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Supplementary Material Available: Projections showing the molecular packing observed in the two molecules, listings of observed and calculated structure amplitudes (×10), and thermal parameters (32 pages). Ordering information is given on any current masthead page.

Direct and Indirect Electrochemical Oxidation of (Benzene)tricarbonylchromium and Its Derivatives in *N*,*N*-Dimethylformamide

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In *N*,*N*-dimethylformamide, benchrotrenyl, $XC_6H_5Cr(CO)_3$ (X = H, $COCH_3$, $N(CH_3)_2$), complexes exhibit a three-electron irreversible oxidation at the glassy carbon electrode. It is suggested that the first electron loss is followed by a fast decomposition of the intermediate Cr(I) complex, with the further formation of Cr(III). The electrooxidation can be carried out indirectly, by homogeneous redox catalysis, by means of catalyst redox couples whose oxidized forms are active. They include ferrocenes, tetrathiafulvalenes (TTF), and an aromatic amine. A quantitative study in cyclic voltammetry shows that the catalytic process corresponds to the limiting case of a kinetic control by the follow-up chemical reaction with the homogeneous electron transfer as a preequilibrium. It is shown that the presence of an electron-donating substituent on the benzene ring does not improve the stability of the intermediate Cr(I) species. When benchrotrenyl and catalyst groups belong to the same molecule, the induced oxidation of the former by the latter can occur in certain conditions which are filled for the chalcones $R_1COCH{=}C(CH_3)R_2$ (R_1 = TTF, R_2 = $C_6H_5Cr(CO)_3$; R_1 = $C_6H_5Cr(CO)_3$, R_2 = TTF).

In a recent study of the electrochemical redox properties of mixed chalcones derived from tetrathiafulvalene (TTF) and metallocenes, we have reported the abnormal behavior of the chalcones 1 and 2 in cyclic voltammetry performed

$R_1(C{=}O)CH{=}C(CH_3)R_2$
1, R_1 = TTF, R_2 = $C_6H_5Cr(CO)_3$
2, R_1 = $C_6H_5Cr(CO)_3$, R_2 = TTF
$XC_6H_5Cr(CO)_3$
3, X = H
4, X = $COCH_3$
5, X = $N(CH_3)_2$

at platinum electrode in *N*,*N*-dimethylformamide (DMF).[1] Despite the electron-withdrawing power of the C=CH-C=O group contained in these molecules, the oxidation of the benchrotrenyl unit occurs at potentials less positive than in (benzene)tricarbonylchromium (3); the respective values of the anodic peak potential, E_{pa}, of 1, 2, and 3 are 0.68, 0.75, and 0.83 V vs. SCE, respectively, when the scan rate is 0.1 V s^{-1}.

We now report on the direct and indirect electrochemical oxidations, through homogeneous redox catalysis,[2] of (benzene)tricarbonylchromium (3) and its derivatives 4 and 5, in DMF as solvent. Furthermore, it is shown that, in 1 and 2, the abnormal behavior observed in cyclic voltammetry results from the induced oxidation of the benchrotrenyl unit by the TTF group contained in the same molecule.

Table I. Half-Wave Potential ($E_{1/2}$) and Limit Current (i_l) of the Waves of 3-5 and of *N*,*N*-Dimethylaniline[a]

	anodic wave		cathodic wave	
substrate	$E_{1/2}$, V	i_l, μA	$E_{1/2}$, V	i_l, μA
3	0.82	224	−2.35	144[b]
4	0.87	242	−1.65	80[c]
			−2.51	75[c]
5	0.55	208	−2.50	140
	0.85	144		
N,*N*-dimethylaniline	0.83	150		

[a] Substrate concentration = 2×10^{-3} M°, angular velocity of the RDE = 115 s^{-1}. [b] Two-electron process; see ref 11. [c] One-electron processes; see ref 8-10.

We have applied several electrochemical techniques including voltammetry at stationary (SDE) and rotating disk electrodes (RDE), coulometry, and preparative electrolyses at a controlled potential. In order to prevent the electrode coating which is observed on platinum and which causes the appearance of a new anodic wave,[1] we have performed the voltammetric experiments with use of a glassy carbon electrode and the electrolyses and coulometric experiments with use of a glassy carbon cloth as the anode.

