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Metal stabilized carbanions

XIII *. The mechanism of migration of the $\text{Cr}(\text{CO})_3$ unit from the six- to the five-membered ring in indenyl anions

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Abstract

The potassium salts of η^6 -indenyl-, η^6 -(1-phenyl)indenyl-, and η^6 -(1,3-diphenyl)indenyl- $\text{Cr}(\text{CO})_3$ anions have been prepared in THF solution at -30°C and fully characterized by ^1H NMR spectroscopy. At higher temperatures, the $\text{Cr}(\text{CO})_3$ group migrates from the benzo- to the cyclopentadienyl-ring, the migration being slowest for the 1,3-diphenyl-substituted species. A kinetic study indicates that an intra-molecular pathway through an η^3 intermediate is preferred.

Introduction

Intramolecular migrations in bicyclic polyene- ML_n complexes in which the inorganic unit migrates from one coordination site to the other have been observed for both neutral [2] and charged [1,3] systems. Extended Hückel calculations [4] indicate that such rearrangements will tend to have high activation energies, at least for FeCp (Cp = cyclopentadienyl) and $\text{Cr}(\text{CO})_3$ units. In *ortho*-condensed $4n + 2\pi$ -electron systems, such as naphthalene-, indenide- and fluorenyl- $\text{Cr}(\text{CO})_3$ complexes (in the fluorenyl anion only the electrons involved in the two coordination sites are considered), the least motion pathway across the bond shared by the two rings is the highest energy route and a circuitous path via the periphery of the rings is energetically favoured.

Kinetic studies, carried out on naphthalene- and dimethoxynaphthalene- $\text{Cr}(\text{CO})_3$ in non-coordinating solvents [5] and on fluorenyl- $\text{Cr}(\text{CO})_3$ [6a,c] and benzocyclo-

* For Part XII see ref. 1

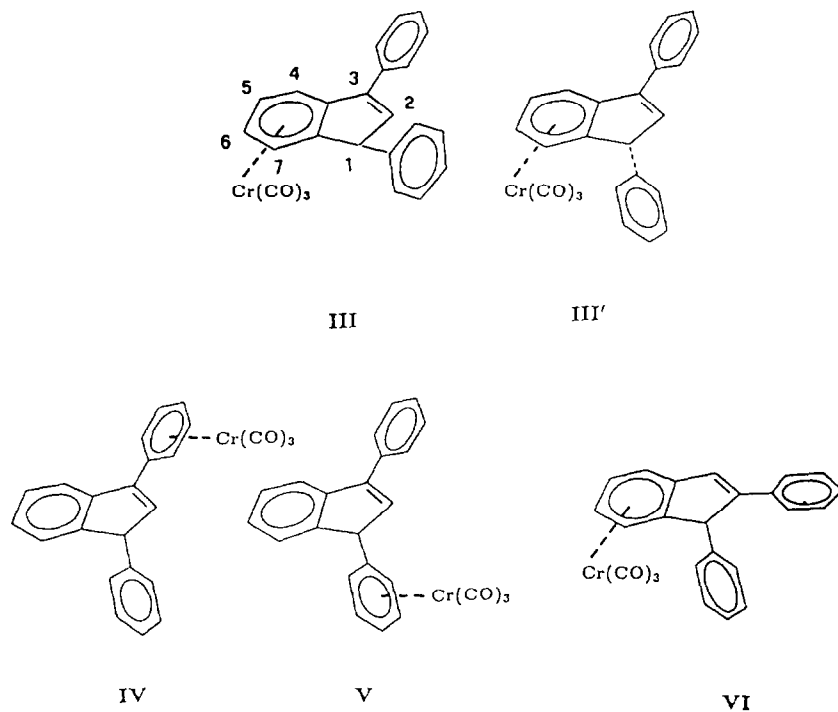
heptatrienyl-Cr(CO)₃ potassium [6d] in coordinating solvents, suggest that the migration occurs along a peripheral path involving the formation of an η^3 allyl-type intermediate. On the other hand, no kinetic information is available for haptotropic shifts in indenyl-ML_n systems even though there is experimental evidence for occurrence of this slippage [7]. In particular, deprotonation of η^6 -indene-Cr(CO)₃ at room temperature leads directly to the η^5 -indenyl-Cr(CO)₃ anion, observation of the η^6 -isomer being possible only at -78°C [8].

