Journal of Organometallic Chemistry, 312 (1986) 207–219
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

STEREOSELECTIVE ELECTROCHEMICAL SYNTHESIS AND CATHODIC BEHAVIOUR OF (9-*exo*-BENZYL-η^6-FLUORENE)CHROMIUM TRICARBONYL

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(Received March 14th, 1986)

Summary

The one-electron electrochemical reductive cleavage of (η^6-fluorene)$Cr(CO)_3$ gives the (η^6-fluorenyl)$Cr(CO)_3$anion. This anion reacts at 0°C in DMF with benzyl chloride present in excess during electrolysis to give (9-*exo*-benzylfluorene)$Cr(CO)_3$ stereoselectively in 64% yield. At higher temperatures there is competing formation of the *exo* and *endo* isomers. The reaction of $Cr(CO)_6$ with 9-benzylfluorene is neither stereoselective nor regioselective, and gives moderate yields of the *exo* and *endo* isomers (26 and 17%, respectively). The one-electron reduction of the *exo* isomer generates the conjugated base which initiates the *exo–endo* transformation. In the presence of benzyl chloride, the base-catalyzed isomerization competes with a slow benzylation of the base, and (9,9′-dibenzylfluorene)$Cr(CO)_3$ can be isolated.

Introduction

The stereoselective deprotonation of (η^6-fluorene)$Cr(CO)_3$ (**1**) with bases such as t-BuOK, n-BuLi or KH [1–4] leads to the unstable *exo* η^6-anion **2** which isomerizes to the η^5-anion **3** [1–7], through an intramolecular haptotropic rearrangement [6] (Scheme 1). In THF, the transformation **2** → **3** occurs above −20°C [2–7]. The synthesis of the anions **2** and **3** has been much used by Nesmeyanov, Ustynyuk et al. to produce 9-alkylated complexes [2,3,7–9] and Scheme 1 (X = I) summarizes a part of their work. Methylation of **2** and **3** with methyl iodide proceeds stereoselectively to give the *exo*-**4** and *endo*-**5** isomers, respectively [2,3] (Scheme 1). The *endo* isomer **5** results from an inner-sphere "ricochet" rearrangement in which the methyl group, which is initially σ-bonded to the metal, migrates to the π-ligand [2–4]. The isomers **4** and **5** can be also prepared, but only in very low yield, by treatment of 9-methylfluorene with $Cr(CO)_6$ [2]. In the first investigation [7] benzylation of **2** and **3** with benzyl iodide was shown to lead to the *endo* isomer **7** in 11% yield, no *exo* isomer **6** being obtained at low temperature, but very recently it has been found that at low temperatures the *endo* isomer **7** can be obtained in 20% yield [9].

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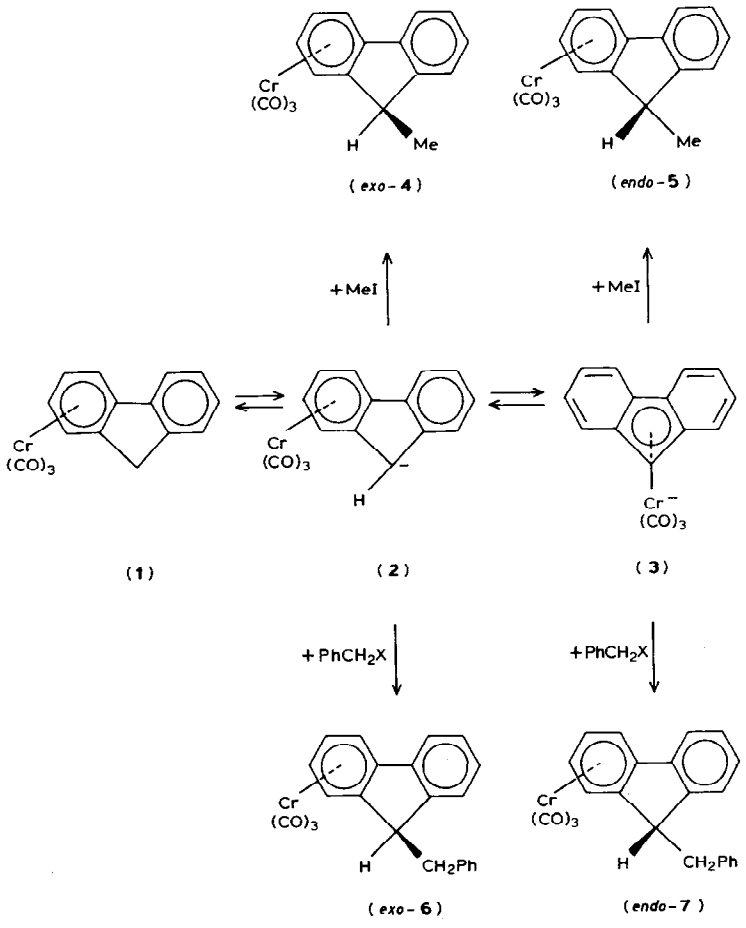
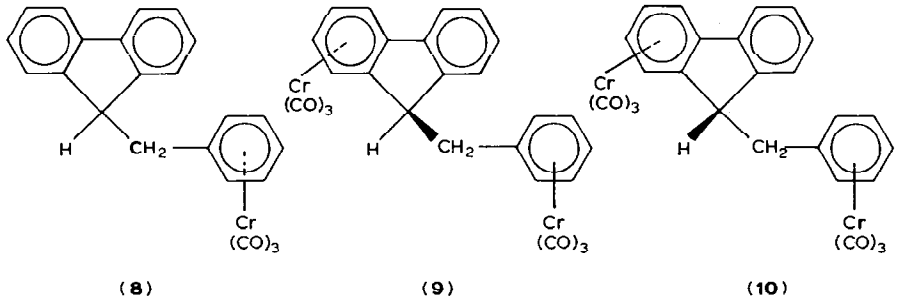