Prior to this report, the electrochemical oxidation of (arene)tricarbonylchromium complexes has been studied at the rotating Pt electrode in acetonitrile (MeCN)[3] and methylene chloride.[4] In the case of 3 in MeCN, a single

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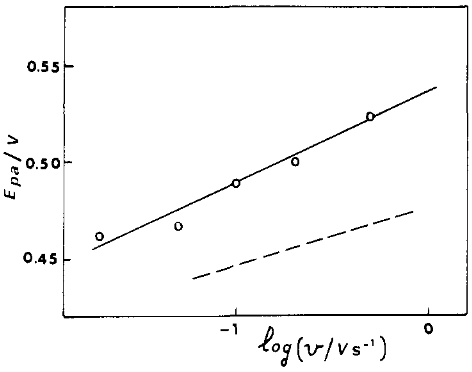

Figure 1. Influence of the sweep rate v on E_{pa} (compound **5** (10^{-3} M)). The dashed line gives the theoretical slope obtained in the case of an EC mechanism kinetically controlled by the chemical step.[12]

anodic wave is observed, whose height is about twice that of ferrocene.[3] In methylene chloride, the oxidation of **3** is characterized by two one-electron processes accompanied by electrode coatings.[4] All these oxidations are complicated by rapid follow-up reactions, so that overall multielectron processes along with destruction of the complex are observed; however, the oxidation mechanism has not yet been clearly established, neither in MeCN nor in methylene chloride. In a recent report,[5] stable cations of (arene)tricarbonylchromium complexes of dimethyldiphenyltin have been obtained electrochemically in propylene carbonate.

Results and Discussion

Direct Electrochemical Oxidation of 3–5. In voltammetry at RDE, a single anodic wave is observed for **3** and **4** and a double wave for **5**; the half-wave potential $E_{1/2}$ of the most positive wave is equal to that of *N,N*-dimethylaniline which is oxidized in the aprotic medium to tetramethylbenzidine.[6] Compounds **3** and **5** present a cathodic wave and **4** presents a double one. The characteristics of the voltammograms are summarized in Table I. For each wave, the limit current i_l is proportional to $W^{1/2}$ (W = angular velocity) and to the concentration of the substrate; it shows that i_l is diffusion controlled and obeys the Levich equation.[7]

A comparison of the values of the limiting currents of the cathodic and anodic waves of **3** and **4** (see Table I) shows that an overall three-electron process occurs upon their oxidation. At the mercury cathode, the successive one-electron reduction steps of **4** have been reported by Gubin[8,9] and Rieke;[10] the two-electron reduction of **3** has been claimed by Dessy.[11] A comparison of the heights of the waves of **3** and **5** leads also to a three-electron process for the first anodic wave of **5**; two electrons are involved in its reduction.

The cyclic voltammograms at SDE are found to be totally irreversible in the scan rate range v = 0.02–20 V s^{-1}. The peak potential values move toward positive values with increasing sweep rates; graphs $\delta E_p/\delta \log v$ are straight lines, the slopes of which are slightly higher than that expected in the case of a reversible electron exchange followed by a fast chemical reaction[12] (Figure 1). These results, together with the observation reported above that, for **5**, the $E_{1/2}$ value of its second anodic wave corresponds to that of *N,N*-dimethylaniline, suggest a fast destruction of complexes **3–5** according to the overall reaction (1).

Table II. Electrochemical Oxidation of 3–5 [a]

substrate	$C°$, M	applied pot, V	F consumed	identified or isolated compds
3	5.0×10^{-3}	1.0	3.4	Cr(III)
4	5.0×10^{-3}	1.26	3.3	Cr(III), $PhCOCH_3$ [b]
4	3.35×10^{-2}	1.2	2.85	Cr(III), $PhCOCH_3$ [c]
5	3.3×10^{-2}	0.65	2.97	Cr(III), $PhNMe_2$ [c]

[a] Coulometries and preparative electrolyses. [b] Identified by its reduction wave at RDE ($E_{1/2}$ = −2.2 V). [c] Isolated.

$$XC_6H_5Cr(CO)_3 - 3e^- \rightarrow XC_6H_5 + Cr(III) + 3CO \quad (1)$$

A series of coulometric experiments and preparative electrolyses has confirmed an overall three-electron mechanism together with the formation of Cr(III) and organic ligands (Table II). The Cr(III) species is electroactive in aqueous media[13–15] and aprotic solvents such as MeCN.[16] In DMF, its reduction at the glassy carbon electrode is accompanied by an electrode coating which causes distortions in the waves. The Cr(III) species electrogenerated in situ can be identified qualitatively from their UV spectroscopic properties[17] (see Experimental Section). Acetophenone and *N,N*-dimethylaniline are isolated upon preparative electrolyses at a controlled potential, performed in the presence of **4** and **5** as depolarizers.