We present here the results of a kinetic study of the $\eta^6 \rightarrow \eta^5$ rearrangement of Cr(CO)₃ in the unsubstituted 1-phenyl- and 1,3-diphenyl-substituted indenyl anions. Information about the structure of the ion pairs in solution has been obtained by IR spectroscopy.

Results and discussion

Synthesis of indene-Cr(CO)₃ complexes

Indene-Cr(CO)₃, I [9], and η^6 -(3-phenyl)-indene-Cr(CO)₃, II [10], were prepared by standard literature methods. Complexation of 1,3-diphenyl-indene at the benzo ring can give rise to two stereoisomers, viz., *exo* and *endo*, depending upon the relative position of the 1-phenyl group with respect to Cr(CO)₃, while complexation of the 1- or 3-phenyl ring can produce two other different structural isomers. The reaction of this ligand with (CH₃CN)₃Cr(CO)₃ in boiling THF gave, after separation by column chromatography, three yellow products, which were identified by



^1H NMR and mass spectroscopy. The first product eluted (3% yield) was shown to be a 1 : 1 mixture of the two stereoisomers III and III', the second (7% yield) a 4 : 1 mixture of isomers IV and V, and compound VI (a few milligrams) in which a phenyl group has migrated from C(3) to C(2).

When complexation was carried out with $\text{Cr}(\text{CO})_6$ in $n\text{-Bu}_2\text{O}/\text{THF}$ 10 : 1 v/v at 120°C the stereoisomer III was obtained in 12% yield together with a 4 : 1 mixture of IV and V (20% overall yield) and traces of VI. It is noteworthy that the *endo*-III' isomer is not formed at the highest temperature, and this may be the result of a ready rearrangement to the more stable III in which the two bulky groups, viz., $\text{Cr}(\text{CO})_3$ and C_6H_5 , are located *anti* to each other with respect to the indene plane.

IR study of the anionic solutions

The infrared spectrum of neutral indene- $\text{Cr}(\text{CO})_3$ complexes is characterized by two absorption bands in the $\nu(\text{C}\equiv\text{O})$ stretching region, i.e. the fully symmetrical vibration of type A_1 at ca. 1960 cm^{-1} , and the degenerate E band at ca. 1885 cm^{-1} [11]. When deprotonation of the complexed indenenes is carried out with KH in THF in the presence of 18-crown-6-ether at -30°C the carbonyl stretching bands appear at lower frequency and splitting of the E band is observed (Table 1). These results indicate a C_s symmetry for the $\text{Cr}(\text{CO})_3$ tripod, the C_{3v} symmetry of the neutral complexes having been lost upon ionization. Probably the perturbation due to the negative charge is enhanced when the potassium cation is trapped by 18-crown-6 ether, so that the η^6 -indenyl- $\text{Cr}(\text{CO})_3$ salts are present as solvent-separated ion pairs (SSIP).

In pure THF the spectral pattern of Ia and IIa is more complicated. In the 1900 cm^{-1} region two bands are observed, the A_1 band due to SSIP's and, at a slightly higher frequency, an A_1' band. This band, when viewed in the light of results obtained by Ustynyuk et al. [12], indicates that contact ion pairs (CIP) are also present in the solution. In addition, a broad band centered at ca. 1830 cm^{-1} is observed and mathematical analysis of this band allows three bands of type E (see Table 1) to be distinguished, two of them belonging to SSIP's and the third at the highest frequency, belonging to CIP's. We attribute the restoration of the C_{3v} symmetry in the CIP's to the quenching of the charge perturbation due to the