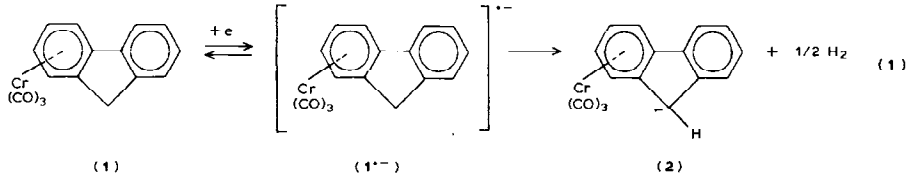
SCHEME 1

Our group has shown previously [10], that electrochemical reduction in DMF of (fluorene)$Cr(CO)_3$ on a mercury pool cathode generates the conjugated base **2** of the complex. Addition of oxygen to **2** has provided a practical route to (fluorenone)$Cr(CO)_3$ [10]. Taking advantage of the electrochemical approach, we have studied the behaviour of **2** in the presence of benzyl chloride and observed the stereoselective electrochemical synthesis in DMF of the *exo*-isomer **6** in good yield (64%). The cathodic behaviour of **6** has been examined. In addition, the reaction of 9-benzylfluorene with $Cr(CO)_6$ has been carried out; and shown to be neither stereoslective nor regioselective since the formation of **6** and **7** is accompanied by that of **8**–**10**.



Results

The polarogram A of Fig. 1 confirms the earlier observation [10] that one electron is involved in the reduction process of fluoreneCr(CO)$_3$ (**1**). Indeed, the limiting current for the single reduction wave (Fig. 1A) is close to the limiting currents of the two successive one-electron reduction steps of (fluorene)Cr(CO)$_3$ (Fig. 1B) [11]. In DMF the electron uptake is followed by cleavage of the CH bond along with the formation of the anion **2** (eq. 1) [10].



(1)

A comparative study of the voltammograms of fluorene in the complexed (Fig. 2A) and free form (dotted curve of Fig. 2A) shows that the reductive cleavage of the CH bond is faster when the fluorene is complexed. Thus the anodic peak corresponding to the oxidation of the intermediate radical anion is visible in the case of fluorene (peak D_2), whereas it does not appear for the complex **1**. These results are consistent with a higher lability of the CH bond in the case of **1** arising from the electron-withdrawing effect of the Cr(CO)$_3$ group. The anodic peak A_2 of Fig. 2A corresponds to the oxidation of the anion **2**. Reversal of the potential beyond −2.8 V (Fig. 2B) generates a reversible peak system B_1/B_2 (standard redox potential $E°$ −2.64 V at 25°C in DMF) with which is associated an anodic peak C. The redox peak system B_1/B_2 cannot correspond to fluorene [12], since this compound is electrochemically active at slightly more negative potentials (about 40 mV, dotted

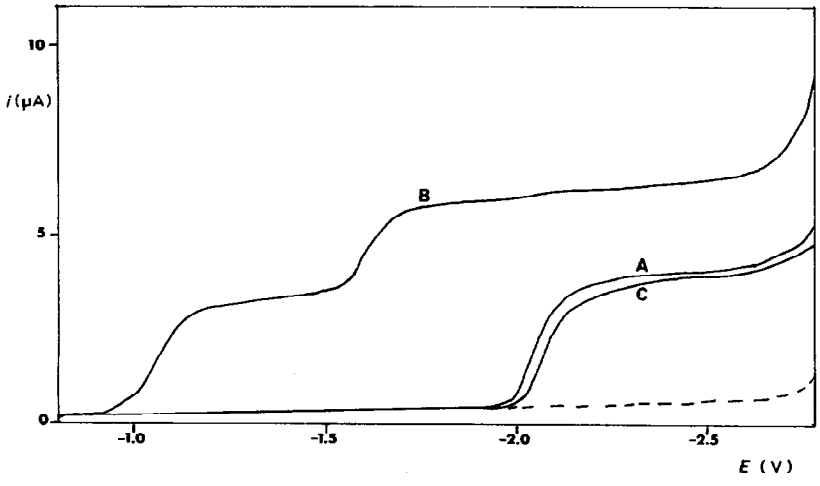


Fig. 1. Polarograms of 1 mmol **1** (curve A), (fluorenone)Cr(CO)$_3$ (curve B) and **6** (curve C).