A possible oxidation mechanism which is consistent with the above results is described by reactions 2–4.

$$XC_6H_5Cr(CO)_3 \overset{-e^-}{\rightleftharpoons} [XC_6H_5Cr(CO)_3]^+ \quad (2)$$

$$[XC_6H_5Cr(CO)_3]^+ \xrightarrow{k} XC_6H_5 + Cr(I) + 3CO \quad (3)$$

$$Cr(I) \xrightarrow{-2e^-} Cr(III) \quad (4)$$

The formation of the unstable cation is followed by the loss of the CO groups and of the organic ligand. Several chemical steps are involved in reaction 3 so that the formation of the intermediate Cr(I) species most probably occurs far from the electrode. Therefore, they are further oxidized to Cr(III) through solution electron transfers (SET mechanisms[18]). In DMF, the oxidation potential of Cr(II)[19] is negative to that of substrates **3–5**.

In the scope of reactions 2–4, the irreversible peaks observed in cyclic voltammetry may correspond to a kinetic control either by the charge transfer step (2) or by the

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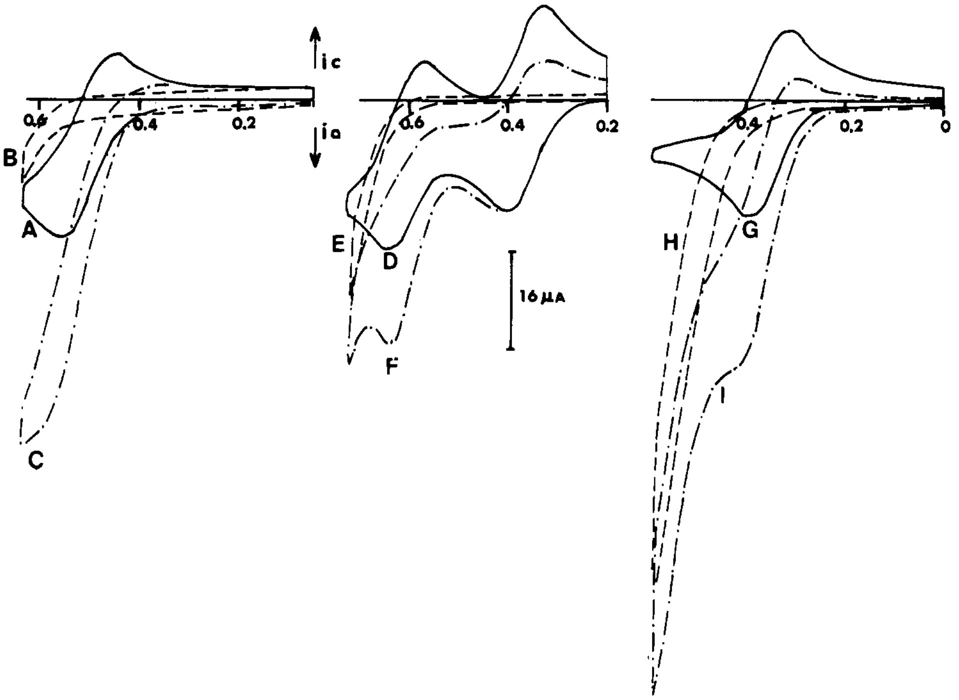


Figure 2. Modifications of the voltammetric peaks of catalysts upon addition of substrates. Catalyst (10^{-3} M) in the absence of substrate: curves A (**13**), D (**11**), and G (**7**). Substrate alone: curves B (**3**, 5×10^{-3} M), E (**3**, 2×10^{-3} M), and H (**5**, 2×10^{-3} M). Catalyst in the presence of substrate: curves C (**13** + **3**), F (**11** + **3**), and I (**7** + **5**).

