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METAL STABILIZED CARBANIONS

VII *. THE HAPTOTROPIC MIGRATION OF THE TRICARBONYLCHROMIUM GROUP FROM THE SIX- TO THE SEVEN-MEMBERED RING IN THE BENZOCYCLOHEPTATRIENYL ANION **

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Summary

The π-$Cr(CO)_3$-benzocycloheptatrienyl anion, produced by proton abstraction in THF, is unstable and the $Cr(CO)_3$ unit migrates irreversibly from the six- to the seven-membered ring. The activation parameters for the process have been obtained. A detailed ^1H NMR analysis and the ^{13}C NMR chemical shifts of the two anions are reported, and the effects of the $Cr(CO)_3$ complexation on the *anti*-aromatic properties of the ligand are discussed for both isomeric anions.

Introduction

There is a large body of informations about the migration of the metal unit from one coordination site to another in monocyclic polyene-metal complexes [2]. In contrast very little is known about the ability of the metal unit to migrate from one ring to another in a multicyclic polyene complex. Evidence for these haptotropic [3] rearrangements in tricarbonylchromium complexes has been found for the reversible $\eta^6 \rightleftarrows \eta^5$ isomerization in the fluorenyl anion [4] and for the degenerate reaction $\eta^6 \rightleftarrows \eta^6$ in the naphthalene system [5]. Slipping of the $Cr(CO)_3$ unit from the six- to the five-membered ring has been observed for the indenyl system [6]. Very recently the rearrangement of some manganese complexes of the fluorenyl anion have been described [7] and an intramolecular mechanism suggested.

We describe below the ready deprotonation of η^6-tricarbonyl(benzo[1.2]cycloheptatriene)chromium(0) and the irreversible migration of the metal unit from the six to the seven membered ring in the anion, (I → II):

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* For part VI see ref. 1.

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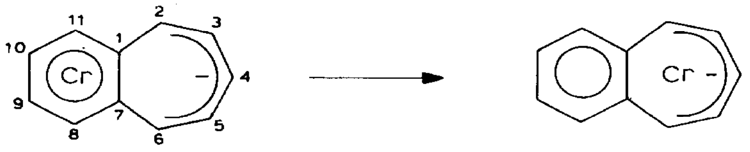
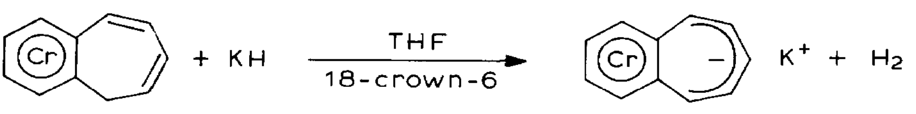


(I) (II)

Results and discussion

The $Cr(CO)_3$-complexed benzocycloheptatriene was converted into the corresponding potassium salt by treating (under argon atmosphere and at room temperature) its THF solution with an excess of KH in the presence of 18-crown-6 ether. The orange-yellow solution of the complexed hydrocarbon quickly turned red-brown and hydrogen was quantitatively evolved according to eq. 1. The reaction is very fast and a pseudo-first order rate constant, $k_{obs} = (2.2 \pm 0.2) \times 10^{-2}$ s^{-1} at 294.0 ± 0.1 K, was calculated.



(1)

Treatment of the solution with aqueous, oxygen free THF just after the formation of the anion immediately restored the orange-yellow color, and the starting complex was recovered unchanged in high yield. Under the same conditions the evolution of hydrogen from the uncomplexed benzocycloheptatriene was much slower and not quantitative, and the system decomposed very quickly.

