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Metal stabilized carbanions

X *. A ^{1}H and ^{13}C NMR spectroscopic study of η^6,η^6-bis(tricarbonylchromium)fluorene and the corresponding carbanion

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Abstract

η^6,η^6-Bis(tricarbonylchromium)fluorene has been metallated with KH in THF to give the corresponding anion. The IR spectrum indicates that the anion exists in solution as a solvent-separated ion pair. Detailed analysis of the NMR parameters suggests that upon ionization the two tricarbonylchromium moieties move towards the junction carbons.

Introduction

Stabilization of exocyclic anions by tricarbonylchromiumphenyl group is well documented [2]. In particular, there have been several reports of stabilization of the closely related fluorenyl and indenyl anions by tricarbonylchromium (TCC) [3]. Haptotropic rearrangement of the η^6-TCC-fluorenyl anion to the η^5 *hapto*-isomer has been reported in some detail [4]. Jaouen, et al. [5] have described the formation of a stable carbanion from bis-(TCC-phenyl)methyl anion, and have given complete ^{1}H and ^{13}C NMR spectroscopic data for this compound.

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* For Part IX see ref. 1.

We have recently reported the synthesis of a large number of mono- and bis-TCC derivatives of diarenes, including fluorene [6]. In this paper we present a complete ^1H and ^{13}C NMR analysis of the neutral and anionic η^6,η^6-bis-TCC-fluorene complexes. Complete proton assignments have been accomplished by NOE (nuclear Overhauser effect) measurements. The formation of the same anion has been briefly described by Ustynyuk, et al. [7]; they have recorded the IR spectrum of this anion, which, however, decomposes under the reaction conditions to give the mono-complexed η^5-species.

Results

The syntheses of η^6,η^6-bis-TCC-fluorene (I) and of η^6-TCC-fluorene (II) were carried out as previously described [6]. The conversion of these complexes into the corresponding anions, Ia and IIa, according to eqn. 1 was performed in anhydrous

$$R{-}H + K^+H \rightarrow R^-K^+ + H_2 \qquad (1)$$

oxygen-free tetrahydrofuran (THF) at 294 K. The red solution of Ia was stable at room temperature for few hours; quenching of the same solution with oxygen-free water regenerated the starting hydrocarbon I in high yield. Rate constants for metallation, voltammetric peak potentials, and IR carbonyl stretching frequencies of I and Ia are listed in Table 1. The data relative to mono-complexes II and IIa are also given.

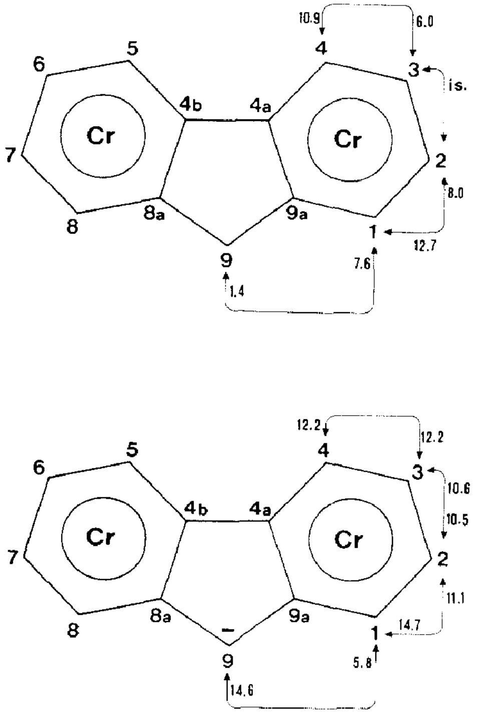

Fig. 1. NOE interaction diagrams for neutral, I, and anionic, Ia, η^6,η^6-bis(tricarbonylchromium)fluorenes. is. signifies isochronous or nearly isochronous resonances.

Table 1

Metallation rate constants, k [a], voltammetric reduction potentials, E [b], and IR stretching frequencies, $\nu(C{\equiv}O)$ [c], for I, Ia, II, and IIa

Complex	k (s^{-1})	E (V)	$\nu(C{\equiv}O)$ (cm^{-1})	
			A-band	E-band(s)
I	0.088 ± 0.005	−1.66	1958	1894
Ia	–	–	1922 [d]	1854 [d] 1834 [d]
II	0.078 ± 0.002	−1.92	1968	1895
IIa	–	–	1921	1832 1805

[a] Solvent, THF; T 294 K. [b] Solvent, DMF; supporting electrolyte, Et_4NClO_4; potential sweep rate, 0.25 V s^{-1}; the potentials are given against an Ag, AgCl electrode in Et_4NCl-saturated acetonitrile/dimethylformamide 3/1 v/v solution, $E(Ag, AgCl, Cl^-) - E(SCE) = 0.31 \pm 0.01$ V. [c] Solvent, THF; $\Delta\nu = \pm 1$ cm^{-1}. [d] Nearly identical values have been measured in the presence of 18-crown-6 ether (1921, 1853, and 1831 cm^{-1}).