Table III. Standard Potential of the Redox Couples Fc/Fc$^+$ ($E°_1$), TTF/TTF$^+$ ($E°_2$), and TTF$^+$/TTF^{2+} ($E°_3$) for Compounds 6–12

	6	7	8	9	10	11	12
$E°_1$, V	0.45	0.355	0.64	0.69	0.57,^{a} 0.72^a		
$E°_2$, V						0.35^a	0.45
$E°_3$, V						0.60^a	0.65

^{a} See ref 1.

elimination reaction (3) or by both steps concomitantly. But in any other scheme describing the overall reaction, (1) cannot be excluded a priori.

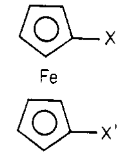
It has been shown by Sevêant and his group that short-lived intermediates may be generated by homogeneous redox catalysis.[2,18,20,21] The method has been illustrated by the indirect reduction of aromatic and heteroaromatic halides (see, for instance, ref 22). In the following part of this report, the catalytic indirect oxidation of (arene)chromiumtricarbonyl complexes such as **3–5** is described.

Indirect Electrochemical Oxidation of 3–5. Instead of electron transfers occurring at the electrode surface, the electron-exchange reactions (eq 5) are carried out in solution by means of catalyst redox couples P/Q whose standard potential $E°$ is negative with respect to the oxidation potential of the substrates.

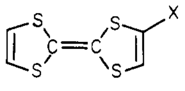
$$P \underset{}{\overset{-e^-}{\rightleftharpoons}} Q$$

$$Q + XC_6H_5Cr(CO)_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P + [XC_6H_5Cr(CO)_3]^+ \quad (5)$$

We have selected three types of stable redox systems as catalyst couples, P/Q. Compounds **6–10** belong to the ferrocene (Fc) series for which the active form Q of the catalyst couple is the ferricinium group. The standard potential is designated as $E°_1$. The $E°_1$ values of **6–10** in DMF are summarized in Table III. They are determined either at RDE from the $E_{1/2}$ value of their anodic wave or at SDE, in cyclic voltammetry, from the value (E_{pa} + E_{pc})/2, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. They had been measured previously in MeCN in the case of **6**, **7**, and **9**[23,24] and in water for **8**.[25] In the tetrathiafulvalene (TTF) series to which compounds **11** and **12** correspond, the active form is either the cation TTF$^+$ or the dication TTF^{2+}.[26] The corresponding standard potentials are $E°_2$ and $E°_3$; they are given in Table III. The aromatic amine **13** represents the last type of catalyst. Its oxidation leads to a stable cation



6, X = X' = H
7, X = X' = C_2H_5
8, X = Br, X' = H
9, X = $COCH_3$, X' = H
10, X = $CH_3C{=}CHC({=}O)Fc$, X' = H



11, X = H
12, X = SePh

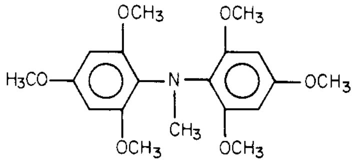


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Table IV. Oxidation of 3 (2×10^{-3} M) as Catalyzed by a Series of Catalysts P (10^{-3} M)[a]

	P					
	6	12[b]	13	10[b]	11[c]	8
$\Delta E_{1/2}$	0.37	0.37	0.32	0.25	0.22	0.18
$i_p/^3\gamma i_{pd}$	0.19	0.20	0.24	0.41	0.25	0.73

[a] Scan rate = 87 mV s^{-1}. Influence of the wave separation $\Delta E_{1/2}$. [b] First oxidation step. [c] Second oxidation step.

in MeCN[27,28] and in DMF; its standard potential is 0.50 V in DMF.

Three examples of the increase in the catalyst cyclic voltammetric peak upon addition of benchrotrenyls **3** and **5** are given in Figure 2. In the first case, the active catalyst species is the radical cation of **13**; in the second case, it is TTF^{2+}, and in the last one, it is the ferricinium derivative of **7**. In all examples, the catalytic effect is clearly seen from the increase in the anodic peak height and from the decrease in reversibility. On the other hand, a partial overlapping of the catalyst and substrate waves occurs. It has been shown by Savéant et al.[21,22] that this phenomenon appears to be in general the limiting case of the kinetic control by a chemical reaction. In the scope of the mechanism discussed previously, a kinetic control by reaction 3, with (5) as a preequilibrium, may account for the partial overlapping.

