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ELECTRODE-CATALYZED SUBSTITUTION OF $M(CO)_4$bipy (M = Cr, Mo, W) INITIATED BY REDUCTION *

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Summary

One CO group is labilized and substituted by triphenylphosphine in radical anions formed by the electrochemical reduction of $M(CO)_4$bipy (bipy = 2,2-bipyridyl; M = Cr, Mo, W). The reaction proceeds as an electrode-catalyzed process. It is shown that the release of the CO group following the electrode reduction is the rate-determining step. The redox "cross"-reaction proceeding in the bulk of the solution plays the dominant role in propagation of the catalytic chain. Similarities between electrochemical and photochemical labilization are discussed.

It is shown that constant potential electrolysis can be conveniently used to study electrode-catalyzed substitutions in systems with slow chemical rate-determining steps coupled to reversible processes, and can be employed for preparative purposes.

Introduction

The first electrode-catalyzed reaction ** was described in 1959 by Elving et al. [1] for the case of the reduction of chromium(II) ions. Feldberg and Jeftic [2] analyzed the general mechanism leading to an electrode-catalyzed process:

$$A \underset{n_1}{\overset{E_1^\circ}{\leftrightarrow}} B \qquad (1)$$

$$B + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \qquad (2)$$

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* Dedicated to Prof. J. Halpern.

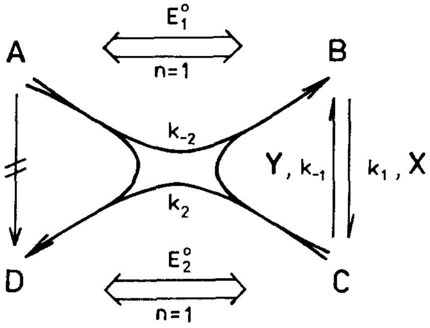
** It is preferable to call these reactions "electrode-catalyzed" processes as the injection of a highly sub-stoichiometric amount of charge from the electrode initiates the catalytic cycle. The term "electrochemical catalysis" is not adequate as it denotes quite a broad group of mechanistically different processes. Electron-transfer catalysis, initiated by a homogeneous redox transfer, does not include the possibility of propagation of the cycle via a reverse electrode reaction (cf. Scheme 1).

$$\mathrm{D} \underset{n_2}{\overset{E_2^\circ}{\leftrightarrow}} \mathrm{C} \tag{3}$$

$$\mathrm{A} + \mathrm{C} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{D} + \mathrm{B} \tag{4}$$

The set of processes 1–4 can be depicted schematically (Scheme 1).

SCHEME 1



The necessary condition for Scheme 1 to operate as a catalytic cycle is

$E_1^\circ > E_2^\circ$ for A → B being reduction

$E_1^\circ < E_2^\circ$ for A → B being oxidation

In 1–4, A is the substrate and D is the final product, in the same oxidation state as A. B and C are intermediates, which in the case for organic and many organometallic systems might be radical anions or cations. The direct reaction A → D proceeds very slowly, if at all, compared with reactions 1–4.

Although various electrode-catalyzed processes have been described recently (cf. refs. given in ref. 3, 4), the most vital point of the overall mechanism, the cross-reaction 4, has not always been fully recognized and taken into account.

We have recently analyzed the system (Scheme 1), considering especially the effect of the relative rates of eqs. 2 and 4 on the conditions under which electrode-catalyzed processes can be detected by various electrochemical techniques [3]. All the previous studies used mostly dc polarography, cyclic voltammetry or chronoamperometry, all of which require reaction 2 to be rather fast. We deduced, and were able to show experimentally [3], that mechanism (1) can be detected even for low values of k_1, using constant potential electrolysis at mercury pool electrodes. Moreover, constant potential electrolysis enables the electrode-catalyzed reactions to be used as a convenient electropreparative method, which, for large values of k_2, can be triggered merely by a short electrolytic pulse.

In the system we studied previously, reaction 3 was fully irreversible so that the propagation of the catalytic chain was maintained by the cross-reaction 4 only. In the present paper, we report an electrode-catalyzed substitution reaction for a system in which both electrode reactions 1 and 3 are electrochemically fully reversible and the catalytic chain is initiated by a reduction process.

Experimental

Chemicals

Tetrahydrofuran (Merck) was used throughout as solvent after purification using the "ketyl method", i.e. boiling with metallic sodium and benzophenone [5,6]. Tetrabutylammonium hexafluorophosphate (Fluka), dried in vacuo at 350 K, was used as the supporting electrolyte (0.1 *M*).