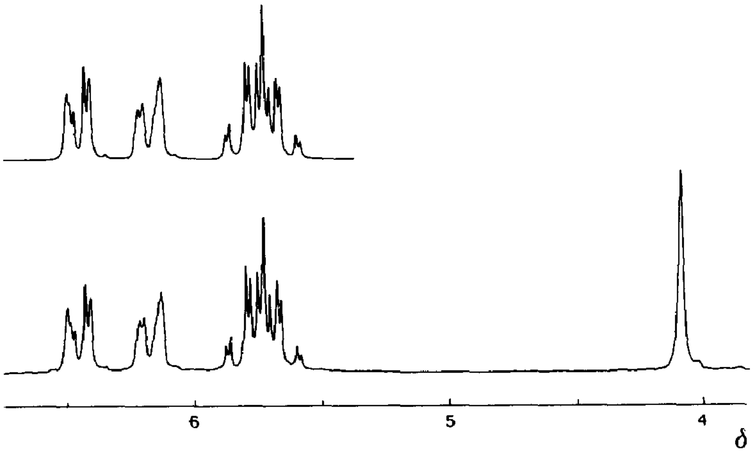

Fig. 2. Experimental and computer simulated spectra for neutral η^6,η^6-bis(tricarbonylchromium)fluorene (I) in acetone-d_6.

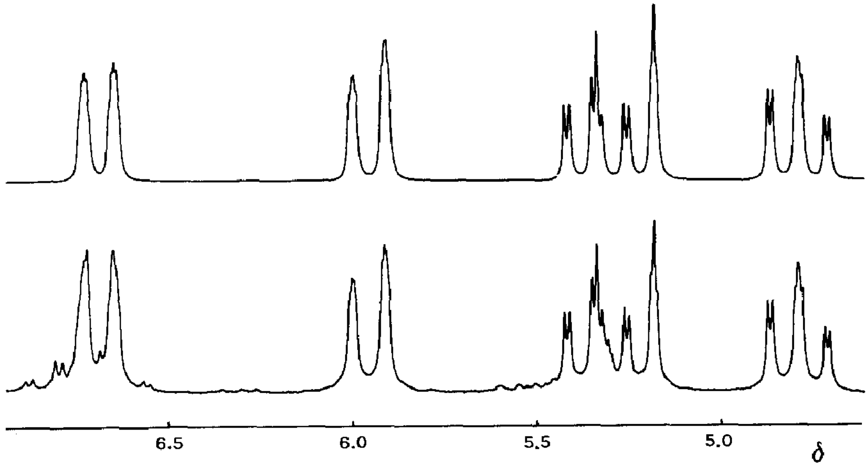

Fig. 3. Experimental and computer simulated spectra for anionic η^6,η^6-bis(tricarbonylchromium)fluorene (Ia) in THF-d_8.

Table 2

^{1}H NMR parameters for I, Ia, II, and IIa obtained by computer simulation of the experimental spectra

			Complexed ring			Free ring		
H_i [a]	Chemical shifts [e]		H_i [a]	Chemical shifts [e]		H_i [a]	Chemical shifts [e]	
	I [b]	Ia [c]		II [b]	IIa [d]		I [b]	IIa [d]
1 = 8	6.167	5.950	1	6.221	6.033	8	7.554	7.279
2 = 7	5.777	5.336	2	5.716	5.318	7	7.407	6.977
3 = 6	5.680	4.791	3	5.671	4.739	6	7.375	6.640
4 = 5	6.449	6.486	4	6.532	6.856	5	7.815	7.819
9	4.078	5.180	–	–	–	9	3.946 [f]; 4.119	5.567
i, *j*	$J_{i,j}$ (Hz)		*i*, *j*	$J_{i,j}$ (Hz)		*i*, *j*	$J_{i,j}$ (Hz)	
1,2 = 7,8	6.46 ± 0.04	7.10 ± 0.01	1,2	6.45 ± 0.05	7.19 ± 0.04	7,8	7.66 ± 0.06	8.08 ± 0.01
1,3 = 6,8	0.99 ± 0.04	1.03 ± 0.01	1,3	0.91 ± 0.05	1.01 ± 0.04	6,8	1.39 ± 0.06	0.90 ± 0.01
1,4 = 5,8	0.51 ± 0.03	0.58 ± 0.01	1,4	0.47 ± 0.04	0.55 ± 0.05	5,8	−0.45 ± 0.04	0.98 ± 0.02
1,9 = 8,9	−0.53 ± 0.04	0.0 [g]	1,9	0.6 [g]	0.0 [g]	8,9	0.90 ± 0.03	0.0 [g]
2,3 = 6,7	6.39 ± 0.03	5.92 ± 0.01	2,3	6.23 ± 0.05	5.76 ± 0.03	6,7	7.51 ± 0.05	6.79 ± 0.01
2,4 = 5,7	0.88 ± 0.04	1.16 ± 0.01	2,4	1.04 ± 0.05	1.09 ± 0.03	5,7	1.36 ± 0.07	1.11 ± 0.02
3,4 = 5,6	6.43 ± 0.04	6.54 ± 0.01	3,4	6.61 ± 0.05	6.56 ± 0.03	5,6	7.49 ± 0.07	7.84 ± 0.02
4,9 = 5,9	0.00 [g]	0.69 ± 0.01	4,9	0.0 [g]	0.86 ± 0.02	5,9	−0.4 [g]	0.86 ± 0.02
–	–	–	–	–	–	9,9′	−21.80 ± 0.06	–

