tables 4, 5 and 6.

The isomerization was carried out in sealed NMR tubes at four different temperatures and monitored by ^{1}H NMR spectroscopy. Use of the first order equation for an irreversible reaction gave satisfactory plots ($r \geqslant 0.998$) up to 90% of reaction. Rate constants and activation parameters, calculated from Eyring plots ($r = 0.999$), are listed in Table 7, together with the kinetic data relative to 3-(η^6-phenyl-TCC)pentadienyl anion (IVa) taken from ref. 4.

The intramolecular nature of the metal migration was demonstrated by carrying the reactions in the presence of ligands with high complexation ability towards TCC. Thus, when the isomerization was performed after addition of hexamethylbenzene or potassium fluorenide no cross products could be detected.

Treatment of the solutions of IIb and IIIc with aqueous oxygen-free THF under argon gave η^6-3-(phenyl)indene-TCC and η^6-9-(phenyl)fluorene-TCC in high yield, but similar quenching of the solution of Ib caused decomplexation and formation of unidentified products.

The formation of anions Ia, IIa, and IIIa by metallation of the neutral complexes I, II, and III with KH in THF solution also took place in the absence of 18-crown-6 ether, but under these conditions Ia did not isomerize in the range of temperatures used for the other anions, and when higher temperatures were used only decomposition was observed. In contrast, metal slippage still took place in the case of IIa and

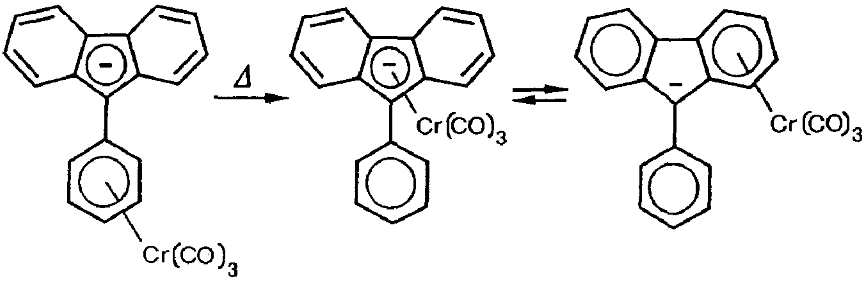
Table 3

^{1}H NMR parameters for III, IIIa, and IIIc

H_i	III [a]	IIIa [b]	IIIa [c]	IIIc [c]
	Chemical shifts, δ_i (ppm)			
$o = o'$	5.530	5.983	5.910	7.707
$m = m'$	5.610	5.801	5.637	7.255
p	5.679	4.937	4.779	6.852
1	7.799	7.929	7.874	6.458
2	7.395	7.095	7.002	5.309
3	7.470	6.761	6.675	4.800
4	7.923	7.947	7.828	6.803
5	7.923	7.947	7.828	7.850
6	7.470	6.761	6.675	6.717
7	7.395	7.095	7.002	7.025
8	7.799	7.929	7.874	7.728
9	5.002	–	–	–
i,j	Coupling constants, $J_{i,j}$ (Hz)			
$o,m = o',m'$	6.56 ± 0.03	7.31 ± 0.03	7.30 ± 0.03	7.96 ± 0.05
$o,p = o',p$	1.06 ± 0.03	1.41 ± 0.03	1.14 ± 0.03	1.25 ± 0.04
$o,m' = o',m$	0.30 ± 0.04	0.12 ± 0.03	0.11 ± 0.03	0.46 ± 0.05
o,o'	1.81 ± 0.05	1.71 ± 0.05	1.58 ± 0.05	2.01 ± 0.07
$m,p = m',p$	6.34 ± 0.03	6.12 ± 0.02	6.02 ± 0.03	7.34 ± 0.05
m,m'	1.17 ± 0.06	1.72 ± 0.05	1.85 ± 0.05	1.35 ± 0.07
$o,9 = o',9$	0.3 [d]	–	–	–
$m,9 = m',9$	0.1 [d]	–	–	–
$p,9$	0.0 [d]	–	–	–
1,2	7.67 ± 0.01	8.20 ± 0.02	8.29 ± 0.06	7.30 ± 0.02
1,3	1.08 ± 0.01	0.96 ± 0.02	1.04 ± 0.05	0.99 ± 0.02
1,4	0.71 ± 0.01	0.80 ± 0.02	0.75 ± 0.05	0.52 ± 0.02
1,9	0.9 [d]	–	–	–
2,3	7.45 ± 0.01	6.85 ± 0.02	6.84 ± 0.06	5.72 ± 0.02
2,4	1.14 [d]	1.30 ± 0.02	1.27 ± 0.07	1.17 ± 0.02
2,9	0.0 [d]	–	–	–
3,4	7.68 ± 0.01	7.71 ± 0.02	7.67 ± 0.05	6.51 ± 0.02
3,9	0.7 [d]	–	–	–
4,9	0.25 [d]	–	–	–
5,6	7.68 ± 0.01	7.71 ± 0.02	7.67 ± 0.05	7.78 ± 0.01
5,7	1.14 ± 0.01	1.30 ± 0.02	1.27 ± 0.07	1.24 ± 0.01
5,8	0.71 ± 0.01	0.80 ± 0.02	0.75 ± 0.05	0.75 ± 0.02
5,9	0.25 [d]	–	–	–
6,7	7.45 ± 0.01	6.85 ± 0.02	6.84 ± 0.06	6.81 ± 0.01
6,8	1.08 ± 0.01	0.96 ± 0.02	1.04 ± 0.05	1.01 ± 0.02
6,9	0.7 [d]	–	–	–
7,8	7.67 ± 0.01	8.20 ± 0.02	8.28 ± 0.06	8.18 ± 0.02
7,9	0.0 [d]	–	–	–
8,9	0.9 [d]	–	–	–

