Journal of Organometallic Chemistry, 386 (1990) 37–50
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20614

The electrochemical properties of the (μ-η^6,η^6-naphthalene)dichromium compounds and bis(η^6-naphthalene)chromium

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(Received August 28th, 1989)

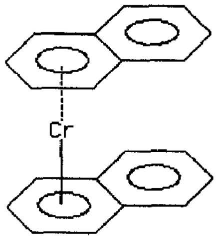
Abstract

The electrochemistry of the novel macromolecular organometallic polymer poly[(μ-η^6,η^6-naphthalene)chromium] is delineated through the study of its precursor (bis(η^6-naphthalene)chromium) and an oligomeric model ((μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium) in order to observe the degree of intervalence charge transfer between chromium sites in the multinuclear species. Theoretical studies have indicated that the multidecker sandwich compound poly[(μ-η^6,η^6-naphthalene)chromium] should be an electrical conductor in its oxidized state; no electrical conductivity is observed in the zero valent state. The inferred mechanism of the ligand exchange process of bis(η^6-naphthalene)chromium in tetrahydrofuran through an η^2-THF,η^4,η^6 intermediate is supported by the CE mechanism of the $Cr^{0/+}$ couples observed by the Nicholson and Shain method of kinetic analysis in (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium).

The cyclic voltammetry of bis(η^6-naphthalene)chromium and (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium) in tetrahydrofuran, and bis(η^6-naphthalene)chromium and poly[(μ-η^6,η^6-naphthalene)chromium] in ethylenediamine are described to delineate the electrochemical behavior of chromium compounds incorporating η^6-naphthalene and μ-η^6,η^6-naphthalene moieties. In addition to the various kinetic processes, characteristic $Cr^{0/+}$ and relatively unusual $Cr^{+/2+}$ couples were observed; ligand (naphthalene)(0/ –) and (– /2 –) redox couples were also observed. While the second reduction of the μ-η^6,η^6-naphthalene moiety was inhibited by the first reduction, mixed valence interaction between the metal sites was not observed electrochemically.

Introduction

We became interested in the ligand exchange reactions of bis(η^6-naphthalene)chromium as a possible route to the formation of binuclear organometallic com-



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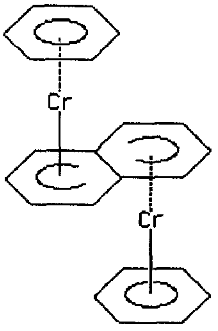

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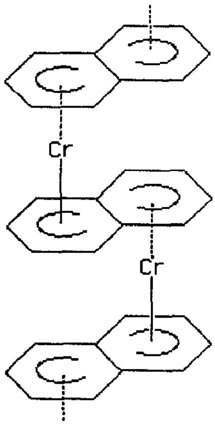


(III)

pounds for the purpose of studying electronic interactions between metal centers through bridging groups [1]. Most of the oligomeric or polymeric organometallics investigated in recent years consist of structures incorporating organic connecting groups between the metallocene units [2]. In such structures, the metallocene moieties are either pendent or are a component of the chain.

When the slipped triple-decker, (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium was isolated and analyzed [3], the novel bridging μ-η^6,η^6-naphthalene moiety became our focus of study; the report by Burdett and Canadell [4] predicting the band structure, and thus conductivity properties, of poly[(μ-η^6,η^6-naphthalene)chromium] further piqued our interest. Whereas the usual organometallic polymer is often an arrangement of metallocene moieties connected by organic groups, poly[(μ-η^6,η^6-naphthalene)chromium] is an organometallic polydecker sandwich compound containing no uncomplexed organic moieties.

The electronic interaction between the chromium sites, and the μ-η^6,η^6-naphthalene moieties, were studied by cyclic voltammetry on representative compounds incorporating these structural units, namely bis(η^6-naphthalene)chromium (I), (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium (II) and poly[(μ-η^6,η^6-naphthalene)-chromium] (III).

Although the extreme reactivity of these compounds made experimental progress difficult, this same reactivity provides insight into the phenomena observed.

Results and discussion

Representative cyclic voltammograms are presented in Fig. 1 through 5. Comparison of the features that appear in Fig. 1, 2 and 3 shows a commonalty of behavior in THF; the $Cr^{+/2+}$, $Cr^{0/+}$, $Np^{0/-}$, $Np^{-/2-}$ (Np = naphthalene) couples are clearly identified by intercomparison as indicated. Likewise, comparison of the electrochemical behavior between bis(η^6-naphthalene)chromium and poly[(μ-η^6,η^6-naphthalene)chromium] in ethylenediamine results in an unambiguous conclusion: the $Cr^{0/+}$ and $Np^{0/-}$ couples overlap, by comparison to the one electron $Np^{-/2-}$ wave in both Fig. 4 and 5.