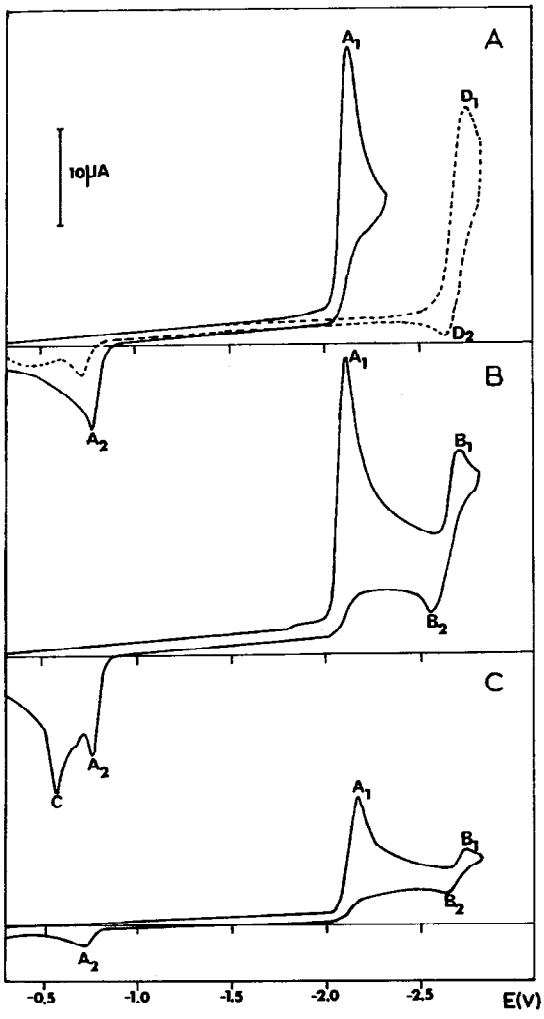


Fig. 2. Cyclic voltammograms in DMF of **1** (2 mmol) at 0.25 V s^{-1}. Curves A and B are obtained at 22°C and curve C at −37°C. The dotted curve corresponds to fluorene (1.8 mmol) at 22°C.

curve of Fig. 2A). The peak system B_1/B_2 tends to disappear at low temperatures (Fig. 2C). In THF it is negligible at temperatures below −25°C (Fig. 3).

Benzyl chloride is somewhat more difficult to reduce than **1** (see curves B and A of Fig. 4). In the presence of benzyl chloride, the resulting current (curve C) does not correspond to the simple juxtaposition of the reduction currents of both species (curve D). It shows that benzyl chloride interferes in the reduction process of **1**.

A large-scale electrolysis of **1** carried out at 0°C in the presence of benzyl chloride in excess indicates a partial reduction of **1** after consumption of only one electron. When it is carried on for a longer time and stopped after consumption of 2 electrons per mole of **1**, the *exo*-isomer **6** is obtained regioselectively as the major product (64%) together with some parent 9-benzylfluorene (22%) and traces of starting material **1** (< 5%) (electrolysis no. 1 of Table 1). Similarly, in THF at 0°C

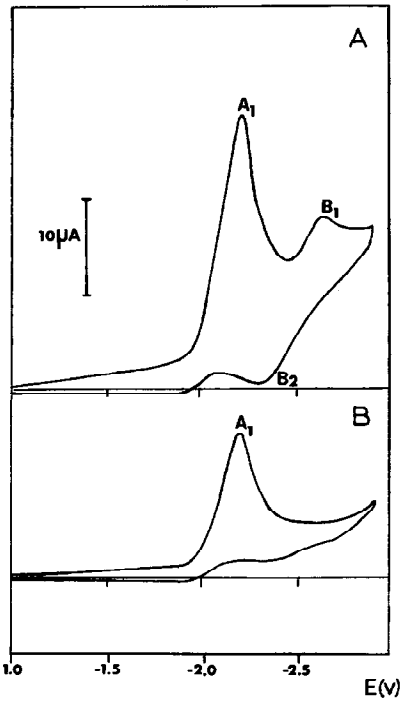


Fig. 3. Cyclic voltammograms in THF of **1** (2 mmol) at 0.25 V s^{-1}. Curve A is obtained at $-5°C$ and curve B at $-38°C$.