[a] 10^{-2} M in acetone-d_6; T 300 K. [b] 10^{-2} M in THF-d_8, counter-ion K^+; T 300 K. [c] 10^{-2} M in THF-d_8/18-crown-6 ether, counter-ion K^+; T 300 K. [d] Not refined by iteration.

IIIa although more slowly (see rate constants for IIIa in Table 7). Moreover, in contrast to the result observed in the presence of 18-crown-6 ether, the isomerization of IIIa gave rise to an equilibrium mixture of the isomers IIIb and IIIc:



IIIa IIIb IIIc

Table 4

^{13}C NMR chemical shifts [a] for I, Ia, and Ib

C_i	I [b]	Ia [c]	Ib [c]
$o = o'$	91.64	85.22	126.02
$m = m'$	95.22	98.02	128.03
p	92.85	83.76	124.52
j	107.19	125.56	141.13
1	143.50	112.82	100.44
2	131.24	107.00	81.79
3	133.36	111.31	81.90
4	135.25	111.31	81.90
5	41.64	107.00	81.79
CO	234.74	237.55	246.17

[a] ppm from internal TMS. [b] 0.1 *M* in acetone-d_6; *T* 300 K. [c] 0.1 *M* in THF-d_8/18-crown-6 ether, counter-ion K$^+$; *T* 300 K.

Table 5

^{13}C NMR chemical shifts [a] for II, IIa, and IIb

C_i	II [b]	IIa [c]	IIb [c]
$o = o'$	94.16	86.46	129.01
$m = m'$	94.85	99.93	128.25
p	93.79	84.42	125.15
j	106.71	126.75	140.95
1	38.72	102.23	72.19
2	135.44	120.95	91.96
3	145.58	101.31	93.32
3*a*	142.84	129.60	107.15
4	121.20	118.72	124.12
5	127.01	117.55	121.02
6	126.13	116.02	120.44
7	125.07	120.11	126.57
7*a*	141.16	135.44	106.09
CO	234.30	238.36	245.58

[a] ppm from internal TMS. [b] 0.1 *M* in acetone-d_6; *T* 300 K. [c] 0.1 *M* in THF-d_8/18-crown-6 ether, counter-ion K$^+$; *T* 300 K.

Table 6

^{13}C NMR chemical shifts [a] for III, IIIa, and IIIc

C_i	III [b]	IIIa [c]	IIIc [c]
$o = o'$	94.52	86.59	128.43
$m = m'$	94.26	99.19	128.52
p	95.04	82.16	121.37
j	114.78	129.78	140.48
1	126.17	117.44	83.16
2	128.25	122.75	93.53
3	129.01	114.37	78.91
4	121.02	119.00	93.70
4a	141.71	129.58	97.30
4b	141.71	129.58	127.31
5	121.02	119.00	119.57
6	129.01	114.37	114.23
7	128.25	122.75	123.42
8	126.17	117.44	116.41
8a	145.44	138.15	142.14
9	51.86	92.83	94.79
9a	145.44	138.15	118.19
CO	234.56	237.80	239.68

[a] ppm from internal TMS. [b] 0.1 M in acetone-d_6, T 300 K. [c] 0.1 M in THF-d_8/18-crown-6 ether, counter-ion K^+, T 300 K.