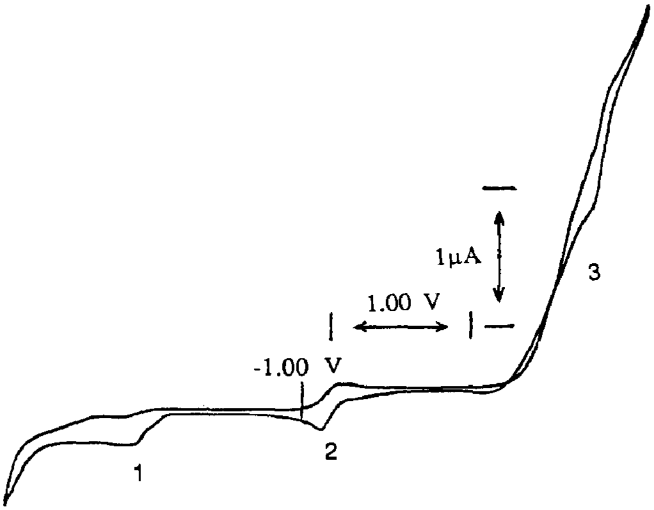


Fig. 1. Cyclic voltammogram of bis(η^6-naphthalene)chromium/THF.

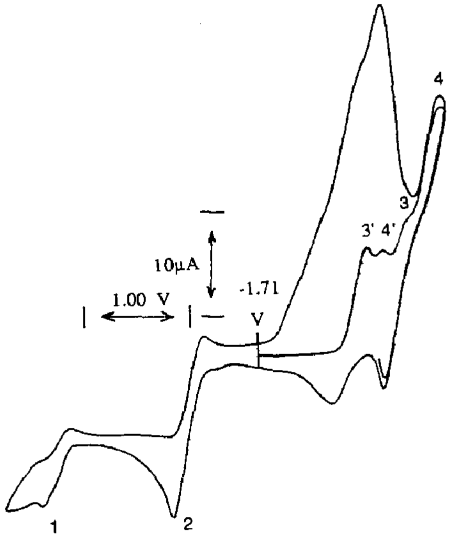


Fig. 2. Cyclic voltammogram of bis(η^6-naphthalene)chromium/THF/wet.

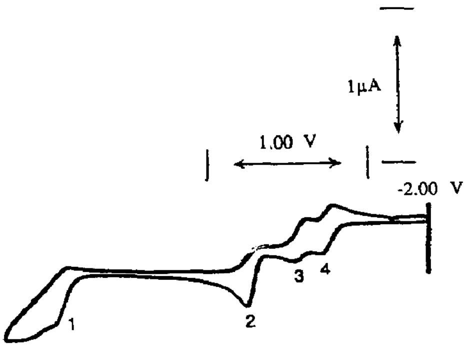


Fig. 3. Cyclic voltammogram of (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium/THF.

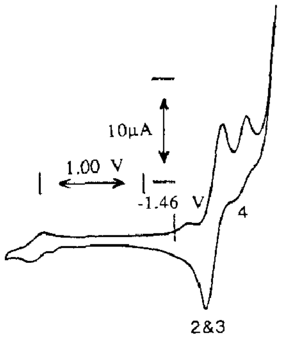


Fig. 4. Cyclic voltammogram of bis(η^6-naphthalene)chromium/ethylenediamine.

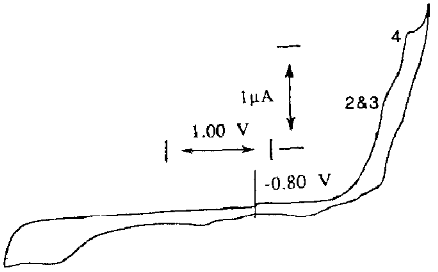
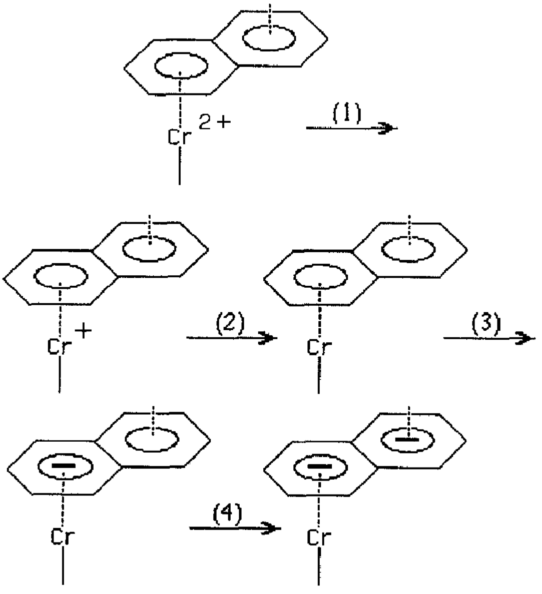


Fig. 5. Cyclic voltammogram of poly[(μ-η^6,η^6-naphthalene)chromium]/ethylenediamine.