Synthesis of $M(CO)_4bipy$ complexes

The tungsten compound was prepared by a modified method of Wrighton [7]: 780 mg of $W(CO)_6$ (Fluka) and 350 mg of bipyridine (GFS Chem. Company) in 100 ml of toluene were irradiated by a mercury lamp in a glass vessel under argon atmosphere. The directly formed crystals of $W(CO)_4$bipy were washed with petroleum ether and dried in vacuo. Yield 46%.

Chromium and molybdenum complexes were prepared by boiling a toluene solution of the corresponding hexacarbonyl and bipyridine under reflux for 1.5 h. The following procedure was identical with that for the tungsten species.

Chemical preparation of $M(CO)_3PPh_3bipy$ complexes

Stoichiometric quantities of $M(CO)_4$bipy and triphenylphosphine (Merck) were heated in xylene solution under reflux in argon atmosphere for 2 h. Afterwards, the reaction mixture was cooled to room temperature and the crystals formed were separated, washed with several portions of n-heptane, and dried in vacuo. Yield, ~ 90%.

All the prepared complexes were identified by IR and UV-VIS spectra. The IR spectra of our product were almost identical to those described for *fac*-$M(CO)_3PPh_3$bipy complexes [8] and indicate that the compound formed is a *fac*-isomer.

Electrochemical preparation of $M(CO)_3PPh_3bipy$

The typical procedure for the synthesis of $M(CO)_3PPh_3$bipy using electrode catalysis will be described for the molybdenum species: 0.15 mmol of $M(CO)_4$bipy and 0.45 mmol of triphenylphosphine were added to 15 ml of 0.1 *M* Bu_4NPF_6 in THF solution and electrolyzed under argon atmosphere with exclusion of direct illumination.

The potential of the mercury pool electrode was kept potentiostatically at −1.55 V (SCE). At the same time, the charge passed through the cell was measured. The progress of the electrolysis was monitored by dp-polarography as well as by IR spectra. In about 1 h the conversion of $Mo(CO)_4$bipy into $Mo(CO)_3PPh_3$bipy was completed. The resultant solution was reduced by vacuum-distillation to about half of the original volume and diluted with benzene. After standing for about 30 min, the precipitated supporting electrolyte was filtered off and the solution evaporated to dryness. The residue was washed with four portions of n-pentane and dried in vacuo. The remaining crystals were shown to be identical to $Mo(CO)_3PPh_3$bipy prepared by the chemical method, i.e. the compound formed electrochemically is also a *fac*-isomer. Yield 95%.

TABLE 1

Dp-PEAK POTENTIALS OF THE ONE-ELECTRON REDUCTION STEPS OF M(CO)$_3$Lbipy IN THF (0.1 *M* Bu_4NPF_6) IN V vs. SCE

M	L	1st reduction		2nd reduction	
		E_1°	E_2°	E_1°	E_2°
Cr	CO	−1.61		−2.16	
	PPh$_3$		−1.73		−2.26
Mo	CO	−1.53		−2.10	
	PPh$_3$		−1.64		−2.21
W	CO	−1.45		−2.02	
	PPh$_3$		−1.59		−2.19

Electrochemical measurements and instrumentation

In all the electrochemical measurements, a three-electrode system was used. The working electrode was a dropping mercury electrode (t_1 2 s) in dc- and dp-polarographic experiments, and a mercury pool electrode (7 cm^2) in potential-controlled exhaustive electrolysis. As the auxiliary electrode, Pt-wire was used in polarographic experiments and a graphite rod in exhaustive electrolysis. An aqueous saturated calomel electrode was used as the reference electrode. The aqueous and non-aqueous parts of the cell were separated by a bridge containing 0.1 *M* Bu_4NPF_6 in THF. All measurements were made in a modified electrochemical cell described previously [6]. To minimize the residual water content, freshly activated alumina (Merck) was added to all the solutions investigated. All transfer of solutions and electrolysis were carried out in argon atmosphere.