Thus, in agreement with the observations of Ustynyuk et al. [8], the position of the $\eta^5 \rightleftarrows \eta^6$ metallotropic equilibrium involving the species IIIb and IIIc is influenced by additives that solvate the alkali metal cation, and it is almost completely shifted over to the η^6-isomer in the presence of an excess of 18-crown-6 ether.

The ^{1}H NMR spectra of IIa, IIb, and IIIa in pure THF solutions were also analyzed by computer simulation and the derived parameters are shown in the Tables 1, 2 and 3. Because of the almost complete overlap of the resonances for the two species, it was not possible to analyse the spectrum of the equilibrium mixture of IIIb and IIIc.

Table 7

Rate constants and activation parameters for the $\eta^6 \rightarrow \eta^5$ haptotropic rearrangements

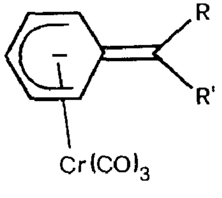
Anion	10^4 k (s^{-1}) (T, K)	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (cal mol^{-1} K^{-1})
Ia [a]	1.03 ± 0.03(325); 2.32 ± 0.01(332); 3.85 ± 0.02(337); 6.21 ± 0.02(342)	22.7 ± 0.4	−7.1 ± 1.1
IIa [a]	1.30 ± 0.02(324); 4.32 ± 0.02(335); 7.86 ± 0.03(341); 12.5 ± 0.2(346)	22.3 ± 0.4	−7.6 ± 0.6
IIIa [a]	1.08 ± 0.01(338); 1.84 ± 0.01(343); 3.15 ± 0.06(348); 5.20 ± 0.06(353)	24.3 ± 0.2	−2.6 ± 0.7
IIIa [b]	0.407 ± 0.010(333); 1.95 ± 0.05(348); 3.47 ± 0.01(353)	24.1 ± 0.4	−6.5 ± 1.3
IVa [a,c]	0.71 ± 0.01(304); 2.00 ± 0.01(314); 7.87 ± 0.02(324)	22.9 ± 0.5	−2.4 ± 1.0

[a] In THF/18-crown-6 ether. [b] In pure THF. [c] Data from ref. 4.

Discussion

Structure and conformation of the η^6 and η^5 anions

The molecular symmetry of the anions Ia and IIIa as suggested by their ^1H and ^{13}C NMR spectra could result either from free rotation around the σ-bond connecting the complexed and uncomplexed moieties of the organic ligand or from a conformation in which the two residues lie in the same plane. However, the equivalence of the *o,o′* and *m,m′* hydrogen and carbon atoms of the complexed phenyl ring, found also for the homologous structurally asymmetric IIa, rules out the possibility of a rigid coplanar conformation. Therefore, the η^5-benzylidenecyclohexadienyl electronic structure, V, which is responsible for freezing of rotation of the complexed phenyl ring around the exocyclic bond in 3-(η^6-phenyl-TCC)pentadienyl (IVa) [4], and TCC-complexed di- and tri-phenylmethyl carbanions [9], must contribute to a minor extent to the resonance hybrid of the anions Ia–IIIa. This is clearly evidenced by the large fall in the magnitude of the effect of ionization on the ^{13}C chemical shifts for the *ortho, para,* and carbonyl carbon atoms, namely $\Delta i = \Delta i(\text{anion}) - \Delta i(\text{hydrocarbon})$, observed upon the closure of the pentadienyl skeleton (cf. the Δi values for the "open" IVa with those for the "closed" Ia–IIIa in Table 8). This feature is reflected also in the small values of the differences between the vicinal coupling constants for the complexed phenyl ring protons, $\Delta^3J(\text{H,H}) = {}^3J_{o,m} - {}^3J_{m,p}$, found for Ia–IIIa and those of the corresponding parameter for IVa (cf. Table 8).