[a] For proton numbering, see Fig. 1. [b] Solvent, acetone-d_6, T 298 K. [c] Solvent THF-d_8, counter-ion K^+, T 298 K. [d] Solvent THF-d_8, counter-ion K^+, T 254 K. [e] Ppm from internal Me_4Si. [f] This proton is in the *exo* position relative to the $Cr(CO)_3$ group. [g] Not refined by iteration.

Table 3

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

				Complexed ring				Free ring, others			
C_i [b]	δ (ppm)		Δ_i^- [g]	C_i [b]	δ (ppm)		Δ_i^- [g]	C_i [b]	δ (ppm)		Δ_i^- [g]
	I [c]	I [a]			II [c,f]	IIa [e,f]			II [c,f]	IIa [e,f]	
1 = 8	91.35	85.10	−6.25	1	91.6	85.2	−6.4	8	127.5	117.6	−9.9
2 = 7	93.36	94.64	1.28	2	93.1	94.5	1.4	7	127.9	122.7	−5.2
3 = 6	91.98	80.56	−11.42	3	92.0	77.1	−14.9	6	129.1	113.0	−5.2
4 = 5	87.73	92.23	4.50	4	87.9	93.5	5.6	5	120.9	119.5	−1.4
9	37.29	80.40	43.11	–	–	–	–	9	37.5	83.1	45.6
4a = 4b	108.77	93.30	−15.47	4a	112.0	92.7	−19.3	4b	139.7	126.6	−13.1
9a = 8a	112.70	95.70	−17.00	9a	114.3	122.6	8.3	8a	143.2	143.3	0.1
C≡O	233.77	238.42	4.65	–	–	–	–	C≡O	234.3	240.3	6.0

[a] ppm from internal Me_4Si. [b] For carbon numbering, see Fig. 1. [c] Solvent, acetone-d_6; T 298 K. [d] Solvent, THF; counter-ion, K^+; T 298 K. [e] Solvent, THF; counter-io, K^+; T 254 K. [f] Data from ref. 4b. [g] $\Delta_i^- = \delta_i$ (anion) − δ_i (neutral).

The results of NOE experiments on I and Ia are shown in Fig. 1. The numbers at the tip of the arrows indicate the % enhancements upon saturation of the connected nucleus. Cross experiments may give different numerical answers because of different relaxation effects associated with the various nuclei.

The NOE analysis allowed the unambiguous assignment of ^1H resonances. In turn, the ^{13}C line assignment was based on selective proton decoupling experiments and partially relaxed spectra. The complete analysis of the ^1H resonance patterns was accomplished through computer simulation. Experimental and simulated spectra are compared in Figs. 2 and 3. The ^1H and ^{13}C parameters for compounds I and Ia are listed in Tables 2 and 3, together with the corresponding parameters for II and IIa (^{13}C data are taken from a previous paper [2a], whereas the ^1H spectra of II and of IIa were determined by computer simulation).

Discussion

The equivalence of protons 9 and 9′ observed in the ^1H NMR spectrum of I (Fig. 2, Table 2) indicates that the two TCC groups are positioned *anti* to one another with respect of the plane of fluorene skeleton. Moreover, the ^1H and ^{13}C NMR parameters of the complexed ring of II are not significantly modified when the other ring is complexed with the second TCC group to give I (cf. Tables 2 and 3), suggesting that in the bis-complex the benzene rings behave as two non-interacting π-electron systems. The very similarity of the values for the rate constants of metallation of bis- and mono-complexed fluorenes suggests that after the anion is stabilized by one TCC group the presence of a second such group provides little extra stabilization. In contrast, the voltammetric reduction potential, E, is markedly changed on going from the mono- to the bis-complexed fluorene ($\Delta E = +0.26$ V, Table 1). This result can be accounted for by the fact that the electrochemical reduction of both I and II is a two-electron process and the negative charges carried by the produced dianion are better stabilized by two electron-withdrawing TCC groups. Details of the electrochemical behaviour of these systems will be presented elsewhere.