Dc- and dp-polarographic * measurements as well as slow cyclic voltammetry (scan rate < 200 mV s^{-1}) were performed using a PA 3 Polarographic analyzer (Laboratorní přístroje, Prague). Dp-polarograms were registered with a modulation amplitude of 12.5 mV. Potentiostatic control of the electrolysis was carried out using a specially designed potentiostat developed in the Heyrovský Institute. For coulometric measurements, an Amel Integrator 558 was used. Fast Fourier Transform Faradaic Admittance (FFTFA) measurements were performed using apparatus described previously [9]. UV-VIS spectra were measured on a Cary 17D spectrometer; IR spectra on a Nicolett MX 1-N spectrometer. EPR spectra were recorded using a Varian E4 spectrometer.

Results

The polarographic behaviour of M(CO)$_4$bipy (M = Cr, Mo, W) in dimethoxyethane [10,11] and acetonitrile [12] was briefly described previously. That of tributylphosphine derivatives of molybdenum species in dimethylformamide is reported in [13].

The behaviour in THF is essentially the same as in other solvents: there are two reduction steps, the dp-polarographic potentials of which are summarized in Table 1. Oxidation processes were also observed for all the species investigated and their analysis will be reported in detail elsewhere.

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* dc- stands for direct current and dp- for differential pulse polarography.

TABLE 2

PREPARATION OF $M(CO)_3PPh_3bipy$ BY THE ELECTRODE-CATALYZED SUBSTITUTION REACTION IN THF

M	Number of equivalents PPh_3	T [b] (K)	n [c] (n_{app})	Composition of final solution [a]	
				$M(CO)_4bipy^-$	$M(CO)_3PPh_3bipy$
Cr	–	291	1.25	0.7_5	–
	–	260	1.09	0.9	–
	3	291	0.75	0	0.6_5
	3	260	0.24	0	0.8_5
Mo	–	291	1.1	0.9	–
	–	260	1.01	1.0	–
	3	291	0.2	0	0.9_5
	3	260	0.38	0.2_5	0.7_5
W	–	291	1.07	0.9_5	–
	–	260	1.02	1.0	–
	3	291	0.23	0	0.9_5
	3	260	0.50	0.4_5	0.5_5

[a] Molar ratio of products identified by IR and/or UV-VIS spectra and dc-, dp-polarography. [b] Temperature of solutions. [c] Electron number, in F mol^{-1}, consumed for total conversion.

The first reduction step is fully reversible, both electrochemically and chemically. The second reduction step is electrochemically reversible, but chemically irreversible as shown by Kalousek polarography or cyclic voltammetry (20 V s^{-1}) at lower temperatures.

The one-electron primary products have been identified, by EPR and IR spectroscopy, as radical-anions, in agreement with previously published data [11,13]. Although Kalousek polarography, cyclic voltammetry and preliminary FFTFA measurements have shown no indication of a follow-up reaction of the primarily formed radical, the detailed analysis of the exhaustive electrolysis measurements combined with IR and EPR spectra indicates the existence of slow side-reactions to the main electrolytic process. This side-reaction is most pronounced for chromium compounds. Even in this case, however, the side-reaction does not exceed 10% of the total conversion (see Table 2).

As can be seen by inspection of the data in Table 1, the redox potentials of both groups of complexes, i.e. $M(CO)_4bipy$ and $M(CO)_3PPh_3bipy$, fulfill the basic condition necessary for the operation of an electrode-catalyzed substitution reaction, i.e.

$$E^\circ(M(CO)_4bipy) > E^\circ(M(CO)_3PPh_3bipy)$$

so that the formation of phosphine-substituted species could be expected to follow the reduction of $M(CO)_4bipy$ in the presence of triphenylphosphine.

Solutions containing $M(CO)_4bipy$ species and an excess of triphenylphosphine do not exhibit any observable change in their electrochemical behaviour when dc-, dp- or Kalousek-polarography or cyclic voltammetry techniques are used. These results point to the conclusion that the reaction between the radical-anions formed primarily and phosphine proceeds, if at all, at a rate much slower than would be required for the time scale of these methods. Furthermore, solutions containing $M(CO)_4bipy$

and triphenylphosphine do not show any time change of the polarographic behaviour or UV-VIS or IR spectra, so that direct substitution (reaction A → D in Scheme 1) also does not proceed under the given experimental conditions (290 K, reduced illumination, 60 min time of observation).