V

However, it is noteworthy that the closure of the pentadienyl skeleton causes a large downfield shift of the *ortho* phenyl ring proton resonances, and the sequence of chemical shifts, $\delta_m > \delta_o > \delta_p$, observed for IVa, changes into $\delta_o > \delta_m > \delta_p$ for Ia–IIIa (see Table 9). This effect can be explained in terms of the contribution to δ_o of the anisotropic current in the cyclopentadienyl ring, and the downfield direction of the shift reveals the preferred planar conformations of the organic ligand.

Table 8

Ionization effects on ^{13}C NMR chemical shifts [a] for the anions Ia–IVa

Anion	Δo	Δm	Δp	Δj	Δ_{CO}	Δ^3J(H,H) (Hz)
Ia	−6.42	+2.80	−9.09	+18.37	+2.80	1.18
IIa	−7.70	+5.08	−9.37	+20.04	+4.06	1.11
IIIa	−7.93	+4.30	−12.91	+15.00	+3.24	1.28
IVa [b]	−21.77	+6.33	−19.57	+21.58	+5.44	1.98

[a] $\Delta i = \delta_i$ (anion) − δ_i (hydrocarbon), ppm. [b] $\delta(^{13}C)$ values for the neutral hydrocarbon (in acetone-d_6, ppm from internal TMS): 234.50 (CO), 113.92 (*j*), 96.31 (*o,o′*), 94.96 (*p*), 93.56 (*m,m′*). For IVa, see ref. 4.

Table 9

Selected ^1H NMR chemical shifts for the anions Ia–IVa

Anion	δ_o	δ_m	δ_p
Ia	5.713	5.662	4.916
IIa	5.703	5.497	4.722
IIIa	5.910	5.637	4.779
IVa [a]	4.559	5.055	4.463

[a] Data from ref. 4.

On the basis of the above observations, the occurrence of a fast exchange (on the NMR time scale) between the two equivalent and energetically favoured conformations having the two ring systems situated on the same plane can be confidently proposed. This view is supported by the results of NOE experiments. As shown in Fig. 1 the NOE values observed for Ia, Ib, IIa, and IIb indicate that the dipolar interaction between the *ortho* protons of the phenyl ring and the nearest protons of cyclopentadienyl residue decreases greatly on going from the η^6 to the η^5 hapto isomers. This implies that the distance between these pairs of protons must be shorter in the η^6-species, and it can easily be confirmed that the dipolar interaction is at a maximum when the ligand adopts a planar arrangement.

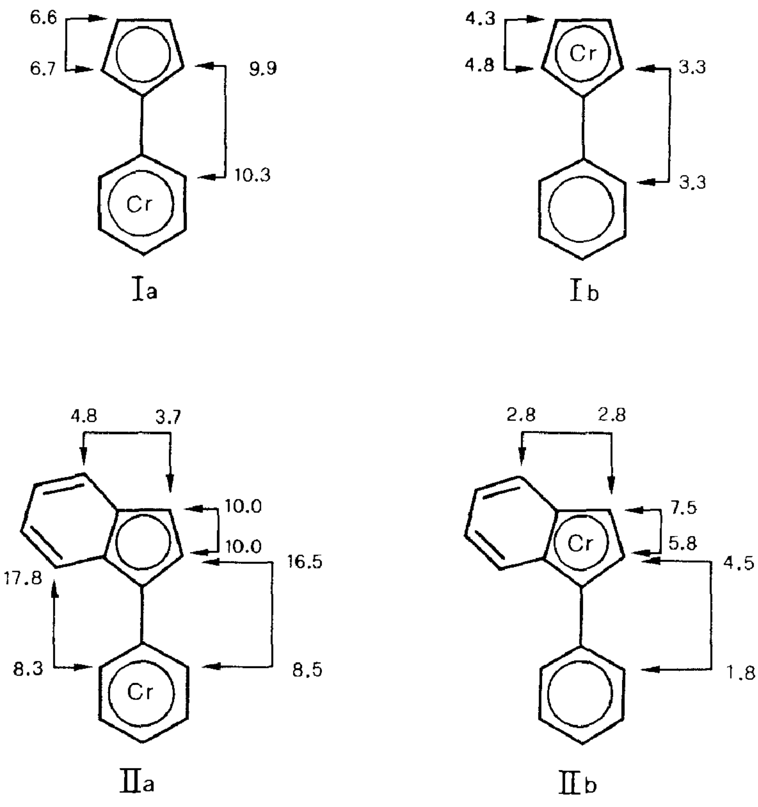


Fig. 1. ^1H-{^1H} NOE enhancements (T 300 K). The numbers at the tip of the arrows indicate the percentage enhancements upon saturation of the connected nucleus.