Scheme 1 provides a key relating the assignment of electrochemical events in Fig. 1–5 to the corresponding half wave potentials reported in Table 1, the scan rate is constant (50 mV/s) throughout this series or experiments. The electroactive moie-



Scheme 1

Table 1

Potentials of representative cyclic voltammograms shown in Fig. 1 through 5

	Process			
	(1) $Cr^{+/2+}$	(2) $Cr^{0/+}$	(3) $Np^{0/-}$	(4) $Np^{-/2-}$
Fig. 1, Bis(naphthalene)chromium/THF	+0.196 [a]	−1.190	−3.126	-
Fig. 2, Bis(naphthalene)chromium/THF/wet	+0.22	−1.05	(3′) −2.76 [b] −2.41 [c] −3.15 [d] −2.91 [e]	(4′)−2.91 [b] −3.46 [d]
Fig. 3, (μ-naphthalene)bis(benzene)-dichromium/THF	+0.38	−0.80	−1.10	−1.27
Fig. 4, Bis(naphthalene)chromium/ ethylenediamine	-	−1.84	−1.84	−2.09
Fig. 5, Poly[(μ-naphthalene)chromium]/ ethylenediamine	-	−2.04	−2.04	−2.24

[a] Anodic wave. [b] Cathodic adsorption prewave. [c] Anodic adsorption prewave. [d] Cathodic diffusion wave. [e] Anodic diffusion wave.

ties depicted in Scheme 1 differ in stoichiometric proportion from one experiment to another, but not in identity in the series of experiments depicted by the data.

Electrochemistry in THF

Bis(η^6-naphthalene)chromium. The electrochemistry of bis(η^6-naphthalene)chromium in THF is complicated by the reactivity of the compound with the solvent. The slow ligand exchange reaction of bis(η^6-naphthalene)chromium with itself [5] to form the insoluble poly[(μ-η^6,η^6-naphthalene)chromium] or oligomers thereof causes the concentration of bis(η^6-naphthalene)chromium to change slowly over the course of a series of cyclic voltammetry experiments. In a scrupulously dry cell (Fig. 1) the $Cr^{0/+}$ couple is observed at −1.19 volts, the $Cr^{+/2+}$ anodic peak at +0.196 volt, and the complexed naphthalene (0/−) couple at −3.126 volts, all reported versus $Ag/AgNO_3$.

The standard method of probing electrochemical processes using variable scan rates had to be modified in our experiments because the resistance of the circuit increased after the first scan (e.g. Fig. 2), which we attribute to the formation of an insoluble product on the electrode surface. Accordingly the working electrode was polished before the beginning of each single cyclic scan, and the scan rates varied over several orders of magnitude.

For the $Cr^{0/+}$ couple, plots of $i_p/(v)^{1/2}$ versus scan rate (v) suggest reversible charge transfer; likewise a plot of i_{pa}/i_{pc} versus scan rate indicates reversible charge transfer, especially at higher scan rates were kinetic processes exert a smaller influence. For the $Cr^{+/2+}$ anodic peak, the plots of $i_p/(v)^{1/2}$ versus scan rate is inconclusive; the lack of a cathodic return wave (Fig. 1) suggests an irreversible charge transfer, or following kinetics. For the process that is presumed to the complexes naphthalene (0/−) couple (see Fig. 1), the close proximity to the negative solvent limit combined with apparent adsorption phenomena preclude the usual kinetic analysis; no complexed naphthalene (−/2−) couple could be discerned in this system. It is possible that the complexed naphthalene (0/−) couple assigned in Fig. 1 consists of overlapping complexed naphthalene (0/ –) and (– /2 –) couples, or that the (– /2 –) couple is obscured by the reductive solvent limit. Extrapolation of ΔE_p of the complexed naphthalene (0/ –) couple to zero scan rate suggests a relatively small ΔE_p (tending towards reversibility), compared to the case of the complexed naphthalene (0/ –) and (– /2 –) couples under conditions were strong adsorption phenomena are observed (Fig. 2).