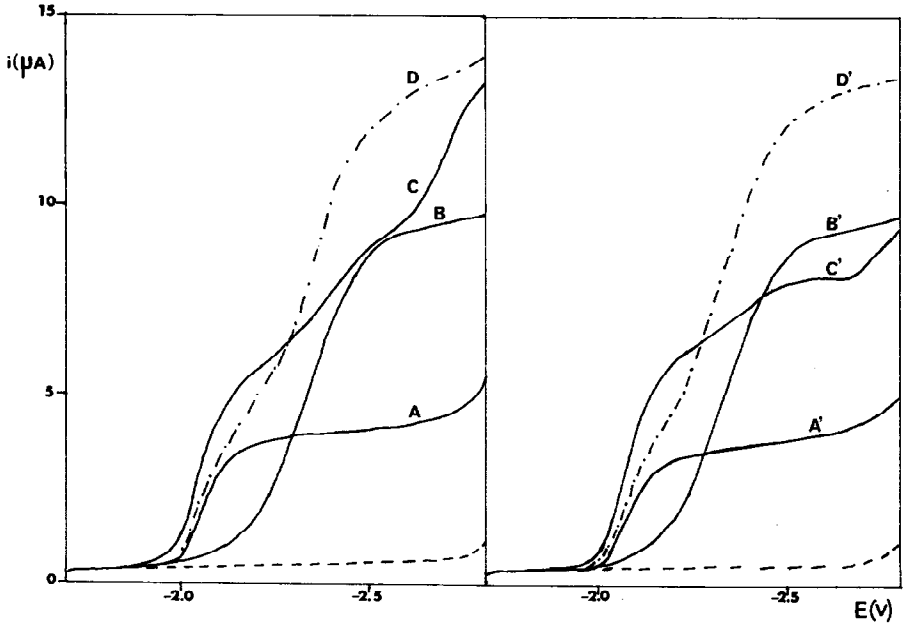


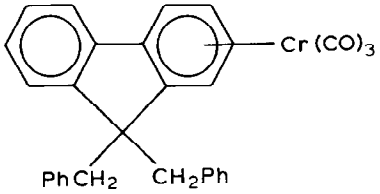
Fig. 4. Modification of the polarogram of **1** (1 mmol) and **6** (1 mmol) upon addition of benzyl chloride (1 mmol). Curves A and A′ correspond to **1** and **6** alone and curves B and B′ to benzyl chloride alone. Upon addition of benzyl chloride, curves C and C′ are obtained experimentally and curve D and D′ are drawn by juxtaposition of the Faradaic currents of A + B (curve D) and A′ + B′ (curve D′).

TABLE 1

ELECTROCHEMICAL REDUCTION OF (FLUORENE)$Cr(CO)_3$ (**1**) AND (*exo*-9-BENZYLFLUORENE)$Cr(CO)_3$ (**6**) IN THE PRESENCE OF BENZYL CHLORIDE (2.5 equiv.)

Electrol. no.	Complex (mmol)	Solvent	Applied potential (V vs. SCE)	*n*	*T* (°C)	Compounds isolated (% yield)	
						Arene	Arene $(CrCO)_3$
1	**1** (2.0)	DMF	−1.80 to −1.85	2.0	0	Fluorene (traces)	**1** (5)
						9-Benzylfluorene (22)	**6** (64)
2	**1** (2.0)	THF	−1.60 to −1.88	2.0	0	Fluorene (5)	**1** (35)
						9-Benzylfluorene (5)	**6** (27)
							7 (5)
3	**6** (0.8)	DMF	−1.91 to −1.95	1.0	22	9-Benzylfluorene (4)	**6** (39)
							7 (9)
							11 (20)

the *exo*-isomer **6** is obtained as the predominant reduction compound (electrolysis no. 2 of Table 1); however, much starting material **1** is still present after consumption of 2 electrons per mole of **1**, and traces of the *endo*-isomer **7**. When the temperature is increased to 22°C and the electrolysis carried out in DMF, the electrochemical synthesis is not regioselective. Some *endo* isomer **7** can be isolated (13%) together with traces of (9,9-dibenzylfluorene) $Cr(CO)_3$ (**11**) and its parent arene, 9,9-dibenzylfluorene. Complexes **6**, **7** and **11** are moderately stable in solution in DMF. Their decomposition leads to the free arenes.

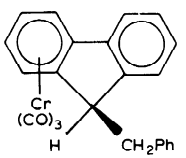
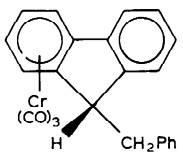
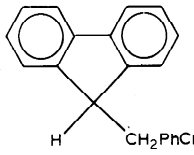
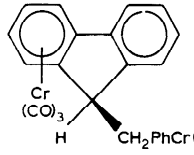
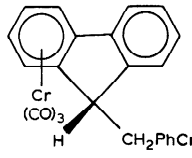


(**11**)

The electrochemical behaviour of the *exo*-isomer **6** is very similar to that of **1**. In the absence of benzyl chloride, the cathodic reduction is again an one-electron process, and it takes place at potentials slightly more negative than in the case of **1** (compare polarograms A and C of Fig. 1). When benzyl chloride is added, the resulting current (curve C′ of Fig. 4) does not correspond to the simple addition of the cathodic currents of **6** and benzyl chloride (curve D′ of Fig. 4), in line with the observations in the case of **1**. When large-scale electrolysis of **6** is performed at room temperature in the presence of benzyl chloride much starting material **6** (39%) is still left after consumption of one electron (electrolysis no. 3 of Table 1) and some of the *endo*-isomer **7** (9%) and **11** (20%) can be isolated. If the electrolysis is prolonged (until 2 electrons are consumed) **7** can no longer be isolated, and **11** is the major product (34%) but a large amount of 9-benzylfluorene (32%) is also formed.