Thus, it appears that the $\eta^6 \rightarrow \eta^5$ metal shift is accompanied by an increase in the distance between the two ring systems, and this probably results from the lack of stability of the ligand planar conformations in the η^5 species. As a consequence, in the η^5 hapto isomers the phenyl ring is no longer available to withdraw the negative charge by a conjugative mechanism. In fact, the charge is mainly delocalized from the five-membered ring into the inorganic unit, as indicated by the large downfield shift experienced by the carbonyl carbon resonances upon isomerization ($\Delta\delta(CO) = +8.62$ and $+7.22$ for Ib and IIb, respectively). This situation is also indicated by the absence in the case of the η^5-TCC-cyclopentadienyl anions of structural effects on the carbonyl carbon chemical shifts, which appear not to be affected by substituents on the penta-atomic ring, and exhibit $\delta(CO)$ values at about 246 ppm (π-cyclopentadienyl-TCC $\delta(CO) = 246.9$ [10], Ib $\delta(CO) = 246.17$, and IIb $\delta(CO) = 245.58$).

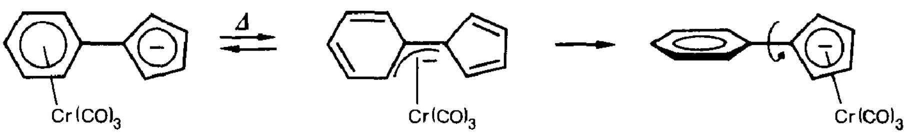
Kinetics of the $\eta^6 \rightarrow \eta^5$ haptotropic rearrangement

Comparison of the rate constants for the $\eta^6 \rightarrow \eta^5$ intramolecular migration of TCC from a phenyl to a pentadienyl coordination site through a σ-bond shows that the rate depends on the structure of the penta-atomic frame, and is markedly higher when the metal slippage occurs towards an "open" pentadienyl skeleton; for example, at $T = 325$ K the rate constant ratio for the isomerization of Ia and IVa is about 1/8 (cf. Table 7). Examination of the activation parameters indicates that differences of reactivity are mainly due to variations in the entropic term (see Table 7). The negative values of $\Delta S^{\ddagger}$ found for all the investigated substrates, together with their further decrease observed when the isomerization is carried out in the absence of the 18-crown-6 ether (eg., isomerization of IIIa, see Table 7), may be the result of solvent reorganization around the alkali metal cation during the TCC slippage. This behaviour probably arises from the incomplete solvation of K^+, and, as a consequence, the ionic state of the η^6 species must consist of contact ion-pairs in equilibrium with solvent-separated ion-pairs. In the case of contact ion-pairs, during the TCC migration the alkali metal moves away from the pentadienyl residue and becomes solvated by solvent molecules, to be eventually released to the η^5 isomer to form another contact ion-pair in which the cation interacts with one carbonyl oxygen atom, as usually found for TCC-cyclopentadienyl anions [8,11]. Clearly such a process cannot occur in the case of solvent-separated ion-pairs, where K^+ is always trapped by the crown ether.

As far as the $\Delta H^{\ddagger}$ values are concerned, it can be seen that they are little affected by structural modification of the ligand, such as closure of pentadienyl skeleton and its benzanellation, a significant increase being found only for the fluorenyl system (see Table 7).

These observations suggest that in all the investigated substrates the inorganic unit moves along the same path.