Strong adsorption phenomena of bis(η^6-naphthalene)chromium. In a cell containing slightly wet THF (Fig. 2), the electrochemical results suggests strong adsorption phenomena. The baseline cyclic voltammograms of this THF electrolyte solution appeared normal if not cleaner than the baseline found in the completely dry system. The electrochemistry of bis(η^6-naphthalene)chromium reported by Saji et. al. [6] is probably incorrect because of the source of their sample; the methods of Hein and Kleinwachter [7] to synthesize bis(η^6-naphthalene)chromium results in at least the partial hydrogenation of the species formed [8]. Unless care is taken to remove the hydrogenated products, the reported electrochemical results can be ambiguous. The $Cr^{0/+}$ couple as we have identified it occurs at –1.05 volts; the electrochemical results, $i_{pa}/i_{pc} > 1$, suggest weak adsorption of bis(η^6-naphthalene)chromium on the electrode [9]. The cathodic adsorption prewaves of the complexed naphthalene (0/ –) and (– /2 –) couples were observed at –2.76 and –2.91 volts, respectively, while a single anodic prewave was observed at –2.41 volts. The cathodic prewaves possess a characteristic symmetry associated with strong adsorption [10a].

The relative wave shapes of these couples indicate a greater current is passed for the complexed naphthalene (0/ –) cathodic peak, compared to the complexed naphthalene (– /2 –) cathodic peak; this relationship suggests that the $Cr^{0/+}$ adsorption cathodic peak overlaps with the complexed naphthalene (0/ –) peak. The known reaction chemistry of bis(η^6-naphthalene)chromium [5] suggests that the adsorbed species is poly[(μ-η^6,η^6-naphthalene)chromium] or oligomers thereof.

After the first cycle, the adsorption peaks grow until they dominate the voltammogram; the increasing resistance spreads and obscures the peaks during successive scans (Fig. 6). It was necessary to polish the working electrode before every scan, to remove the non-electroactive material which coated it. The cathodic diffusion peaks of complexed naphthalene (0/ –) and (– /2 –) were observed at –3.15 and –3.46 volts, respectively; a single anodic peak was observed at –2.91 volts. Presumably these couples are associated with a weak adsorption phenomena, but the proximity of the reductive solvent limit precludes analysis.

(μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium. The $Cr^{+/2+}$, $Cr^{0/+}$, complexed naphthalene (0/ –) and (– /2 –) couples were observed at $E_{1/2}$ values of +0.38, –0.80, –1.10 and –1.27 volts versus $Ag/AgNO_3$, respectively. Because the electrode became coated with a non-electroactive material after only one scan, it was necessary to polish it before the beginning of each individual scan. Plots of the current function $(i_p/(v)^{1/2})$, and i_{pa}/i_{pc} versus scan rate, were used to help identify the kinetic processes occurring.

The absence of a cathodic return wave for the $Cr^{+/2+}$ couple, suggests charge transfer followed by a chemical reaction which is consistent with the conclusions deduced from the plot of the current function versus scan rate; the instability of a chromium-arene moiety carrying two positive charges has been observed previously [11]. For the $Cr^{0/+}$ couple the current function versus scan rate plot suggests a

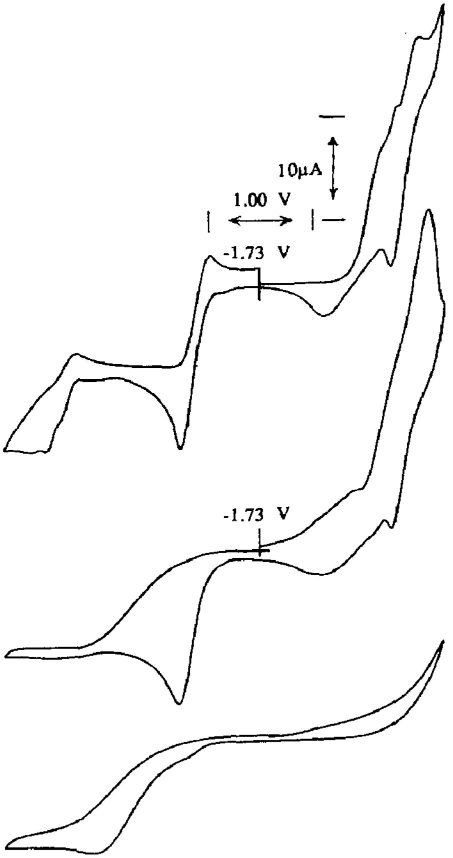
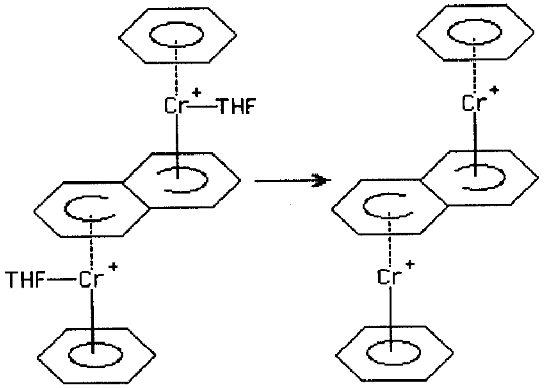