Table 1

IR spectral data in the $\nu(\text{C}\equiv\text{O})$ region of η^6 -indene- $\text{Cr}(\text{CO})_3$ and of η^6 - and η^5 -indenyl- $\text{Cr}(\text{CO})_3$ anions^a

1,3-Substituents	Indenes		η^6 -Anions				η^5 -Anions					
	A_1	E	SSIP ^b		CIP ^c		SSIP ^b		CIP ^c			
			A_1	E	A_1'	E	A_1	E	A_1	E		
R = R' = H	1960	1884	1914	1825	1802	1922	1828	1895	1791	1896	1793	1751
R = C_6H_5 , R' = H	1960	1884	1918	1834	1811	1921	1832	1896	1795	1897	1799	1755
R = R' = C_6H_5	1964	1889	1918	1831	1814	1921	1832	1896	1798	1897	1802	1759

^a Solvent, THF; frequency value uncertainties are $\leq 2\text{ cm}^{-1}$. ^b Counter-ion, K^+ /18-crown-6-ether. ^c Counter-ion, K^+ .

increased interaction of the anions with K^+ . In the case of IIIa a very small amount of contact ion pairs can be detected even in the absence of 18-crown-6-ether.

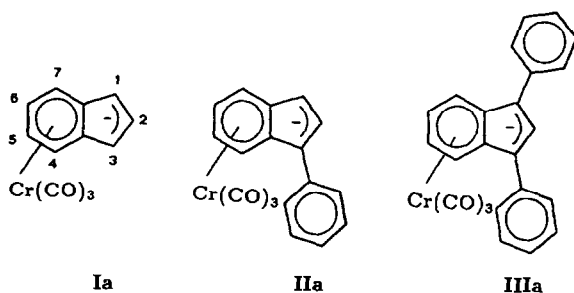
Although the IR analysis does not allow a quantitative determination of the ratio of the two different ion pairs, a rough estimate indicates that in pure THF the ionic state of η^6 -indenyl- $Cr(CO)_3$ potassium salts changes with the substituents: i.e., the parent anion is mostly in a CIP state in equilibrium with a minor amount of SSIP; whereas in the 1,3-diphenyl- $Cr(CO)_3$ anion the ratio is reversed, the contact interaction with potassium cation being unimportant. The effect of the two phenyl rings in favouring the free ion over the contact ion pair can be ascribed both to polar and steric effects. In the light of the results obtained for fluorenyl- $Cr(CO)_3$ anions [12], a likely structure for the CIP's is one in which the potassium cation lies over the five membered ring *anti* to $Cr(CO)_3$. The presence of two phenyl groups in the 1,3-positions of the indenyl frame would lower the anion-cation interaction both by reducing the amount of negative charge on the five membered ring and by sterically hindering the approach of the potassium ion. It is relevant to recall that even the η^6, η^6 -fluorenyl- $[Cr(CO)_3]_2$ potassium salt exists in SSIP form in pure THF [3b] since the cation cannot lie over the five membered ring for steric reasons.

When deprotonation of the complexed indenenes is carried out at room temperature, the IR spectra indicate that the $\eta^6 \rightarrow \eta^5$ metallotropic shift takes place. In the presence of 18-crown-6 ether, two bands are observed, and the spectrum is similar to that reported for the cyclopentadienyl- $Cr(CO)_3$ anion in a symmetrical solvent environment [13] (see Table 1). In pure THF three distinct absorptions are observed, the lowest frequency one (in the range $1750-1760\text{ cm}^{-1}$) being indicative of a direct $C\equiv O \cdots K^+$ interaction. Thus, for the η^5 anions of all the investigated substrates only contact ion pairs of local C_s symmetry are present in pure THF.