The simplest and most attractive mechanistic scheme for the isomerization, which is consistent with the kinetic and conformational results involves the formation of a η^3-allyl intermediate, as shown in eq. 2 for the process Ia → Ib:

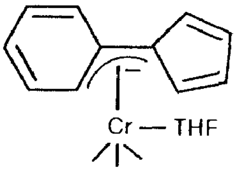


(2)

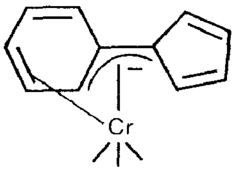
It is assumed that the energetically-favoured coplanar conformations between the two coordination sites in the initial η^6 anion meet the essential requirement for the occurrence of the intramolecular TCC rearrangement along the σ-bond. The spectroscopic data indicate that this condition is no longer met in the case of the η^5 anions, and this could be the reason for the irreversible character of the isomerization process. The planar geometry of the organic ligand is required also by the η^3-allyl structure of the intermediate, which must be the same for the forward and back reaction. In this respect, the results of quenching of the η^5 anion solutions are instructive; reaction of IIb and IIIb with water quickly produces η^6-3-(phenyl)indene-TCC and η^6-9-(phenyl)fluorene-TCC, respectively, while similar treatment of Ib and IVb leads to decomposition products only. In the case of the anions IIb and IIIb, protonation of the five-membered ring takes place concomitantly with the TCC shift towards the *ortho* condensed benzo ring, no metal rearrangement towards the σ-bonded phenyl ring being observed. When the structure of the ligand is such that no coplanar coordination sites are available, as in Ib and IVb, protonation at the pentadienyl residue is not accompanied by the shift of TCC to the phenyl residue, and the protonated complex can only undergo decomplexation.

In a theoretical analysis of TCC migration between *ortho*-condensed aromatic rings, Albright et al. [3] proposed a reaction path involving formation of an η^3-allyl intermediate. The kinetics of this process have been studied for indenyl [12] and fluorenyl [1b,1c] anionic systems, and it has been found that the activation enthalpy is 18–19 kcal mol^{-1}, a value much lower than that found when the metal migration is between σ-bonded coordination sites (22–24 kcal mol^{-1}, see Table 7). The larger $\Delta H^{\ddagger}$ values in the second case can be attributed to steric interactions between the phenyl ring and the substituents in the 2- and 5-positions of the (cyclo)pentadienyl skeleton, arising from the shortening of the central junction bond required for the formation of the allyl intermediate. The higher energy barrier observed when the isomerization takes place in the more hindered IIIa complex is consistent with this interpretation.

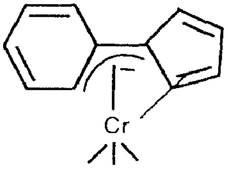
The proposed allyl intermediate is a species in which the metal is an electron deficient centre, and can be stabilized through the binding of a THF molecule as in (**a**):



(**a**)



(**b**)



(**c**)

A different type of stabilization could result from the interaction of the metal with a neighbouring double bond, situated either on the phenyl or on the pentadienyl residue, to give rise to coordination with a penta-atomic fragment in a planar "sickle" conformation, as illustrated in (**b**) and (**c**). In our opinion, this possibility accounts well for the fluxional nature of these haptotropic rearrangements. We are not aware of the existence of any stable complexes in which chromium is bonded to a pentadienyl ligand in a "sickle" conformation, but this possibility is supported by the recent isolation of a molybdenum complex in which there is a preference of the group VIb metal for η^5-coordination towards a "sickle" pentadienyl ligand [13].

Experimental

The ^1H and ^{13}C NMR spectra were obtained on a Bruker WP-200 SY spectrometer operating in the FT mode. The proton spectra were analyzed by computer simulation on an Aspect-2000 Bruker computer using the Bruker PANIC program. The ^{13}C lines assignment was based on selective proton decoupling experiments and partially relaxed spectra. For ^1H-$\{^1H\}$ NOE measurements the usual procedure for gated experiments was modified [14], and the selected multiplet was saturated by a 8 s cyclic perturbation of all lines with a 42 dB attenuation of a nominal 0.2 W decoupling power. The percentage enhancements were obtained from the multiplier of the reference spectrum which brings the multiplet to exact matching of the perturbed spectrum; errors are ca. 0.3%.

The products of electrophilic quenching of the anion solution were purified by column chromatography and identified by ^1H NMR spectroscopy and TLC.

In the kinetic runs the aquisition of the FID's were carried out under fully-relaxed conditions. The integrals of the various proton multiplets were normalized against the signal from a trace of cyclohexane used as internal standard for the integration. The very high signal-to-noise ratio for the spectra meant that the uncertainty in the integral determination was less than 1%.

In the competition experiments, 2 to 10 equivalents of the scavengers were added to the starting neutral complex. In our experimental conditions, while hexamethylbenzene was found to be completely unreactive towards KH, fluorene reacted very rapidly to give the corresponding fluorenyl anion.

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