Fig. 6. Successive cyclic voltammetric scans showing resistance induced by adsorption of poly[(μ-η^6,η^6-naphthalene)chromium] (or oligomers thereof) from a solution of bis(η^6-naphthalene)chromium in THF.

chemical process preceding charge transfer (the CE mechanism). The plot of i_{pa}/i_{pc} versus scan rate confirms unambiguously that indeed a chemical process is occurring before charge transfer. A misdiagnosis of the CE mechanism based on the plot of i_{pa}/i_{pc} versus scan rate could occur if a weak adsorption of the electroactive species onto the electrode surface does not produce obvious concomitant changes in wave shape associated with strong adsorption phenomena. If the increase in i_{pa}/i_{pc} were to level off at unity as the scan rate became slow, the product of the electron transfer process could be diagnosed as being weakly adsorbed on the electrode surface. However in this case the values of the ratio of i_{pa}/i_{pc} ($i_{pa}/i_{pc} > 1$) do not level off at unity as the scan rate decreases; we have no evidence to support the considered possibility that weak adsorption is present in the electrochemical processes of this system [9]. This is an important conclusion, because the analysis that a CE mechanism is involved suggests that the solvent plays a role in the process. The CE mechanism is consistent with a process in which an individual chromium atom shifts from an η^2-THF-η^4-naphthalene-η^6-benzene configuration, to an η^6-naphthalene-η^6-benzene configuration before electron transfer (Scheme 2), a process that is in accord with the known reaction chemistry of bis(η^6-naphthalene)-chromium [5], and the inferred mechanism of ligand exchange [3].



Scheme 2

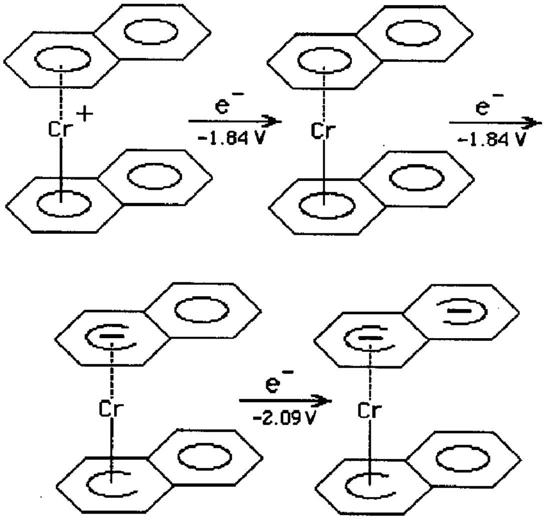
The (0/ −) and (− /2 −) waves associated with the complexed naphthalene moiety are sufficiently close ($\Delta E_{1/2}$ −170 mV) to interfere with each other and, thus, render a proper kinetic analysis of the data for these processes difficult to interpret. This EE process exhibits normal behavior for the case where the first reduction inhibits the second reduction [12]. There is no indication of strong adsorption based on wave shape criteria, nor is weak adsorption indicated by the plot of i_{pa}/i_{pc} versus scan rate which should level off at unity. The fact that the apparent i_{pa}/i_{pc} is greater than unity suggests that chemical processes precede electron transfer in the naphthalene (− /2 −) couple. The plot of ΔE_p versus scan rate, extrapolated to zero scan rate suggests that the $Cr^{0/+}$, naphthalene (0/ −) and (− /2 −) couples are reversible charge transfer processes, a conclusion which is consistent with the CE mechanism for $Cr^{0/+}$.

The existence of a $Cr^{+/2+}$ wave for bis(η^6-naphthalene)chromium, suggests that the $Cr^{+/2+}$ wave of (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium is a two electron process where the two chromium moieties undergo oxidation independently of each other. Likewise the $Cr^{0/+}$ wave appears to be a two electron process with both chromium moieties behaving independently of each other.

Electrochemistry in ethylenediamine

Bis(η^6-naphthalene)chromium. The cyclic voltammograms of bis(η^6-naphthalene)chromium in ethylenediamine are remarkably different than those observed in THF. Two couples near the reductive solvent limit were observed by cyclic voltammetry for bis(η^6-naphthalene)chromium in ethylenediamine (Fig. 4), the first at $E_{1/2}$ −1.84 volts draws approximately twice the cathodic current as the second wave, at $E_{1/2}$ −2.09 volts, both measurements being made at a 50 mV/s scan rate.