In conclusion, the results of the IR study indicate that in THF, in which the rates of $\eta^6 \rightarrow \eta^5$ migration have been measured (see below), the ionic state of the initial η^6 -anions depends upon the presence of phenyl substituents, i.e., there is a change from a situation in which contact ion pairs dominate (parent anion) to a situation in which the free ions (or SSIP's) are the most important species present in solution (diphenyl-substituted anion). In contrast, in η^5 -isomers the interaction with the potassium does not change with the substituents, the contact oxygen-metal ion pair being the dominant species for all substrates. Thus, when the haptotropic rearrangement takes place in the absence of solvating agents two migration processes occur, namely, the $Cr(CO)_3$ slippage from the benzo to the *ortho*-condensed cyclopentadienyl ring and the transfer of the potassium cation from the top of Cp ring (or from a symmetrically solvated state) to the oxygen atom of one of the carbonyls.

NMR and kinetic measurements

The initially yellow THF solutions of the neutral complexes I, II, and III quickly became red orange upon addition of KH at 243 K, and quantitative evolution of hydrogen gas occurred. Quenching of the reaction mixture with aqueous oxygen-free THF immediately restored the yellow colour and the starting neutral complexes could be recovered unchanged in high yield. The low temperature 1H NMR spectra of the anionic solutions in THF- d_8 indicate the formation of the η^6 -indenyl anions Ia-IIIa:



The chemical shifts and the coupling constants obtained by computer simulation of the experimental spectra are given in Table 2. The ^1H NMR spectrum of Ia is shown in Figure 1A.

Table 2

 ^1H NMR parameters ^a for Ia, Ib, IIa, IIb, IIIa, and IIIb

	Ia	Ib	IIa	IIb	IIIa	IIIb
<i>Chemical shifts, ^b δ_i</i>						
H_i						
1	5.720	4.850	5.792	4.916	—	—
2	6.870	4.756	7.105	5.203	7.328	5.635
3	5.720	4.850	—	—	—	—
4	6.391	7.239	6.825	7.690	6.801	7.755
5	4.860	6.566	4.912	6.689	5.021	6.760
6	4.860	6.566	4.950	6.633	5.021	6.760
7	6.391	7.239	6.342	7.304	6.801	7.755
<i>o, o'</i>	—	—	7.588	7.689	7.640	7.753
<i>m, m'</i>	—	—	7.167	7.212	7.208	7.240
<i>p</i>	—	—	6.789	7.035	6.851	7.062
<i>Coupling constants, ^c J_{ij}</i>						
<i>i, j</i>						
1,2	3.55 ± 0.01	2.91 ± 0.02	3.85 ± 0.03	2.99 ± 0.01	—	—
1,3	2.68 ± 0.04	2.84 ± 0.03	—	—	—	—
1,4	1.22 ± 0.02	1.33 ± 0.03	0.88 ± 0.02	0.77 ± 0.01	—	—
1,7	-0.58 ± 0.02	-0.62 ± 0.03	-0.30 ± 0.03	0.00	—	—
2,3	3.55 ± 0.01	2.91 ± 0.02	—	—	—	—
3,4	-0.58 ± 0.02	-0.62 ± 0.03	—	—	—	—
3,7	1.22 ± 0.02	1.33 ± 0.03	—	—	—	—
4,5	6.98 ± 0.02	8.56 ± 0.02	7.00 ± 0.08	8.72 ± 0.02	7.11 ± 0.04	8.72 ± 0.04
4,6	1.12 ± 0.02	1.05 ± 0.02	1.20 ± 0.09	1.05 ± 0.02	1.15 ± 0.04	0.99 ± 0.04
4,7	0.52 ± 0.03	0.92 ± 0.02	0.50 ± 0.05	0.86 ± 0.01	0.50 ± 0.05	0.87 ± 0.03
5,6	5.71 ± 0.02	6.47 ± 0.02	5.90 ± 0.06	6.48 ± 0.02	5.58 ± 0.05	6.33 ± 0.04
5,7	1.12 ± 0.02	1.05 ± 0.02	1.00 ± 0.07	1.08 ± 0.02	1.15 ± 0.04	0.99 ± 0.04
6,7	6.98 ± 0.02	8.56 ± 0.02	7.00 ± 0.07	8.55 ± 0.02	7.11 ± 0.04	8.72 ± 0.04
<i>o, m = o', m'</i>	—	—	8.04 ± 0.04	7.89 ± 0.03	7.91 ± 0.04	7.79 ± 0.04
<i>o, p = o', p</i>	—	—	1.14 ± 0.04	1.26 ± 0.03	1.24 ± 0.04	1.20 ± 0.03
<i>o, m' = o', m</i>	—	—	0.30 ± 0.04	0.50 ± 0.03	0.51 ± 0.04	0.63 ± 0.04
<i>o, o'</i>	—	—	2.52 ± 0.06	1.83 ± 0.05	2.17 ± 0.05	1.81 ± 0.06
<i>m, p = m', p</i>	—	—	7.30 ± 0.03	7.39 ± 0.03	7.35 ± 0.03	7.41 ± 0.03
<i>m, m'</i>	—	—	1.21 ± 0.06	1.63 ± 0.04	1.38 ± 0.06	1.53 ± 0.07