The freshly-prepared anion I is not stable, and the $Cr(CO)_3$ unit migrates irreversibly to the seven-membered ring to form the isomer II. This isomerization was followed by ^1H NMR spectroscopy at four different temperatures. Use of the equation for a first-order irreversible reaction gave satisfactory plots ($r > 0.999$). From the rate constant values, $10^5 \times k_{is}$ (T, K): 2.25 (293); 10.50 (303); 22.60 (308); 43.0 (313), s^{-1}, the activation parameters $\Delta H^{\neq} = +26 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\neq} = +11 \pm 2$ e.u. were calculated. Treatment of the solution with aqueous THF at the end of the isomerization did not restore the starting hydrocarbon and rapid decomplexation and decomposition of the system took place.

The experimental and computer-simulated ^1H NMR spectra of isomers I and II are reported in Fig. 1 and Fig. 2, respectively. The ^1H NMR spectral parameters and the ^{13}C NMR chemical shifts of the two isomers are listed in Table 1 together with literature data [9] for the free benzocycloheptatrienyl anion. The spectrum of I consists of one AA'BB' pattern relative to the benzo protons and one AA'BB'C pattern due to the seven-membered ring protons. The broadening of the high field component of the AA'BB' system is due to small inter-ring coupling constants, and this allowed unambiguous assignment of the benzo proton chemical shifts. A similar spectral pattern is found for the isomer II.

The ^1H NMR data will be discussed by taking into account the spectral parameters of the uncomplexed anion. The ^1H NMR spectrum of the potassium benzocycloheptatrienide is typical of an antiaromatic $4n$–π electron system; because of the induced paramagnetic ring current [9a] in the magnetic field, all the proton resonances appear at very high fields relative to those observed for anions having aromatic character [10].

Usually complexation with $Cr(CO)_3$ induces an upfield shift of 1.8 ÷ 2.0 ppm for the resonances of protons directly bonded to the ring engaged in the coordination,

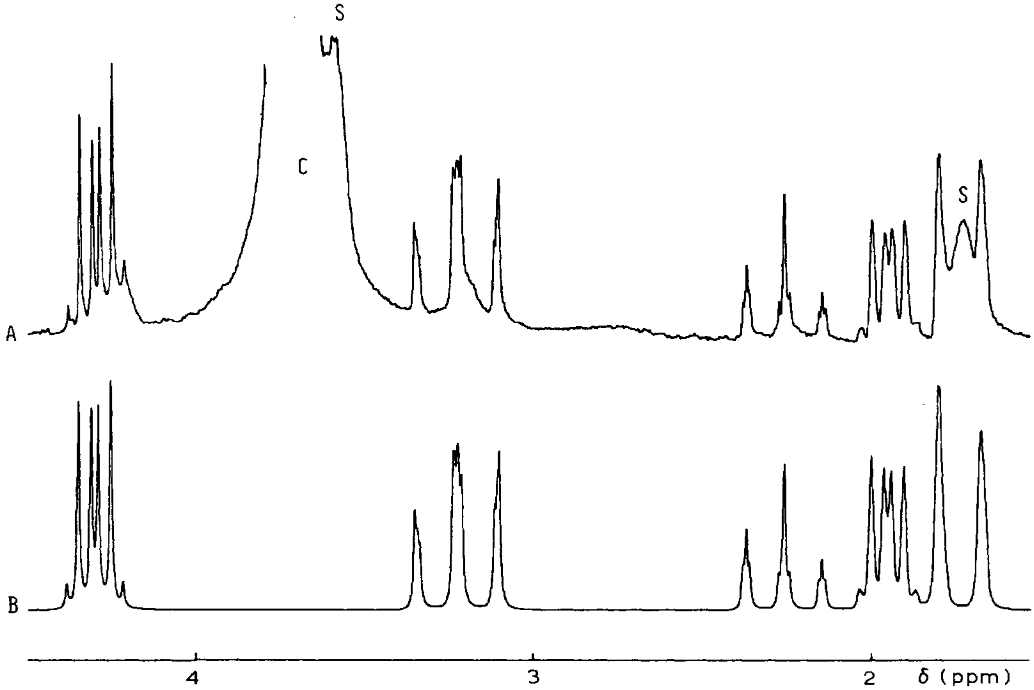


Fig. 1. 80.13 MHz ^{1}H NMR spectrum of I in THF-d_8, T 293 K. A, experimental spectrum. B, computer simulation, C, 18-crown-6 ether resonance, S, solvent resonances.