The stereoisomers **6** and **7** can be obtained in moderate yields from the reaction of $Cr(CO)_6$ with 9-benzylfluorene. Refluxing $Cr(CO)_6$ (7.8 mmol) and 9-benzylfluorene (1 equiv.) [13] for 36 h in a mixture of di-n-butyl ether (100 ml) and THF

TABLE 2. PHYSICAL AND SPECTROSCOPIC DATA FOR **6–10**

	 (*exo*-**6**)	 (*endo*-**7**)	 (**8**)	 (*exo*-**9**)	 (*endo*-**10**)
M.p. (dec.) (°C)	148–150 (ref. 9: 140–141)	182 (ref. 7: 153–155)	111–112	193–200	234
Analysis C	70.35	70.12	69.94	58.92	58.14
Found (calcd.)(%)	(70.41)			(59.09)	
H	3.90	3.87	4.13	2.97	2.87
	(4.08)			(3.03)	
Cr	13.05	13.41	13.30	19.45	19.16
	(13.26)			(19.70)	
IR (KBr); ν(C≡O) (cm^{-1})	1962, 1952 1888, 1851	1948 1875, 1858	1958 1882, 1858	1968, 1955 1872	1969 1898, 1878, 1852
^{1}H NMR [a] (ppm)					
C*H*	4.28 (pt)	4.33 (pt)	4.21 (t)	4.22 (t)	4.22 (pt)
CH$_2$Ph	2.80–3.35	2.98–3.45	3.02		2.70–3.26
	(m*, ^2J(A–B) 12.8 Hz)	(m*, ^2J(A–B) 13.9Hz)	(d, ^3J(A–X) 5.9 Hz)	2.91 (d)	(m*, ^2J(A–B) 13.9 Hz)
CH$_2$*Ph*	7.18–7.45 (5H)	7.10–7.60 (5H)			
Ph part from FlCr(CO)$_3$	7.18–7.45 (4H)	7.10–7.60 (4H)		7.31–7.51 (m, 4H)	7.35–7.59 (m, 4H)
CH$_2$*Ph*Cr(CO)$_3$			4.85 (d, 2H);)	4.90 (t, 2H);	5.08 (t, 1H)
			5.02–5.20 (m, 3H)	5.17–5.38 (m, 5H)	(m, 5.59–5.85 (7H)
				5.70 (t, 1H)	5.82d (1H)
				5.94 (t, 1H)	
PhCr(CO)$_3$ part from	5.96 (d, 1H)	4.98 (1H) 5.35–5.58 m, 2H);			
FlCr(CO)$_3$	5.26 (m, 3H)	5.79 (d, 1H)			
Ph part from fluorene			7.25–7.50 (m, 6H)		
			7.63–7.72 (m, 2H)		

[a] In $CDCl_3$ at 28°C; d = doublet, t = triplet, pt = pseudotriplet, m = multiplet, m* = two doublets of doublets.

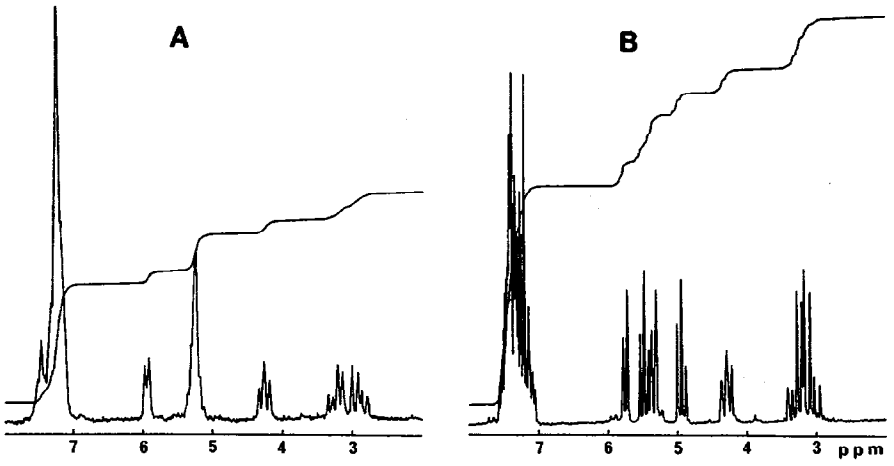


Fig. 5. ^1H NMR in $CDCl_3$ of **6** (curve A) and **7** (curve B).

(10 ml) gives the three monocomplexed arenes **6** (26%), **7** (17%) and **8** (22%) together with smaller amounts of the dicomplexed arenes **9** (11%) and **10** (4%).

The physical and spectroscopic properties of the complexes **6–10** are summarized in Table 2. The complexes are yellow crystals, which can be recrystallized from a methylene chloride/hexane mixture. The melting points observed for **6** and **7** indicate that our samples are purer than those described in refs. 9 and 7, respectively.

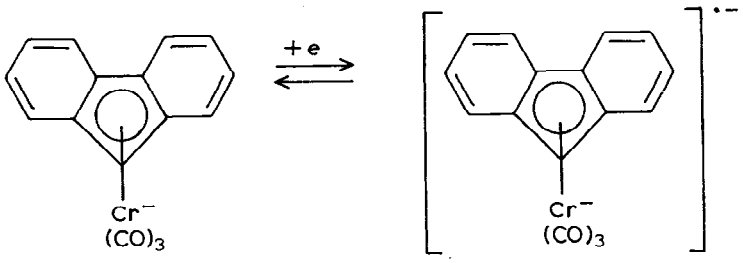
The NMR spectra in $CDCl_3$ of the complexes **6**, **7** and **10** are consistent with their chiral structures (diastereotopy of the two benzylic protons which correspond to the AB part of an ABX system). For complex **9** this diastereotopy is observable in C_6D_6 (see the Experimental section) but not in $CDCl_3$ (Table 2). Such behaviour has been observed precedingly [14].