The 2/1 current ratio suggests that the first wave is comprised of two single electron transfer reactions occurring at approximately the same potential, while the second wave corresponds to a single, one-electron transfer process. The overlap of two, one-electron transfer processes in the first wave and the proximity of the second wave to the solvent limit render kinetic analysis impossible. The double reduction wave of naphthalene is observed in other similar systems, e.g. (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium and the previously mentioned adsorption waves of bis(η^6-naphthalene)chromium dissolved in THF. The 2/1 current ratio of the first wave suggests that it is comprised of the $Cr^{0/+}$ couple and the naphthalene



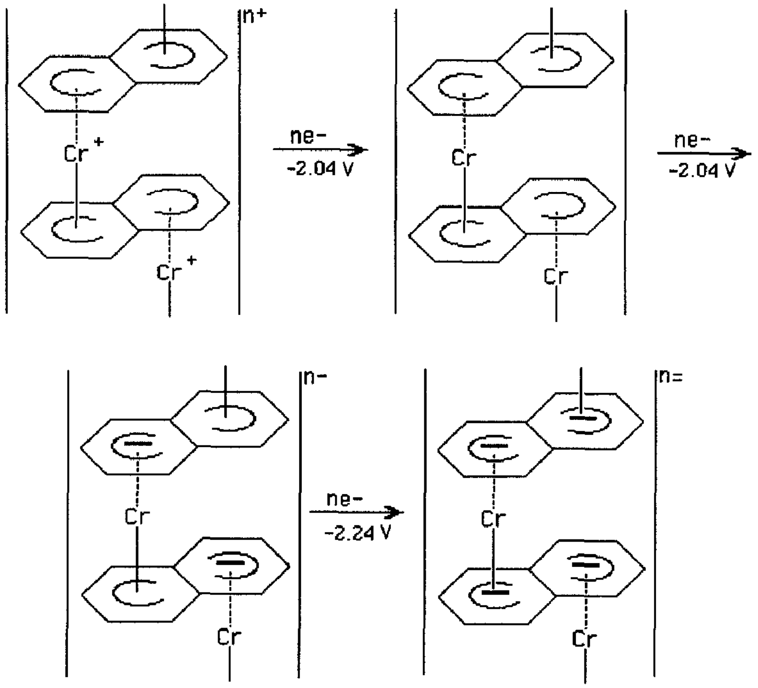
Scheme 3

(0/ −) couple, while the second wave is the naphthalene (− /2 −) couple (Scheme 3).

It was not necessary to polish the working electrode when ethylenediamine is used as the solvent, primarily because the electrochemical process in ethylenediamine does not form a non-electroactive film over the electrode as it does in THF, and, secondarily, because poly[(μ-η^6,η^6-naphthalene)chromium] is soluble in ethylenediamine whereas it is insoluble in THF. The plot of ΔE_p versus the scan rate extrapolated to zero scan rate shows that the first wave of bis(η^6-naphthalene)chromium in ethylenediamine has a ΔE_p of over 100 mV as does the $Cr^{0/+}$ couple in THF. This not only suggests quasi-reversibility for the $Cr^{0/+}$ process, but that the two electron wave of bis(η^6-naphthalene)chromium in ethylenediamine arises in part from the $Cr^{0/+}$ couple.

Poly[(μ-η^6,η^6-naphthalene)chromium]. The electrochemical behavior of poly[(μ-η^6,η^6-naphthalene)chromium] is complicated by its virtual insolubility in THF, fortunately the compound is sufficiently soluble in ethylenediamine for analysis. Poly[(μ-η^6,η^6-naphthalene)chromium] dissolves in a 0.1 *N* tetra(n-butyl)ammonium hexafluorophosphate solution of ethylenediamine to form a relatively intense brown-green colored solution; an intense emerald green color is observed in the vicinity of the dissolving solid. To avoid decomposition by water, the ethylenediamine solvent was vacuum distilled three successive times from a solution of ethylenediamine equilibrated with (NaK) [13].

The proximity of the reductive solvent limit of ethylenediamine to the redox couples observed for poly[(μ-η^6,η^6-naphthalene)chromium] (Fig. 5) precludes kinetic analysis. Like bis(η^6-naphthalene)chromium in ethylenediamine, only two waves are observed for poly[(μ-η^6,η^6-naphthalene)chromium]; in addition the first couple ($E_{1/2}$ −2.04 volts versus Ag/Ag^+) also appears to have a larger peak current than the second wave ($E_{1/2}$ −2.24 volts) for poly[(μ-η^6,η^6-naphthalene)chromium] at 50 mV/s scan rate. This suggests that the wave at −2.04 volt is comprised of both the $Cr^{0/+}$ and the complexed naphthalene (0/ −) couples, whereas the couple at −2.24 volts is the complexed naphthalene (− /2 −) couple (Scheme 4).



Scheme 4

The results of the plot of ΔE_p versus the scan rate extrapolated to zero scan rate, suggests reversible charge transfer processes for both waves.