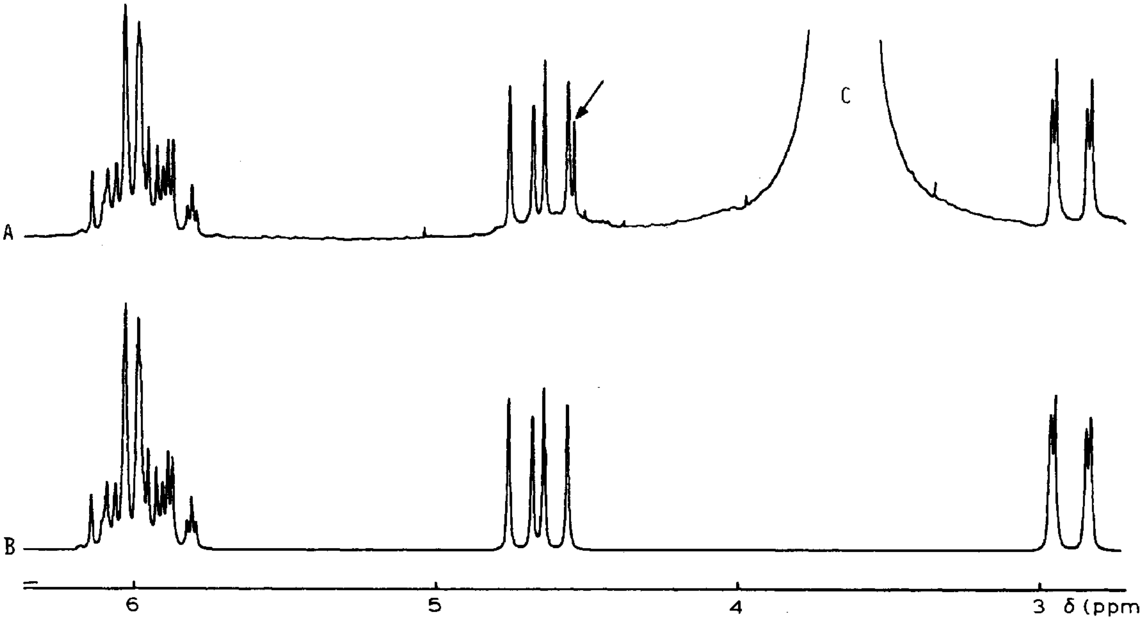


Fig. 2. 80.13 MHz ^{1}H NMR spectrum of II in THF-d_8, T 293 K. A, experimental spectrum. B, computer simulation. C, 18-crown-6 ether resonance. The arrow indicates an unidentified impurity.

TABLE 1

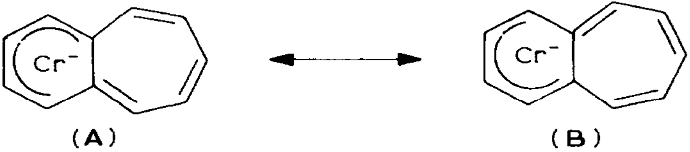
^{1}H AND ^{13}C NMR PARAMETERS [a] FOR THE FREE [b] AND THE TWO ISOMERIC $Cr(CO)_3$-COMPLEXED [c] BENZOCYCLOHEPTATRIENYL ANIONS

	$\delta(H_i)$					$\delta(C_i)$						
	2,6	3,5	4	8,11	9,10	1,7	2,6	3,5	4	8,11	9,10	CO
L [d]	−0.40	1.63	−0.66	2.05	3.81	161.9	90.7	151.2	108.0	121.4	126.8	-
I [e]	1.74	3.22	2.26	1.95	4.29	131.7	110.0	137.1	112.2	84.2	90.2	242.5
II [f]	2.90	4.66	5.89	5.95	6.07	148.9	71.6	104.3	91.3	123.0	124.5	242.7