The NMR spectra which we have obtained at 28°C for **6** and **7** in deuterated chloroform (Table 2 and Fig. 5) and benzene (see Experimental section) differ, in some cases, from those described by Ustynyuk et al., in Table 1 or ref. 9, in which temperatures were not specified. In the case of **7**, the spectral parameters obtained at 28°C in C_6D_6 are different from those described in ref. 9; however, the latter values are similar to those we observed at 50°C. Hence, the ^1H NMR spectra in C_6D_6 of **7** are very sensitive to temperature modifications. Such variations might explain why the NMR characteristics obtained in $CDCl_3$ at 28°C for **6** (Fig. 5A) differ so much from those reported in ref. 9 as far as the protons of the complexed benzene ring are concerned. We have not tried to elucidate this point. However, the spectrum obtained for **6** in C_6D_6 at 50°C (see the Experimental section) is similar to that described in ref. 9.

The polarographic reduction of the complexes **7**, **9** and **10** occurs at potentials close to those for **1** and **6** ($E_{1/2}$ -2.05 ± 0.04 V), suggesting again a monoelectronic reductive cleavage of the CH bond, with formation of the corresponding complexed anion. The polarographic reduction of **8** occurs at more negative potentials ($E_{1/2}$ -2.29 V) and is probably related to the reduction of the complexed phenyl ring [15].

Discussion

The one-electron reductive cleavage of **1** leads to the unstable (η^6-fluorenyl)Cr-$(CO)_3$ anion **2** which is oxidized anodically at the potentials of peak A_2 (Fig. 2), and which rearranges to the η^5-anion **3** [1–7]. On the time scale of the voltammetric study depicted in Figures 2B and 2C, the redox peak systems B_1/B_2 must correspond to the one-electron reversible reduction of the η^5-anion **3** (eq. 2), and the presence of the anodic peak C can be associated with a moderate stability of $\mathbf{3}^{\cdot-}$.



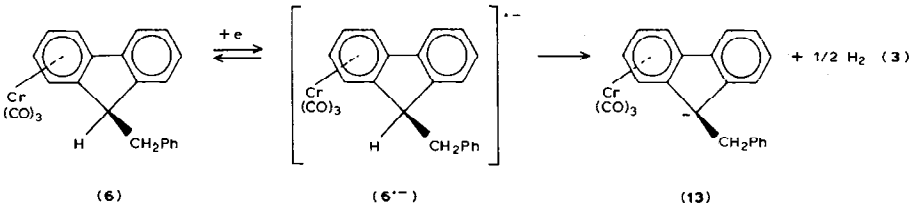
(3) (3$^{\cdot-}$) (2)

It has been shown that the transformation **2** → **3** is slower as the temperature is lowered, and does not take place below −20°C in THF [1–3]. It is compatible with the voltammetric study performed at low temperature in THF and presented in Fig. 3. No peak systems B_1/B_2 are observed at −38°C in THF. In contrast, in DMF, the peaks B_1/B_2 are still observed at −37°C (Fig. 2C), which indicates that the transformation **2** → **3** occurs more readily in DMF than in THF. Furthermore, the transformation is much faster in DMF under the experimental conditions of Fig. 2 than in THF at room temperature, where the half-life of the ion pair **2**, K^+ is about 10 min [2,4,5]. It was possible to carry out the electrochemical synthesis of the *exo*-isomer **6**, stereoselectively in 64% yield at 0°C in DMF. At higher temperatures the competing formation of the *endo*-isomer **7** cannot be avoided (electrolysis no. 3 of Table 1). These results show that in DMF at 0°C the transformation **2** → **3** is too slow to compete with the benzylation reaction **2** → **6** (cf. Scheme 1 where X = Cl) whereas at room temperature these reactions compete, and so the simultaneous formation of the isomers **6** and **7** cannot be avoided. In THF where the intermediate anion **2** is more stable, this competition should be less favourable and so the concomitant formation of isomers **6** and **7** is surprising (electrolysis no. 2 of Table 1). Traces of the *endo*-isomer **7** must arise in that case from either a slow attack of **2** by benzyl chloride or, more probably, to a base-catalysed transformation **6** → **7** (vide infra).

Although the electrochemical synthesis at 0°C of the isomers **6** and **7** is a one-electron process (eq. 1), several electron equivalents have to be consumed in order to achieve complete removal of the initial complex **1**. At the potentials used during electrolysis, the concomitant reduction of benzyl chloride cannot be avoided, and so the current efficiency is only 33% in the best case, with DMF as the solvent.