^a Solvent, THF- d_6 ; T 253 K for Ia and IIa, 273 K for IIIa, 303 K for Ib, IIb, and IIIb. For proton labelling, see text. ^b δ (ppm) from internal Me_4Si ; the uncertainties are ≤ 0.002 ppm. ^c Values given in Hertz.

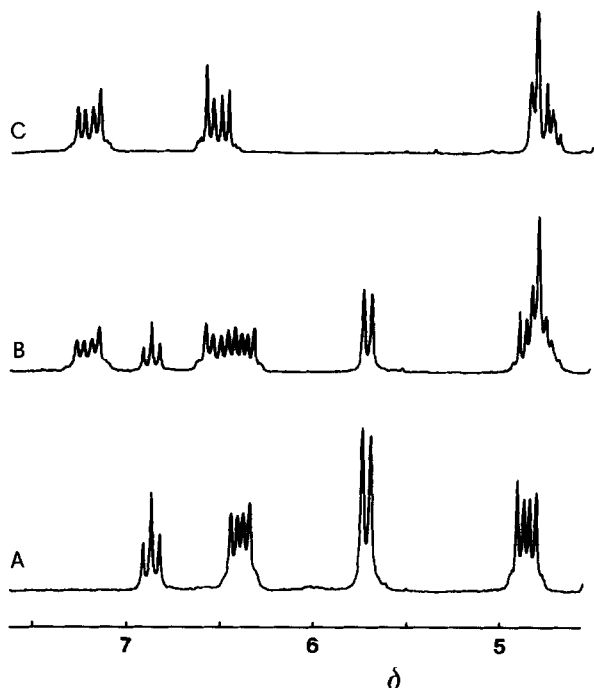


Fig. 1. 80.13 MHz ^1H NMR spectra of the indenyl- $\text{Cr}(\text{CO})_3$ potassium salt in $\text{THF-}d_8$. A, spectrum of Ia, T 253 K. C, spectrum of Ib, T 289 K. B, ca. 1:1 mixture of Ia and Ib at $t = t_{1/2}$, T 289 K.

In the symmetrical complexes Ia and IIIa the protons of the complexed benzo ring exhibit an AA'BB' pattern, while in the unsymmetrical IIa they appear as an ABCD system. Phenyl substitution for hydrogen in 1 and 3 positions induces a large downfield shift of the H(2) resonance ($\Delta\delta = 0.235$ and 0.458 ppm for one and two phenyls, respectively) and a significant shift of the benzo hydrogens H(4) and H(7) in the same direction ($\Delta\delta \approx 0.5$ ppm). This effect can be attributed to the contribution to the chemical shifts by the anisotropic current in the phenyl ring, and the downfield direction of the shifts reveals a preferred co-planar conformations of phenyl and indenyl frameworks. However, the equivalence of the *o,o'* and *m,m'* hydrogen atoms of the phenyl rings rules out the possibility of a rigid planar conformation, and a fast exchange on the NMR time scale between the two energetically favoured co-planar conformations can be confidently proposed. The greater stability of co-planar conformations is probably due to the importance of quinone-like structures which contribute to delocalization of the negative charge from the cyclopentadienyl ring.