On the other hand, an essential change in the nature of the products is observed when large-scale electrolysis of $M(CO)_4$bipy is carried out in the presence of triphenylphosphine. When the potential of the working electrode was set about 25 mV positive with respect to the dp-polarographic peak potential of $M(CO)_4$bipy, the final product formed was shown by dp-polarography, UV-VIS and IR spectra (see Figs. 1 and 2) to be the phosphine-substituted species, $M(CO)_3PPh_3$bipy. For molybdenum and tungsten species at room temperature, an almost complete conversion is observed, the charge consumed for this conversion being considerably lower than 1 F mol^{-1} (see Table 2), i.e. the process observed is a true electrode-catalyzed substitution reaction. With the corresponding chromium species, the conversion at room temperature is considerably smaller, the charge consumed being, at the same time, higher than that corresponding to the degree of conversion (see Table 2). In this case, the side-reactions mentioned above obviously operate to a great extent

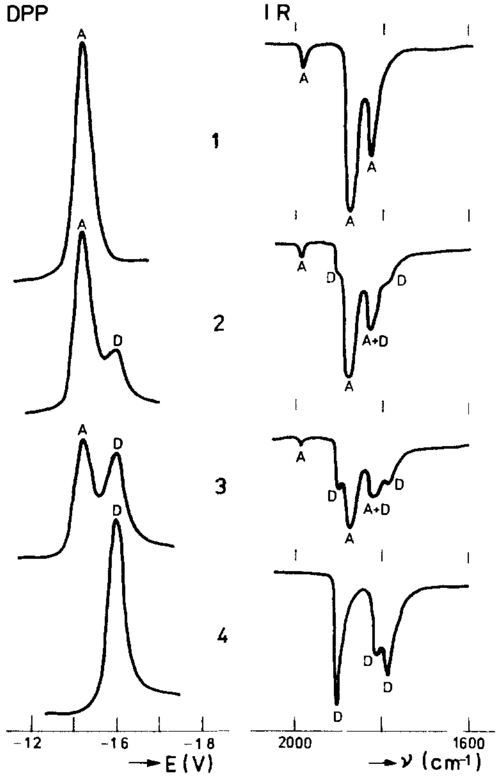

Fig. 1. Electrode-catalyzed preparation of $W(CO)_3PPh_3$bipy as monitored by dp-polarography and IR spectra in THF at T 291 K. (1) 0.01 M $W(CO)_4$bipy, 0.03 M PPh_3; (2) after partial reduction (n_{app} 0.07 F mol^{-1}); (3) solution 2 10 min after interruption of electrolysis; (4) complete conversion (n 0.23 F mol^{-1}). A, dp-peak and CO-bands of $W(CO)_4$bipy; D, dp-peak and CO-bands of $W(CO)_3PPh_3$bipy.

even in the presence of phosphine. However, decrease of the temperature to 260 K suppresses the side-reactions and the catalytic chain operates in an almost clean way with a conversion of about 85%.

The catalysis by the electrode was proved by applying a small electrolytic pulse (under potentiostatic control, a charge corresponding to 0.05 F mol^{-1} was injected) to the system and following the subsequent reaction. As can be seen from Fig. 1, the electrolytic pulse is sufficient to trigger the catalytic chain, and after interruption of the current flow, the conversion of $\mathrm{M(CO)_4bipy}$ to $\mathrm{M(CO)_3PPh_3bipy}$ (M = Mo, W) continues. This finding also gives unambiguous proof that the cross-reaction plays an essential role in propagation of the catalytic chain. For chromium, the same results are observed only at low temperature (260 K).

These results point to the following mechanism for the process:

$$\mathrm{M(CO)_4bipy} + \mathrm{e} \overset{E_1^\circ}{\rightleftharpoons} \mathrm{M(CO)_4bipy^{\cdot-}} \tag{5}$$

$$\mathrm{M(CO)_4bipy^{\cdot-}} + \mathrm{PPh_3} \overset{k_1}{\rightarrow} \mathrm{M(CO)_3PPh_3bipy^{\cdot-}} + \mathrm{CO} \tag{6}$$

$$\mathrm{M(CO)_3PPh_3bipy^{\cdot-}} - \mathrm{e} \overset{E_2^\circ}{\rightleftharpoons} \mathrm{M(CO)_3PPh_3bipy} \tag{7}$$

$$\mathrm{M(CO)_4bipy} + \mathrm{M(CO)_3PPh_3bipy^{\cdot-}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{M(CO)_4bipy^{\cdot-}} + \mathrm{M(CO)_3PPh_3bipy} \tag{8}$$

Due to the slowness of chemical follow-up reactions, reaction 7 seems to play only a minor role in the catalytic cycle.