A general shift towards more negative values of $E_{1/2}$ for the $Cr^{0/+}$, $Np^{0/-}$ and $Np^{-/2-}$ redox processes in going from bis(η^6-naphthalene)chromium to poly[(μ-η^6,η^6-naphthalene)chromium] is observed in ethylenediamine. Thus the difficulty in handling the extremely air sensitive bis(η^6-naphthalene)chromium is greatly exacerbated by polymerization. A steady shift of $E_{1/2}$ towards more negative values is observed in polyferroceneolenes [2] occurs in steps of decreasing size as the number of ferrocene moieties incorporated in the polyferroceneolene increases. Each additional electron donating ferrocene moiety makes it easier to oxidize one of the ferrocene moieties in the chain. While Neuse [2] suggests that a long chain of polyferroceneolene may suffer mono-oxidation spontaneously, the bulk conductivity of poly[(μ-η^6,η^6-naphthalene)chromium] suggests that any accidental oxidation occurring is not sufficient to cause an increase in electrical conductivity as by doping [4].

Conclusions

In each compound studied here (excepting poly[(μ-η^6,η^6-naphthalene)chromium]) the mono- and di-cations of the chromium moieties, and the mono- and di-anions of the complexed naphthalene moieties were observed. Electronic communication between chromium sites through the μ-η^6,η^6-naphthalene bridge appears to be insignificant, since the chromium sites exhibit independent redox properties [12]. The results of theoretical and experimental studies indicate that noninteracting redox centers exhibit voltammetric wave shapes that match exactly those of a corresponding single redox center, only the wave height is different [14]. Had the chromium moieties in our system exhibited standard potentials within 100 mV of each other only one wave would be observed; had these potentials been identical ΔE_p would have decreased to 42 mV [12]. Where structurally identical redox sites in the same molecule (e.g. (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium) do not interact, the electron transfer processes at the two centers are purely statistical. The difference in standard potentials would then be (RT/F(ln 4)) = −35.7 mV (25 ° C) resulting in a ΔE_p of 58 mV, with a wave shape corresponding to that of a single redox site [12]. The case in which the second redox process is facilitated by the first redox process results in ΔE_p decreasing to 28.5 mV at 25 ° C [12]. An interesting example of the second redox process being facilitated by the first redox process is the case of the reduction of (μ-η^6,η^6-biphenyl)bis(chromiumtricarbonyl) to form a stable di-anion [15], resulting in a two electron wave with a ΔE_p of 35 mV. To summarize: no characteristic deviation from the normal reversible or quasireversible behavior was observed, thus no electronic communication effects were observed between the chromium moieties.

The naphthalene moiety exhibits an inhibitory interaction on being reduced from the mono- to the di-anion [12]. The assignment of the mono- and di-anion as being localized on the naphthalene moiety finds support from the work of Rieke [15]. Analysis of the kinetics of the electrochemical processes involving (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium suggests that the substrate undergoes interaction with the solvent (THF) before charge transfer (the CE mechanism); a comparison of the cyclic voltammograms of bis(η^6-naphthalene)chromium in THF and in ethylenediamine indicates enormous solvent effects. In ethylenediamine a solvent effect (complexation) causes the $Cr^{0/+}$ and complexed naphthalene (0/ −) couples of both bis(η^6-naphthalene)chromium and poly[(μ-η^6,η^6-naphthalene)chromium] to occur at the same potentials. We eliminated the possibility of confusing the one electron reduction observed with that of free naphthalene [16], which could be derived from the decomposition of bis(η^6-naphthalene)chromium and poly[(μ-η^6,η^6-naphthalene)chromium] in ethylenediamine; the voltammogram of the mixture formed upon the addition of free naphthalene to the cell after the initial electrochemical experiment indicated that free naphthalene was not present in the original voltammogram of the π-complex.

The formation of the polymer (or oligomer) poly[(μ-η^6,η^6-naphthalene)chromium] was observed as an adsorption wave in the cyclic voltammogram of bis(η^6-naphthalene)chromium using THF as the solvent. The electronic characteristics of poly[(μ-η^6,η^6-naphthalene)chromium] are a result of the naphthalene moiety rather than the topology of the macromolecule [4]. Neuse [2] found the lack of overall electronic delocalization throughout polyferroceneolenes to be due to a blocking function of the metal center [17,18], resulted in a lack of electrical conductivity. Both the naphthalene HOMO and the (occupied) LUMO exhibit non-bonding interactions across the 9–10 bridgehead of the μ-naphthalene moiety, resulting in effective bond localization [3]. The non-delocalized nature of the μ-naphthalene moiety may be the reason for the lack of electrical conductivity observed for poly[(μ-η^6,η^6-naphthalene)chromium(0)].

Experimental

The syntheses and characterization of bis(η^6-naphthalene)chromium [19,20], (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium [3] and poly[(μ-η^6,η^6-naphthalene)chromium] [5] follow those reported in the literature.