[a] Solvent THF-d_8; δ(ppm) from internal TMS; for protons labeling see text. [b] Data from ref. 15a, $J_{2,3}$ 10.8; $J_{3,4}$ 8.2; $J_{8,9}$ 6.4; $J_{8,10}$ 2.8; $J_{9,10}$ 8.0 Hz. [c] In THF-d_8, counter-ion K^+, T 303 K. [d] L = free ligand anion. [e] $J_{2,3}$ 10.22; $J_{2,4}$ 0.75; $J_{2,5}$ 0.38; $J_{2,6}$ −0.08; $J_{2,8}$ 0.52; $J_{2,11}$ −0.52; $J_{3,4}$ 9.02; $J_{3,5}$ 1.09; $J_{8,9}$ 6.18; $J_{8,10}$ 1.47; $J_{8,11}$ 0.00; $J_{9,10}$ 5.81 Hz. [f] $J_{2,3}$ 9.40; $J_{2,4}$ 1.22; $J_{2,5}$ 0.00; $J_{2,6}$ 0.00; $J_{2,8}$ 0.30; $J_{2,11}$ −0.50; $J_{3,4}$ 6.32; $J_{3,5}$ 0.50; $J_{8,9}$ 7.29; $J_{8,10}$ 1.28; $J_{8,11}$ 0.52; $J_{9,10}$ 7.42 Hz.

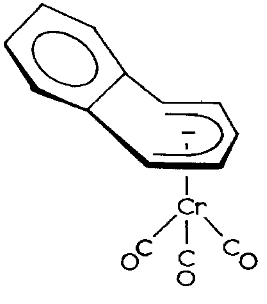
while the effect is very small (0.1 ÷ 0.2 ppm) for other proton resonances [11]. In the case of the benzocycloheptatrienyl anion, complexation of the benzo ring induces a quite different effect, i.e. all the proton resonances exhibit a significant downfield shift, the exceptions only for the H(8) and H(11) proton resonances for which the net effect is practically zero. It is noteworthy that the strongest downfield shift is shown by the protons of the seven-membered ring which is not directly involved in the coordination. This effect can be explained in terms of a marked lowering of the paramagnetic ring current due to the ability of the $Cr(CO)_3$ unit to isolate an electronic π-aromatic sextet, so reducing the peripheral antiaromatic π-circulation in the overall organic skeleton [12].

The relatively high field value of the resonances of H(8) and H(11) protons relative to those of the H(9) and H(10) protons (which is consistent with the presence of a residual paramagnetic ring current [12a,13]) together with the symmetry of the spectral pattern indicates that the electronic arrangement of the anion I can be represented as a resonance hybrid of two planar (η^5-benzylidene)tricarbonylchromium structures **A** and **B**.



The rather similar values of the vicinal coupling constants $J_{2,3}$ 10.22 Hz and $J_{3,4}$ 9.02 Hz, found in the olefinic moiety are in good agreement with this hypothesis. Furthermore, the fundamental role played by planar η^5-structures has been recently demonstrated for the $Cr(CO)_3$-complexed di- and tri-phenylmethyl carbanions [14].

On going from I to II, the ^{13}C resonances of all the benzo carbons experience a strong downfield shift, while the seven-membered ring protonated carbons are shifted upfield as expected [15] by the change of the coordination site. On the other hand, all the proton resonances (in particular those of the protons bonded to the carbons directly involved in the coordination) are strongly shifted downfield, indicating the total quenching of the extended paramagnetic ring current, and this is confirmed by the absence of differences between the benzo protons chemical shifts. Moreover, the trend $\delta_2 < \delta_3 < \delta_4$, found for the chemical shift values of the olefinic protons, is the same as that observed for (η^5-cyclohexadienyl)tricarbonylchromium anions [16] and for other cyclohexadienyl- and cycloheptadienyl-$M(CO)_3$ complexes (M = Mn, Fe) [17], for which a bent structure was inferred. In contrast in planar (η^5-benzylidene)tricarbonylchromium anions the different trend $\delta_2 < \delta_4 < \delta_3$ was found [14]. The anion II is thus postulated to have the bent 5-hapto structure shown below:

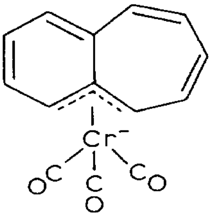


The departure from planarity causes the splitting of the 12 π-electron cloud into two non-interacting π-sextets and this is in agreement with the total quenching of the paratropic properties of the ligand anion. The chemical behaviour of II, i.e. the irreversibility of the isomerization, and the failure to regenerate the starting neutral complex on reaction with water, is also well accounted for by the bent structure. When the migration of $Cr(CO)_3$ occurs without geometric change, as in the case of the fluorenyl anion [4d], the isomerization is reversible and the original complexed hydrocarbon is recovered on treatment with water in the case of both hapto-isomers.

Since the ^{13}C carbonyl chemical shifts can be directly related to the extent of the negative charge delocalization into $Cr(CO)_3$ [4d,18], it is noteworthy that both I and II isomers have the same $\delta(^{13}CO)$ value. This indicates that the driving force for the isomerization does not depend on the charge delocalization requirements, as in the case of the $\eta^6 \rightleftarrows \eta^5$ migration in the fluorenyl-$Cr(CO)_3$ anion [4d], but upon the further stabilization arising from the complete quenching of the antiaromatic electronic distribution in the ligand.

As far as the mechanism of the haptotropic rearrangement is concerned, both an intramolecular and a dissociative mechanism must be considered possible, especially in coordinating solvents [8]. However, some evidence against a dissociative process comes from competitive experiments carried out in the presence of ligands with extraordinary complexation ability [19] versus the $Cr(CO)_3$ group; thus when the isomerization I → II was carried out in the presence of hexamethylbenzene or fluorenyl anion no cross products could be identified, and the kinetic rate constant was not changed. In addition, the positive value of $\Delta S^{\neq}$ contrasts strongly with the negative values observed for arene-exchange in benzene-$Cr(CO)_3$ and derivatives [19].

A possible intermediate in a non-dissociative isomerization path is the η^3-allylic anion shown below:



Experimental

Melting points are uncorrected. Microanalyses were performed by Mr. L. Turiaco, Istituto di Chimica Analitica, Università di Padova. The ^1H and ^{13}C NMR spectra were obtained on a Bruker WP-80 SY spectrometer operating in the FT-mode.

Commercial grade hexamethylbenzene and fluorene (Fluka) were crystallized from ethanol and sublimed in vacuo. The tricarbonyl(1,2-benzocycloheptatriene)chromium(0) was prepared from the ligand and $(NH_3)_3Cr(CO)_3$ in refluxing anhydrous, oxygen free dioxane and purified by column chromatography (degased silica, hexane/diethyl ether mixture as eluent). Yield 68%. M.p 73°C (from hexane, lit. [20], m.p. 73–74°C). (Found: C, 59.80; H, 3.70. $C_{14}H_{10}CrO_3$ calcd.: C, 60.43; H, 3.62%). The ^1H NMR data agreed with literature values [20].

The method of measuring the amount of evolved H_2 has been described elsewhere [14]. The products of electrophilic quenching of the anion solutions were purified by column chromatography and identified by ^1H NMR spectroscopy and TLC.

For the ^1H NMR measurements, 5×10^{-2} *M* solutions of the complexed anion in THF-d_8 were prepared by treatment with KH, as previously described [4d], in the presence of 1.2 equivalents of the 18-crown-6 ether.

The spectral parameters were obtained by computer simulation on an Aspect-2000 Bruker computer using the Bruker PANIC program.

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

In the competitive experiments, 1 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 fluorenyl anion [4d].

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