To establish which of the reactions is rate-determining, EPR and IR spectra of the system were followed after application of a short electrolytic pulse. Immediately after the pulse, the EPR spectrum observed was identical to that of the $\mathrm{Mo(CO)_4bipy^{\cdot-}}$

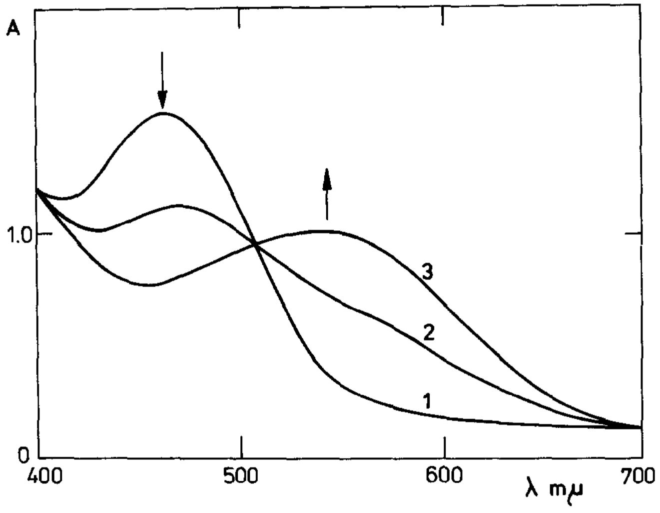

Fig. 2. Changes in the composition of the solution during the electrode-catalyzed preparation of $\mathrm{Mo(CO)_3PPh_3bipy}$ as monitored by UV-VIS spectra. (1) 5×10^{-3} *M* $\mathrm{Mo(CO)_4bipy}$, 1.5×10^{-2} *M* $\mathrm{PPh_3}$; (2) after partial reduction (n_{app} 0.1 F mol^{-1}); (3) solution 2 20 min after interruption of electrolysis.

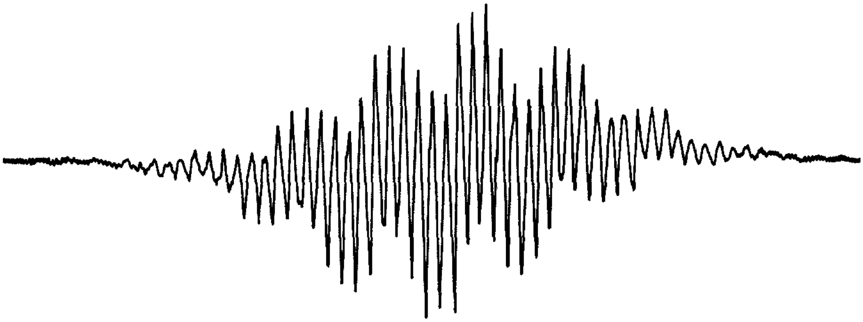

Fig. 3. EPR spectrum of $Mo(CO)_4bipy^-$ in THF at 291 K ($g = 2.004$; hyperfine coupling constants (mT): $a_N = 0.35$; $a_H = 0.12$; 0.10; 0.42; 0.07; $a_{Mo} = 0.16$)

radical anion (Fig. 3). No signal corresponding to the $Mo(CO)_3PPh_3bipy^-$ radical anion appeared after the system was allowed to stand for 20 min. At the same time, the signal of $Mo(CO)_4bipy^-$ was constant, whereas the IR spectra had shown an increase of the concentration of the final product, $Mo(CO)_4PPh_3bipy$, and a concentration decrease of the starting reactant, $Mo(CO)_4bipy$. This experiment proves that the slow rate-determining step in the whole catalytic chain is reaction 6, i.e. substitution of $Mo(CO)_4bipy^-$ by triphenylphosphine, while cross-reaction 8 is much faster. This ratio of rates of consecutive reactions 6 and 8 keeps the concentration of the intermediate $Mo(CO)_3PPh_3bipy^-$ very low, whereas reaction 8, in the given low-conversion stage, keeps the concentration of $Mo(CO)_4bipy^-$ constant. The same behaviour is also observed for the analogous chromium and tungsten systems.