We have derived values of the catalytic efficiency from the values of the peak currents of catalyst P before and after addition of **3–5**. When the substrate undergoes a monoelectronic exchange (EC process), the catalytic efficiency corresponds to the ratio $i_p/\gamma i_{pd}$, where i_p is the catalytic peak current and i_{pd} the diffusion-controlled peak current of P in the absence of substrate.[21] The excess factor γ is the ratio C^0/C^0_p where C^0 and C^0_p are the concentrations of the substrate and P. In the results given below we have applied the theory proposed by Savéant and his group for a two-electron process including a SET mechanism;[21] but we have adjusted this theory to a three-electron process including two SET mechanisms. Therefore, the ratio $i_p/3\gamma i_{pd}$ will be used. The most probable occurrence of two SET mechanisms in the overall three-electron process has been discussed in the first part of this paper.

The catalytic efficiency observed when 2 equiv of **3** are added to a series of catalysts is indicated in Table IV. For the catalysts which exchange a single electron at the electrode, an increase of the catalytic efficiency is observed when the waves of the substrate and of P tend to be closer. Such variations are expected in the context of a redox catalysis.[2] In the case of **11**, the active form of the catalyst TTF^{2+} is generated at the electrode upon a two-electron oxidation. This dictation may undergo either the exchange reaction (5) or the disproportionation reaction (6). A competition between (5) and (6) is consistent with the low value of the catalytic efficiency of **11**.

$$TTF^{2+} + TTF \rightleftharpoons 2TTF^{+} \qquad (6)$$

The influence of the excess factor γ on the catalytic efficiency is shown in Table V. It is interesting to note that the values of $i_p/3\gamma i_{pd}$ keep close when γ is constant and equal to 3.3. In the scope of the oxidation mechanism proposed, evidence is thus obtained for kinetic control by (3), with (5) as a preequilibrium.[21] Under these conditions, it has been shown that the value of kk_1/k_2 can be derived from the catalytic efficiency.[21] From the working curve of Figure 5 in ref 21, we have derived the values of log kk_1/k_2 which are given in Table V. When γ decreases, the catalytic efficiency increases but, as expected, kk_1/k_2 keeps constant and is equal to 1.8×10^{-2} s^{-1}.

Table V. Catalytic Oxidation of 3 by 6 at Various Concentrations[a]

$10^3C^0_p$, M	10^3C^0, M	γ	$i_p/^3\gamma i_{pd}$	log kk_1/k_2
0.4	1.32	3.3	0.15	−1.92
1	3.3	3.3	0.16	−1.85
2	6.6	3.3	0.18	−1.60
4	13.2	3.3	0.17	−1.75
4	5.3	1.33	0.29	−1.75

[a] Scan rate = 42 mV s^{-1}. kk_1/k_2 is expressed in s^{-1}.

Table VI. Catalytic Oxidation of 3–5 (2×10^{-3} M) by Catalysts P (10^{-3} M)[a]

substrate	catalyst	$\Delta E_{1/2}$	$i_p/^3\gamma i_{pd}$
3	**8**	0.180	0.73
4	**9**	0.180	0.43
5	**7**	0.195	0.32
5	**11**[b]	0.200	0.36

[a] Scan rate = 87 mV s^{-1}. [b] First oxidation step.

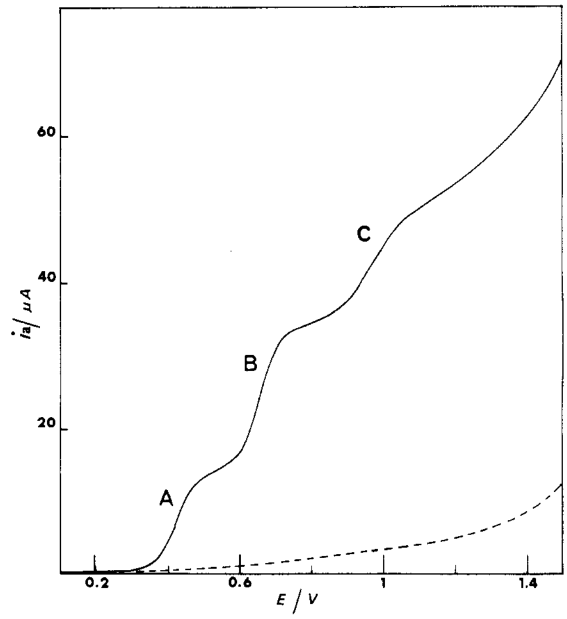

Figure 3. Voltammogram at RDE of **2** (5×10^{-4} M). The angular velocity is 115 s^{-1}. The dashed line corresponds to the supporting electrolyte.