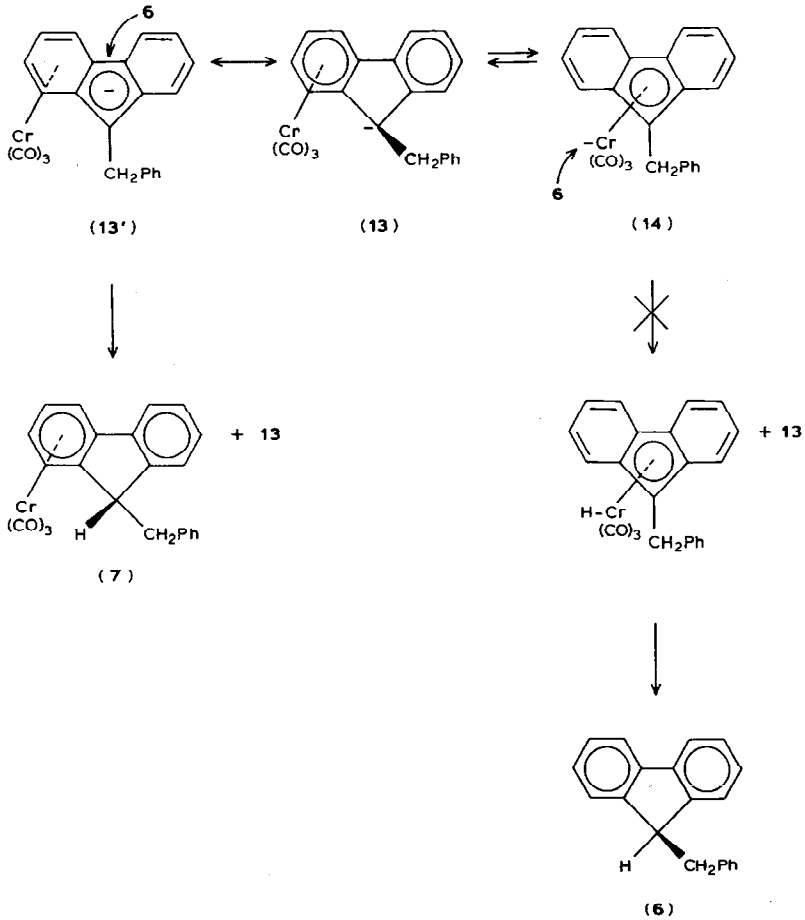
The cathodic reduction of the *exo*-isomer **6** is again a one-electron process with cleavage of the *endo* CH bond. It must be emphasized that the *endo* reductive cleavage takes place even though the $Cr(CO)_3$ unit contained in the complex will

hinder the approach of the CH group towards the electrode surface. The complexed anion **13** is thus initially generated.



(6) (6$^{\cdot -}$) (13)

Electrolysis of **6** in the presence of an excess of benzyl chloride allows the preparation of the dibenzylated complex **11** together with some *endo*-isomer **7** (electrolysis no. 2 of Table 1). Since fluorene is acidic (its pK_a in water is 23 [16]) and the acidity is enhanced by the $Cr(CO)_3$ group in the complex [17], such acidicities have to be taken into account in the case of the *exo* complex **6**. Thus the



(13') (13) (14) (7) (6)

SCHEME 2

formation of the *endo*-isomer **7** can be explained by considering the protonation by **6** of **13'**, a mesomeric form of **13**, and of **14**, the corresponding η^5-complex (Scheme 2). Previous results [2,6,9] have shown that protonation of η^5-fluorenyl complexes leads to the introduction of an *endo* proton. In the case of **14**, protonation by the bulky acid **6** of the Cr site would regenerate the *exo*-isomer **6**. For steric reasons this Cr site is not readily accessible to **6** and so its protonation is hindered. The *exo* protonation of **13'** by the acid **6** might be less hindered, and would lead to the *endo*-isomer **7**.

During electrolysis, the competitive formation of the dibenzylated complex **11** and of the *endo* isomer according to Scheme 2, which summarizes the base-catalyzed transformation **6** → **7**, is compatible with a slow benzylation of the anion **13**. As the electrolysis proceeds, cathodic reduction of **7** occurs, regenerating **13**. Finally, **11** is the only complex isolated.

Conclusion

Electrochemical generation of the conjugated base of (fluorene)$Cr(CO)_3$ in the presence of an alkyl halide provides a convenient stereoselective route to (9-*exo* alkylfluorene)$Cr(CO)_3$. Cathodic reduction of the *exo* isomer generates its conjugated base which initiates the *exo* → *endo* transformation. A new route to (*endo*-9 alkylfluorene)$Cr(CO)_3$ is thus provided.

Experimental

The synthesis of (fluorene)tricarbonylchromium in 75% yield from fluorene and $Cr(CO)_6$ has been reported elsewhere [10]. The synthesis of 9-benzylfluorene is described in ref. 13.

DMF (analytical grade) was carefully dried over neutral alumina and THF was distilled from sodium benzophenone ketyl before use. Tetrabutylammonium hexafluorophosphate (Fluka) was used as supplied.

Elemental analyses were performed by Service Central d'Analyses du C.N.R.S., Lyon, Spectra were recorded with the following instruments: infrared, Perkin–Elmer 530B; ^{1}H NMR, JEOL FX 100; mass spectra Finnigan 3002.

Cyclic voltammograms at a hanging mercury drop electrode or rotating glassy carbon disc electrode were obtained in DMF or in THF with a Tacussel UAP 4 unit and a GSTP function generator, and were recorded on a Ifelec 2025 CX-Y recorder. Polarograms were obtained with a Tacussel Tipol instrument. The characteristics of the capillary were: m 2.7 mg s^{-1}; t 0.70 s. An Amel 552 potentiostat and a Tacussel IG 5-N integrator were used in preparative electrolyses. All the potentials are relative to the aqueous saturated calomel electrode (SCE). Large-scale electrolyses were carried out in a H-type cell the three compartments of which were separated by a glass frit and filled with DMF containing 0.1 M Bu_4NPF_6. The cathode was a mercury pool and the anode a Pt grid. The catholyte (60 ml) was deaerated with argon before the introduction of the complexed substrate and benzyl chloride. After electrolysis, the catholyte was diluted with water and the electrolysis products were extracted with diethyl ether. The ethereal solution was dried, the solvent was removed, and the crude product was subjected to column chromatography.