When the electrolysis was carried out continuously at low temperature, the rate of reaction 6 decreased to such an extent that a larger amount of $M(CO)_4bipy^-$ was formed by electrolysis than could be removed by reaction 6. As the EPR spectra show, the concentration of the primary radical anion increases with time during electrolysis at low temperature. The amount of primary radical anion left immediately after the interruption of the current of exhaustive electrolysis, i.e. after total removal of reactant $M(CO)_4bipy$, is proportional to the rate of reaction 6. The data given in Table 2 indicate the relative order of k_1 (reaction 6 being assumed to be irreversible), $k_{Cr} > k_{Mo} > k_W$.

Discussion

The Redox Orbital Concept [14,15] can be used to discuss changes in the chemical behaviour of a species after its overall number of electrons has been changed. Any increase in the number of anti-bonding electrons directly labilizes that part of the molecule over which the redox orbital is localized. Induced electron density shifts or strong intramolecular interaction (through bond or through space) might exert an indirect labilizing effect. In extreme situation, a spontaneous fragmentation (concerted or follow-up to the redox change) could take place. In most cases, however, merely a latent labilization arises which is put into action only under the influence of another reactant, the reaction with which would reduce the intrinsic instability of the species formed by the redox process.

The reduction of $M(CO)_4$bipy results in an almost complete localization of the extra electron onto the bipyridine ligand [13,16]. Nevertheless, labilization of the coordination sphere is observed, a ligand in the *cis*-position to that which carries the dominant change in the overall number of electrons being labilized. The labilizing effect thus has to be connected with intramolecular transmission of the influence of extra charge on the bipyridine ligand. Insight into the mechanism of the labilization can be obtained by inspecting the properties of the radical anions formed.

Dessy [11] deduced from his study of the IR spectra of $M(CO)_4$bipy and of the corresponding radical anions that a transmission of charge in the radical anion occurs primarily by a σ-effect. On the other hand, an enhancement of the Resonance-Raman intensity of the stretching mode of carbonyls *cis* to bipyridine is observed when $M(CO)_4$bipy complexes are excited within the lowest MLCT band [17]. This enhancement is explained as being due primarily to through-space electron density transfer from bipyridine anion in the excited state on the CO groups in the *cis*-position.

The mechanism of the observed labilizing effect resulting after the electron is accepted dominantly by the bipyridine ligand is most easily understood in terms of partial delocalization of the electron density to the CO ligands *cis* to bipyridine obviously via the through-space interaction. This explanation is analogous to that used to interpret the Resonance-Raman enhancement [17] even though it has to be kept in mind that there is not a complete analogy between the fully reduced state obtained electrochemically and the spectroscopic MLCT state. The observed order of rate constants k_1 fully agrees with the order of the extent of Raman enhancement and thus supports the conclusion on the nature of the labilizing mechanism. The through-space interaction is rather weak and this is also in agreement with the rather low rates observed for the substitution of the *cis*-CO group.

Furthermore, photo-substitution of the *cis*-CO group by phosphine or phosphite was observed following the MLCT excitation of the complex [17] and resulted in products identical with those observed electrochemically. Although, in this case, great care has to be taken when comparing the behaviour of the spectroscopic state (existence of an electron hole on the metal) with fully reduced states, one finds, however, a striking similarity between the rates of substitution in radical anions and the quantum yields observed photochemically.

The rather low rate of reaction 6 is thus connected with the indirect nature of the labilizing effect. A similar indirect labilization was observed recently for the electrode-catalyzed substitution of $R_2C_2Co_2(CO)_6$ [18,19]. In the latter case, the electron is accepted into a dominantly metal-localized orbital, the overall charge-change labilizing one CO ligand. Darchen et al. [20] described CO labilization following one-electron reduction of a tri-iron cluster compound, the charge change being primarily localized in the cluster unit. In these systems, the substitution of the primary radical anion is relatively slow, but still fast enough to be observed on the time scale of cyclic voltammetry. Obviously, the intramolecular transmission of charge change in these cases is much more effective than in our system, which does not show any chemical follow-up reaction on the time scale of dc-polarography or cyclic voltammetry.

The cross-reaction 8 can be looked upon as an electron-transfer process between two organic-conjugated species, i.e. coordinated bipyridine and coordinated bipyridine anion radical. Reactions of such compounds usually proceed very rapidly as there is essentially no internal hindrance to the electron transfer, the π-systems of the redox centres being capable of extensive interaction. The experimental results indicate that this homogeneous electron-transfer process plays the dominant role in the propagation of the catalytic reaction.

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