We have compared the catalytic efficiency of a series of couples, substrate/catalyst, for which the wave separation $\Delta E_{1/2}$ is about the same. The results appear in Table VI. The precision of the values is 10%, owing to the proximity of the direct oxidation of the substrate (cf. Figure 2—curves H and I). In the conditions of Figure 2, the determination of i_p takes into account the current flowing in the absence of catalyst. The indirect oxidation of **5** either by the ferrocenyl derivative **7** or by TTF leads to the same catalytic efficiency. It shows that, as expected for a redox catalysis,[2] the catalytic effect is independent of the nature of the catalyst for a given standard potential. On the other hand, a higher catalytic efficiency and, therefore, a faster decomposition is observed for the unsubstituted substrate **3**. It shows that substituting the phenyl ring by an electron-donating group does not stabilize the intermediate cation. That confirms Rieke's conclusion that the persistence of the cation, when sta-

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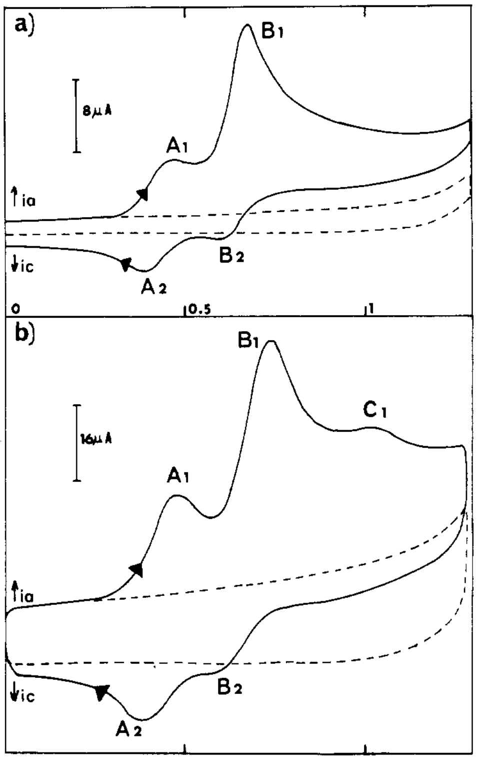

Figure 4. Cyclic voltammograms of **2** (5×10^{-4} M) at two scan rates: (a) 0.05 V s^{-1} and (b) 0.5 V s^{-1}.

bilized, is improved by the presence of bulky substituents around the phenyl ring but not by presence of electron-donating groups.[5]

Electrochemical Oxidation of 1 and 2. On the basis of the preceding results, we have reinvestigated the oxidation mechanism of **1** and **2** which possess a benchrotrenyl group, Bct, and a catalyst unit, TTF, in the same molecule.

Figure 3 presents a voltammogram obtained at RDE in the presence of **2**. Surprisingly, three waves A, B, and C appear at $E_{1/2}$ = 0.42, 0.65, and 0.97 V, although only two reversible peak systems A_1/A_2 and B_1/B_2 are observed at slow scan rate (cf. Figure 4, curve a); in other words, no peak corresponding to the more positive wave C is seen. In ref 1, the peaks A_1/A_2 and B_1/B_2 have been assigned respectively to the redox systems TTF/TTF^+ and TTF^+/TTF^{2+} contained in **2**, the oxidation of the Bct unit being concomitant with that of the TTF^+ moiety at potentials of B_1. When the sweep rate increases, a shoulder C_1 is observed at 1 V (Figure 4, curve b).