Heating of the solutions of Ia, IIa, and IIIa causes migration of the $\text{Cr}(\text{CO})_3$ group from the six to the five membered ring. As shown in Fig. 1C for the parent anion, the ^1H NMR spectra indicate that only one species is present in each case, namely Ib, IIb, and IIIb. In these haptic isomers the absence of $\text{Cr}(\text{CO})_3$ coordination to the benzo ring is shown by the large downfield shift of the benzo proton resonances. In addition, coordinative interaction of the metal with the cyclopenta-

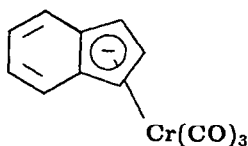
Table 3

Rate constants and activation parameters for the $\eta^6 \rightarrow \eta^5$ haptotropic rearrangement in indenyl- $\text{Cr}(\text{CO})_3$ anions ^a

Anion	$10^4 k, \text{s}^{-1} (T, \text{K})^b$	$\Delta H^\ddagger (\text{Kcal mol}^{-1})$	$\Delta S^\ddagger (\text{cal mol}^{-1} \text{K}^{-1})$
Ia	1.10 (267.5); 2.18 (272.5); 3.60 (277.0); 4.65 (280.0); 8.24 (284.0); 14.60 (289.0)	18.7 ± 0.9	-6.8 ± 2
IIa	1.38 (281.5); 3.08 (288.5); 17.10 (304.0)	18.0 ± 0.7	-11.4 ± 2
IIIa	1.10 (295.0); 3.06 (301.5); 4.88 (306.5); 8.49 (311.0)	22.4 ± 0.8	0.7 ± 1

^a In THF; counter-ion, K^+ . ^b First order kinetic plots ($r \geq 0.998$) up to 90% of reaction.

dienyl ring is revealed by the large upfield shift shown by the H(1), H(2), and H(3) resonances. The importance of electronic structures such as



is suggested by the large values of the differences between the vicinal coupling constants $\Delta^3 J(\text{H}, \text{H}) = {}^3 J(\text{H}_4, \text{H}_5) - {}^3 J(\text{H}_5, \text{H}_6) = 2.0 \text{ Hz}$.

Even though the $\eta^6 \rightarrow \eta^5$ isomerization process is complete for all the substrates investigated, the haptotropic rearrangement is an equilibrium process similar to that observed in the case of the fluorenyl- $\text{Cr}(\text{CO})_3$ anions [6b,6c,12]. Thus quenching of the solutions of the η^5 -indenyl anions with proton donors (e.g. oxygen-free H_2O or MeOH in THF) regenerates the corresponding neutral η^6 -indenes- $\text{Cr}(\text{CO})_3$.

The rate of isomerization was measured at various temperatures and the signals characteristic of the two isomers were monitored by ${}^1\text{H}$ NMR spectroscopy. The observed first order rate constants and the activation parameters calculated from Eyring plots are listed in Table 3.

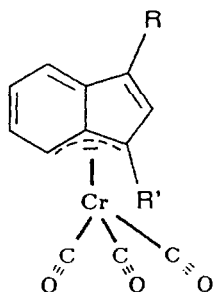
The relative rate constants values (calculated at 288.3 K)

$$k_{\text{H,H}} : k_{\text{H,Ph}} : k_{\text{Ph,Ph}} = 1 : 0.15 : 0.05$$

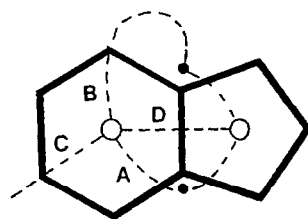
show that the metal migration rate is slowed down by successive phenyl substitution for hydrogen in the position 1 and 3 of the indenyl frame. The comparison of the activation parameters calculated for the three isomerization processes suggests that different effects must be responsible for the trend of k 's. The decrease of the rate constant induced by the introduction of the first phenyl group arises from a lowering ΔS^\ddagger , ΔH^\ddagger being practically unchanged. On the other hand, the lower reactivity of IIIa than of Ia and IIa does not arise from the entropy difference, which operates in the opposite direction, but on a marked increase in the enthalpy term.