Electrochemical reduction of **1** *(2.0 mmol) at 0°C in the presence of benzyl chloride (5 mmol) (electrolysis no. 1 of Table 1)*

The potential changed from −1.80 to −1.85 V during electrolysis and so a constant Faradaic current was maintained (73 ± 5 mA). The electrolysis was stopped after consumption of 2 coulomb equivalents of charge per mole of **1**. Integration of the ^{1}H NMR spectrum of the crude product (0.644 g) indicated that it contained mainly the *exo*-isomer **6** (64%) together with some starting material **1** (5%), fluorene (traces) and 9-benzylfluorene (22%). The crude product was separated by column chromatography with 1/9 diethyl ether/hexane as eluent. The *exo*-isomer **6** is only slightly soluble in this mixture and so could be isolated pure in large amount by filtration. The compounds were eluted in the order: fluorene, 9-benzylfluorene, **6**, and **1**.

Electrochemical reduction of **6** *(0.8 mmol) at 22°C in the presence of benzyl chloride (2 mmol) (electrolysis no. 3 of Table 1)*

The potential changed from −1.91 to −1.95 V during electrolysis which was stopped after consumption of 1 electron. The crude product was separated by column chromatography with 3/7 diethyl ether/hexane as eluent. The compounds were isolated in the order: 9-benzylfluorene (4%), **11** (20%), **6** (39%), **7** (9%).

9,9-Dibenzyl-η^{6}fluoreneCr(CO)$_3$ (11). Yellow crystals. *F* 183°C (CH_2Cl_2/hexane). Analysis: Found: C, 74.51, H,4.84. calcd. C, 74.69; H, 4.56%. ν(C≡O)(KBr) 1858, 1888, 1871 cm^{-1}. NMR ($CDCl_3$): 3.18–3.56 (m, 4H); 4.98–5.18 (m, 1H); 5.44 (d, 2H); 5.79 (d, 1H); 5.26 (d, 2H); 6.62–7.45 (m, 12H).

Treatment of 9-benzylfluorene with Cr(CO)$_6$

A mixture of 9-benzylfluorene (2 g, 7.8 mmol), $Cr(CO)_3$ (1.71 g, 7.8 mmol) and Bu_2O/THF (100 + 10 ml) was refluxed for 36 h under nitrogen. After cooling and filtration to remove unchanged $Cr(CO)_6$ the solvent was distilled off under vacuum. The crude product was adsorbed on Silicagel 60 (Merck) before being chromatographed on a column packed with the same support (4 × 40 cm). The eluent was 1/2 Et_2O/hexane.

The compounds were eluted in the order: 9-benzylfluorene (0.41 g, 1.6 mmol, 20%); **8** (0.63 g, 1.62 mmol, 22%); **6** (0.79 g, 2 mmol, 26%), **7** (0.53 g, 1.36 mmol, 17.5%); **9** (0.46 g, 0.87 mmol, 11.2%); **10** (0.147 g, 0.28 mmol, 3.6%).

All the isolated compounds are yellow solids, and were recrystallized from methylene chloride/hexane. They usually decompose before melting. The main spectroscopic data are reported in Table 2. The infrared spectra exhibit several bands typical of arenechromium tricarbonyl complexes. It is noteworthy that each *exo*-isomer displays two absorptions between 1970–1950 cm^{-1} whereas only one band is observed in this region for the *endo*-isomers.

The ^{1}H NMR spectra described in Table 2 have been obtained in $CDCl_3$. We describe below a few NMR spectra obtained In C_6D_6 (m* = two doublets of doublets): **6** (C_6D_6, 28°C) 2.39—2.86 (m*, 2H); 4.10 (pt, 1H); 4.42 (t, 2H); 4.85 (d, 1H); 5.14 (d, 1H); 6.72–7.10 (m, 9H). **6** (C_6D_6, 50°C) 2.44–2.91 (m*, 2H); 4.12 (pt, 1H); 4.47 (t, 2H); 4.90 (d, 1H); 5.20 (d, 1H); 6.75–7.20 (m, 9H). **7** (C_6D_6, 28°C) 2.40–2.87 (m*, 2H); 4.11 (pt, 1H); 4.43 (t, 2H); 4.87 (d, 1H); 5.16 (d, 1H); 6.80–7.10 (m, 9H). **7** (C_6D_6, 50°C) 3.02–3.10 (m, 2H); 3.84 (t, 1H); 4.16 (t, 1H); 4.72 (t, 1H); 4.90 (d, 1H); 5.05 (d, 1H); 6.85–7.22 (m), **9** (C_6D_6, 50°C) 2.23–2.63 (m*, 2H); 3.74 (t, 1H); 4.06–4.30 (m, 4H); 4.51 (m, 2H); 4.87 (t, 1H); 5.10 (t, 1H).

Acknowledgement

We are grateful to Mrs. Fouquet and Mrs. Compain for technical assistance.

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