The strikingly different behavior of **2** at a stationary and rotating electrode can be explained in the context of the induced oxidation of the Bct unit contained in **2** by the TTF^{2+} dication. At RDE, the reaction layer is thin so that the induced oxidation of the Bct group, at potentials of wave B, competes with its direct oxidation. At SDE and at slow scan rate, the induced oxidation is total; at fast scan rate, it occurs partially and the direct oxidation is seen as a shoulder at 1 V (Figure 4, curve b). The direct and induced oxidation of **2** leads to the TTF^{2+} dication of **14**, which is reduced at potentials of peak B_2 since, as shown in ref 1, the standard redox potentials of the TTF units contained in **2** and **14** are close. Therefore, in Figure 4, the reduction peaks B_2 correspond mainly to the reduction of the TTF^{2+} species in **14**.

$$PhC({=}O)CH{=}C(CH_3)TTF$$
14

The Bct group in **2** is oxidized directly at potentials positive to that of (benzene)tricarbonylchromium (**3**; $\Delta E_{1/2}$ = 0.15 V); it is consistent with the electron-withdrawing power of the unsaturated carbonyl group in **2**.

The behavior of **1** and that of **2**, which is similar, present some similarity with the autocatalytic oxidation scheme which describes the decarboxylation of tetrathiafulvalenemonocarboxylic acid.[29]

Experimental Section

Substrates **3–5** are prepared according to ref 30 or 31. Compounds **6**, **9**, and **11** are commercially available. The synthesis of **1**, **2**, and **10** is described in ref 1. Samples of **7**, **8**, and **13** were kindly provided.

2-(Phenylselenyl)tetrathiafulvalene (12). An ethereal solution of (tetrathiafulvalenyl)lithium[32] (5×10^{-3} M) at −70 °C is admitted (argon pressure) into a flask containing phenylselenyl chloride (5×10^{-3} M) in ether (50 mL) at −70 °C. The solution is allowed to warm to room temperature and left in a freezer for a few hours. Filtration and removal of solvent in vacuo afford a residue. The desired product (0.2 g) is isolated by silica gel chromatography (30% benzene/hexane). The yellow solid has the following characteristics: mp 98–100 °C (isooctane); MS, *m/e* 360 (M^+), 203 (M^+ − SePh), 146, 102.

Anal. Calcd for $C_{12}H_8S_4Se$: C, 40,10; H, 2.24; S, 35.69. Found: C, 40.69; H, 2.29; S, 35.45.

The carbon electrode is a disk made of a rod of V 25 Carbon Lorraine glassy carbon sealed in a piece of glass tubing. Its diameter is 3 mm. Reproducible measurements are obtained when the electrode is cleaned as follows. Between each experiment the electrode is washed with water, polished on alumina (alumine Escil A 3, average dimension of the grains 0.5 μm), and washed again with water and acetone.

Voltammograms at RDE are recorded on a three electrode Tacussel-Tipol and cyclic voltammograms at SDE on an Ifelec 2025 C X-Y recorder, using a Tacussel UAP 4 unit and a GSTP function generator. An Amel-552 potentiostat and a Tacussel IG 5-N integrater are used in coulometry and preparative electrolysis. All the potentials refer to the aqueous saturated calomel electrode (SCE).

General Electrolysis Procedure. The three compartments of a H-type cell are filled with DMF containing Bu_4NPF_6 (0.1 M) as the supporting electrolyte. The cathode is a glassy carbon cloth and the anode a Pt grid. The catholyte (60 mL) is deaerated with argon before introduction of the depolarizer. The electrolysis is stopped when the current has diminished to a negligible value. In preparative electrolyses, the catholyte is diluted with water, and the organic ligand is extracted with diethyl ether. After the solution is dried, the ether is evaporated and the organic ligand is identified by its spectroscopic characteristics.

A UV spectroscopic study of the catholyte shows two maxima characteristic of the Cr(III) species.[17] In our experimental conditions, they are observed at 419 and 585 nm. It has been shown[33] that Cr(III) and amides form complexes which, in certain cases, decompose rapidly in contact with traces of water. We have not tried to determine the nature of the complex which gives maxima at 419 and 585 nm in our experimental conditions so that the UV spectroscopic study corresponds only to a qualitative determination of Cr(III).

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Registry No. **1**, 80753-30-6; **2**, 80753-29-3; **3**, 12082-08-5; **4**, 12153-11-6; **5**, 12109-10-3; **6**, 102-54-5; **7**, 1273-97-8; **8**, 1273-73-0; **9**, 1271-55-2; **10**, 1287-38-3; **11**, 31366-25-3; **12**, 82679-06-9; **13**, 57567-90-5; (tetrathiafulvalenyl)lithium, 63822-37-7; phenylselenyl chloride, 5707-04-0.

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