Electrical conductivity of poly[(μ-η^6,η^6-naphthalene)chromium]: Approximately 5 μg of poly[(μ-η^6,η^6-naphthalene)chromium] was pressed between 0.965 mm diameter steel pistons that were capable of moving within a section of glass capillary tubing. At a distance between the piston faces of 0.005 mm an open circuit was detected using a 20 MΩ setting on a Keithley 191 digital multimeter. Experiments of this kind indicate that the undoped polymer is best described as an insulator.

The voltammetric measurements were made using a PAR Model 173 potentiostat for potential control with a PAR model 175 universal programmer as a sweep generator. Instrumental compensation of solution resistance was generally employed. Fast scan experiments (scan rate greater than 2.0 volts per second) were performed using a Nicolet 1090A Explorer digital oscilliscope, incorporating model D preamplifiers within the Model 93A plug in unit [21*], to collect and store the data. The standard electrochemical experiments [10b] were performed in a one compartment cell [11] incorporating two electrodes (reference and auxiliary) enclosed within small fritted compartments and a platinum button working electrode. The electrolyte, typically tetra(n-butyl)ammonium hexafluorophosphate from Southwestern Analytical Chemicals Inc. 521 East Woodward, Austin, TX., was bulk dried as a fine powder by long term heating under a diffusion pump vacuum (e.g. 120 °C., 24 h, less than 1 micron). The dried electrolyte was weighed in the drybox and loaded into drying pistols which were then capped and removed from the box for use; the electrolyte was introduced into the cell using the usual Schlenk technique. This procedure precluded the need to dry the electrolyte in the cell overnight before each experiment.

The electrolyte and $AgNO_3$ for the reference having been loaded and the sample dumper being in place, the dried solvent (THF or ethylenediamine) was measured in a septum sealed graduated test tube and siphoned into the cell through a cannula. The mixture was stirred until the electrolyte dissolved, and the resulting solution freeze-degassed-force thawed for three cycles to remove any traces of oxygen. The cyclic voltammogram of this solution was then established as a background reference. The sample dumper was then opened allowing the sample container to fall into the solvent and the mixture stirred until the organometallic sample had dissolved. The known oxidation state of the compound in solution as compared to the measured rest potential of the cell was used in identifying oxidative and reductive processes. Finally the cyclic voltammogram of the organometallic substrate was established, altering scan rates and scan limits to define the usual electrochemical parameters for the system [22].

The working electrode was wet polished on felt with 1μ aluminum oxide polishing powder, and dried. The 25μ microelectrode was fabricated by collapsing a glass capillary around a 25μ Pt wire under vacuum, through the use of a helical resistive heating element. The wire was exposed through the use of abrasives and polished with cerium oxide (an abrasive finer than 1μ). The reference silver wire was polished and dipped in concentrated nitric acid, in preparation for use as a silver/silver nitrate reference electrode; or it was polished and oxidized by dipping for one minute in concentrated nitric acid, in preparation for use as a pseudoreference electrode in ethylenediamine. In the latter instance no silver salt was placed in

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* Reference number with asterisk indicates a note in the list of references

the frit. Frits were carefully degreased before cleaning with aqua regia, which was followed by boiling the frits with distilled water and rinsing with methanol prior to oven drying.

A series of compounds were studied in order to provide a basis of comparison among them, unfortunately (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium was not sufficiently soluble in ethylenediamine to obtain useful data and poly[(μ-η^6,η^6-naphthalene)chromium] is insoluble in THF. The cyclic voltammetry experiments were performed in THF and ethylenediamine solutions using 0.1 *N* tetra(n-butyl)ammonium hexafluorophosphate as supporting electrolyte. The THF solvent was purified by stirring with sodium/potassium liquid alloy (NaK, 1/1) until the characteristic blue color was observed, and the pure, dry THF obtained from that mixture by vacuum distillation. The ethylenediamine was thrice vacuum-distilled from successive solvated electron solutions produced by treatment with NaK [13]. The use of ethylenediamine was necessitated by the insolubility of poly[(μ-η^6,η^6-naphthalene)chromium] in THF.

The scan rates in one experiment were varied systematically to obtain data that could be used as diagnostic criteria as defined by Nicholson and Shain [22], viz.: (a) the current function ($i_p/v^{1/2}$) plotted versus scan rate (v), (b) i_{pa}/i_{pc} versus scan rate (v) and (c) $\Delta E_{p/2}/\Delta \log v$ versus the scan rate (v). Criterion (c) was frequently rendered ambiguous by small variations in solution resistance. When these techniques can be applied, they provide insight into the electrochemical processes occurring during the experiment. The tabularized electrochemical data are published elsewhere [23].

Acknowledgment

We thank Dr. H. Steinfink and Mr. Edwin Garcia for helpful discussion. We are grateful for generous support of the Texas Advanced Technology Research Program and the Robert A. Welch Foundation.

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