This non-additive trend of ΔH^\ddagger values strongly suggests that the effect of the phenyl groups is of steric rather than electronic origin. Among the various mechanistic pathways invoked for this type of metallotropic shift the peripheral intramo-

lecular metal slippage, A, through an η^3 -allyl intermediate seems to be the most influenced by steric effects induced by substituents in 1 and 3 positions.



Conversely, other pathways involving the formation of an η^1 intermediate such as B and C and the least-motion path D should not involve significant steric interactions



between the substituents and the migrating unit. An increase in the energy barrier for the FeCp migration in indenyl anion for steric reasons was suggested by Albright et al. in a theoretical analysis [4] in which the allyl intermediate path was revealed to be that of lowest energy. Finally, the dissociative pathway C seems unlikely because of the absence of cross products which would have been detected when the isomerizations were carried out in the presence of ligands with high complexation ability towards $\text{Cr}(\text{CO})_3$ [6d].

The ΔS^\ddagger trend can be understood by taking into account the nature of the ion pairs in pure THF. Since the potassium salts of Ia and IIa are mostly present as contact ion pairs (see above), the potassium cation would become free from the indenyl ligand and solvated by THF molecules on going from the ground to the transition state, and the solvent reorganization around the free K^+ would give rise to the negative ΔS^\ddagger values. On the other hand, the IIIa salt is already present asSSIP in the ground state, and no contribution to ΔS^\ddagger from K^+ solvation can be expected during the haptotropic rearrangement.

Finally, the lower ΔS^\ddagger value found for the 3-phenyl-substituted anion with respect to the parent substrate may be due also to a statistical factor since the phenyl substituent would make one of the two equivalent migration pathways A through the η^3 -allyl intermediate less favoured by steric hindrance.

Experimental

All operations were carried out under purified argon by Schlenk techniques. M.p.'s are uncorrected. Microanalyses were performed by Mr. L. Turiaco, Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, University of Padova. IR and 70 eV electron impact mass spectra were recorded on a Perkin-Elmer 580B

and a VG MM 16 spectrometer, respectively. The ^1H NMR spectra were recorded with a WP-80 SY Bruker spectrometer. The proton spectra were analyzed by computer simulation on a Bruker Aspect-2000 computer by use of the Bruker PANIC program, giving uncertainties in chemical shift values ≤ 0.001 ppm. Commercial grade di-*n*-butyl ether (Bu_2O) (Carlo Erba) and tetrahydrofuran (THF) (Carlo Erba) were distilled before use from potassium and potassium anthracenide, respectively. HPLC grade acetonitrile (Carlo Erba) was dried over P_2O_5 and distilled before use from anhydrous K_2CO_3 . All the solvents used for the syntheses and spectral measurements with chromium derivatives were carefully deoxygenated by repeated freeze-and-thaw cycles. Commercial grade indene (Fluka) was distilled in vacuo. $\text{Cr}(\text{CO})_6$ (Alfa Ventron) was twice sublimed in vacuo before use. 1-Phenylindene [14], 1,3-diphenylindene [14], indene- $\text{Cr}(\text{CO})_3$ [9], and 3-phenylindene- $\text{Cr}(\text{CO})_3$ [15] were made by published methods.

Complexation of 1,3-diphenylindene

(a) Reaction with $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$. A mixture of 1.3 g (4.9 mmol) of the hydrocarbon and $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$ (made from 0.85 g, 3.8 mmol, of $\text{Cr}(\text{CO})_6$ in 10 ml of CH_3CN) in 12 ml of THF was refluxed for 4 h. Filtration of the solution and column chromatography on deoxygenated silica (hexane–diethyl ether mixtures as eluent) gave: (i) a 1 : 1 mixture of isomers III and III' ($\delta(\text{H-1}) = 4.93$ and 4.67, respectively; 3% yield), and (ii) a 4 : 1 mixture of isomers IV and V ($\delta(\text{H-2}) = 6.73$ and 7.02, and $\delta(\text{H-1}) = 4.61$ and 4.84, respectively; 7% yield) and ca. 3 mg of isomer VI.