Upon ionization, the carbonyl stretching frequencies decrease in energy and the carbonyl ^{13}C resonances move downfield relative to those for the corresponding neutral hydrocarbons, the effect being more pronounced for the mono-complexed fluorene (cf. Tables 1 and 3). Both changes reflect an increase in electron density in the chromium moieties. Similar observations were made by Jaouen [5] for the bis-(TCC-phenyl)methyl anion. It is to be noted that in the IR spectrum the degeneracy of the E-band is removed upon ionization, with an associated splitting of ca. 20 cm^{-1}; the same splitting has been observed in the presence of an equimolar amount of 18-crown-6 ether. These facts have led to the suggestion [7] that the K^+ salt of Ia is present as a solvent-separated ion pair even in the absence of the crown ether.

The chemical shift changes of the arene protons of I upon anion formation parallel those observed for the mono-complexed hydrocarbon [4a] and are consistent with the presence of the adjacent strongly electron-donating group. The downfield shift of the proton on carbon 9 is obviously related to the change in hybridization at carbon.

The most interesting feature concerns the ^{13}C chemical shift changes upon ionization (Δ_i^- in Table 3). These changes are expected to reflect both the increase in electron density on going from neutral to anionic hydrocarbon and the relative displacement of the inorganic moiety. The changes upon formation of Ia and IIa are similar in magnitude and direction, the only exceptions being the resonances of junction carbons 8a and 9a. The carbon 9a chemical shift of monocomplexed fluorene moves downfield, whereas the corresponding resonances of carbons 8a and 9a in the bis-complexed fluorene are strongly shifted upfield. We have previously suggested [2a] that the large downfield shift of the signals from the junction carbons in TCC-di- and tri-phenylmethyl anions reflects a major contribution from a η^5-TCC-benzylidene structure in which the junction carbon has lost its coordination with the metal (the less pronounced downfield shift of the junction carbon 9a observed in η^6-TCC-fluorene upon ionization was interpreted in terms of a minor contribution from a η^5 structure). In the present case, the large upfield shift requires a substantial interaction between carbons 8a, 9a and metal. This shift can be interpreted as an indication that in the anion the two chromium units have moved towards the junction carbons. At the same time, the moving away of chromium moieties may account for the smaller upfield shift for the *para*-carbons 3 and 6. Thus the two inorganic units have moved part of the way towards the five-membered ring, as they would in a $\eta^6 \rightarrow \eta^5$ haptotropic rearrangement. The presence of two chromium moieties prevents the completion of the shift, and the metal units settle under dynamic tension at an intermediate position. This tension may be responsible for the lower stability of Ia with respect to IIa. In fact, as observed by Ustynyuk [7], Ia in THF solution slowly loses one TCC group to give the $\eta^6 \rightleftarrows \eta^5$ equilibrium mixture of the mono-complexed anion.

The theoretical analysis of the haptotropic rearrangement of TCC moiety in these compounds predicts exactly this pathway for the movement of the metal from the six- to the five-membered ring [8].

Experimental

The IR and mass spectra were recorded with a Perkin–Elmer 580B and a VG MM16 spectrometers, respectively. The voltammetric measurements were made with an EG&G Princeton Applied Research electrochemical instrument consisting of a model 173 potentiostat equipped with a model 175 function generator, a 4203 signal averager, and a RE 0074 XY recorder. The ^{1}H NMR spectra were recorded on a Bruker WP-80 SY and the ^{13}C NMR spectra on a Bruker WP-200 SY spectrometer. The NOE experiments were carried out on the latter instrument. The samples (I in acetone-d_6, Ia in THF-d_8) were freed from oxygen by sonication under nitrogen purging. The usual procedure for gated experiments was modified [9] and the selected multiplet was saturated by an 8 s cyclic perturbation of all lines with a 42 dB attenuation of a nominal 0.2 W decoupling power. The % enhancements are obtained from the multiplier of the reference spectrum which brings the multiplet to exact matching of the corresponding multiplet of the perturbed spectrum. Errors are ca. 0.3%.

All compounds were handled under carefully-dried oxygen-free argon. The mono- and bis-complexed fluorenes were prepared as previously described [6]; they gave satisfactory elemental analyses, and the molecular ion M^+ was detected in their mass spectra. Anion solutions were prepared with careful exclusion of oxygen by metallation of THF solutions of the neutral hydrocarbons as previously described [2a].

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