(b) Reaction with $\text{Cr}(\text{CO})_6$ in Bu_2O –THF. A mixture of 1 g (3.7 mmol) of the hydrocarbon and 0.75 g (3.4 mmol) of $\text{Cr}(\text{CO})_6$ in Bu_2O containing 10% of THF was refluxed for 40 h. Work-up followed by chromatography as described above gave pure III in 12% yield a 4 : 1 mixture of IV and V (20% overall yield), and traces of VI. No III' was detected by NMR spectroscopy.

1,3-diphenyl-Indene- $\text{Cr}(\text{CO})_3$ (III, nc)

Yellow solid. M.p. 148–149 °C (from THF–hexane; decomp.). (Found: C, 69.7; H, 3.9. $\text{C}_{22}\text{H}_{14}\text{CrO}_3$ calcd.: C, 69.9; H, 3.7%). IR spectrum (THF): $\tilde{\nu}(\text{C}\equiv\text{O})$ 1964 and 1889 cm^{-1} . Mass spectrum: m/z 404 (M^+ , 8.6), 348 ($M^+ - 2\text{CO}$, 3.3), 320 ($M^+ - 3\text{CO}$, 100), 268 ($M^+ - (\text{Cr}, 3\text{CO})$, 22.8), and 52 (Cr^+ , 95.2%). ^1H NMR (acetone- d_6 , ppm from internal Me_4Si): δ 7.7–7.2 (10H, m, 1,3-(C_6H_5) $_2$ protons, not simulated); 6.704 (1H, d, H-2); 6.104 (1H, m, H-4); 5.967 (1H, m, H-7); 5.602 (1H, m, H-5); 5.579 (1H, m, H-6); and 4.935 (d, 1H, H-1); $J(\text{H,H})$ coupling constants: $J_{1,2}$ 2.52 \pm 0.01, $J_{1,7}$ 0.56 \pm 0.01, $J_{4,5}$ 6.45 \pm 0.02, $J_{4,6}$ 0.94 \pm 0.02, $J_{4,7}$ 0.53 \pm 0.01, $J_{5,6}$ 6.39 \pm 0.01, $J_{5,7}$ 0.99 \pm 0.01, and $J_{6,7}$ 6.33 \pm 0.01 Hz.

1,2-diphenyl-Indene- $\text{Cr}(\text{CO})_3$ (VI, nc)

Yellow solid. M.p. 125–128 °C (from THF–hexane; decomp.). (Found: C, 69.1; H, 4.0. $\text{C}_{22}\text{H}_{14}\text{CrO}_3$ calcd.: C, 69.9; H, 3.7%). IR spectrum (THF): $\tilde{\nu}(\text{C}\equiv\text{O})$ 1963 and 1887 cm^{-1} . Mass spectrum: m/z 404 (M^+ , 2.8), 348 ($M^+ - 2\text{CO}$, 3.1), 320 ($M^+ - 3\text{CO}$, 19.7), 268 ($M^+ - (\text{Cr}, 3\text{CO})$, 100), and 52 (Cr^+ , 96.4%). ^1H NMR (acetone- d_6 , ppm from internal Me_4Si): δ 8.0–7.2 (10H, m, 1,3-(C_6H_5) $_2$ protons, not simulated); 6.743 (1H, s, H-3); 6.255 (1H, m, H-4); 5.821 (1H, m, H-6); 5.582 (1H, m, H-7); 5.387 (1H, s, H-1); and 5.264 (1H, m, H-5); $J(\text{H,H})$ coupling

constants: $J_{4,5}$ 6.40 ± 0.01 , $J_{4,6}$ 0.94 ± 0.01 , $J_{4,7}$ 0.51 ± 0.01 , $J_{5,6}$ 6.26 ± 0.01 , $J_{5,7}$ 0.97 ± 0.01 , and $J_{6,7}$ 6.44 ± 0.01 Hz.

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