Voltammetry of carbocations stabilized by coordination with tetrahedral molybdenum- and tungsten-carbon clusters. $[Cp_2M_2(CO)_4\text{-}\mu\text{-}\eta^2{:}\eta^3\text{-}(HCCCR^1R^2)]^+BF_4^-$ (M = Mo, W; R^1, R^2 = H, Me, and Pr^i) complexes

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The electrochemical reduction of the carbocationic complexes $[Cp_2M_2(CO)_4\text{-}\mu\text{-}\eta^2{:}\eta^3\text{-}(HCCCR^1R^2)]^+BF_4^-$, where M/$R^1$, R^2 = Mo/H, H (1^+), Mo/H, Me (2^+), Mo/Me, Me (3^+), Mo/H, Pr^i (4^+), has been studied by polarography and cyclic voltammetry on a Hg-electrode in THF solution. It has been suggested that carbocationic center-directed reversible two-electron reduction of 1^+—4^+ takes place according to an *ECE*-mechanism and results in the carbanionic complexes $[Cp_2M_2(CO)_4\text{-}\mu\text{-}\eta^2{:}\eta^3\text{-}(HCCCR^1R^2)]$ (1^-—4^-) as final products *via* carbon-centered radicals as intermediates. Anions 1^-—4^- are capable of irreversible two-electron reduction at more negative potentials or protonation resulting in their transformation into the corresponding acetylene complexes $[Cp_2M_2(CO)_4(HCCCHR^1R^2)]$, which are also capable of irreversible two-electron reduction. Anions 1^-—4^- and their protonated forms are reduced with cleavage of the Mo—Mo bond. The reduction pathways of complexes 1^+, 2^+, and 4^+ with C—H bonds at the carbon atom of the carbocationic center are different on a Pt-electrode. It is suggested that this difference is due to the abstraction of a H-atom from the intermediate radical species by platinum.

Key words: carbocationic complexes; stabilization of carbocations; polarography; cyclic voltammetry.

The studies of metal-stabilized carbocations, which at first were almost exclusively limited to metallocenyl or semisandwich systems,[1] were then extended to metal-carbon clusters Co_3C,[2] Co_2C_2,[3] Mo_2C_2,[4,5] W_2C_2,[4,6] $CoMoC_2$, and Co_2C_2.[7] Dicarbon systems are traditionally related to binuclear acetylene complexes, and cations based on them are considered to be binuclear complexes containing a coordinate substituted or nonsubstituted propargyl ligand. Among the systems listed above, cations of the dimolybdenum series have been better studied: ^{13}C and ^1H NMR spectra, dynamic behavior in solutions,[8] and thermodynamic stability[9] are known for them, and X-ray analysis has also been performed.[9,10]

Among the metal-stabilized carbocations known at this time, the cations of the molybdenum series are the ones for which the influence of the nature (primary, secondary, or ternary) of the carbocation center on the C^+—metal distance was first established.[9,10] This distance is determined by the degree of interaction between the carbocation center and the metal and can serve as a structural characteristic of the stability of these cations. The stability of the compounds considered is predominantly depend on by the donor properties of the organometallic fragment and not by the nature of the substituents at the carbocation center, which follows from the comparison of the structural data on the stability of dimolybdenum carbocationic complexes; the shorter the C^+—metal distance, which decreases in the series: ternary > secondary > primary, the more stable the complex.[9] Perhaps direct or indirect arguments in favor of this assertion can be obtained by an electrochemical analysis of the dimolybdenum cations. In addition, if the reduction of these complexes is directed to the carbocation center, one may expect it to produce the corresponding carbon-centered radical or anionic complexes, whose stability, reactivity, and acid-base properties are scantily known and, therefore, are of doubtless interest.

In the present work, polarography and cyclic voltammetry (CVA) in THF solutions were used to study the reduction of carbocationic complexes $[Cp_2M_2(CO)_4\text{-}\mu\text{-}\eta^2{:}\eta^3\text{-}(HCCCR^1R^2)]^+BF_4^-$, where

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M/R^1,R^2 = Mo/H,H (**1^+**), Mo/H,Me (**2^+**), Mo/Me,Me (**3^+**), Mo/H,Pr^i (**4^+**), W/H,H (**$1a^+$**), W/H,Me (**$2a^+$**), and W/Me,Me (**$3a^+$**) as well as methylacetylene complex [$Cp_2M_2(CO)_4$-μ-η^2:η^2-(HCCMe)] (**5**).

Results and Discussion

The waves A are observed on the polarograms of **1^+**—**4^+** (Fig. 1) and **$1a^+$**—**$3a^+$** in the −0.5 V region of potentials. The two-electron character of these waves follows from the comparison with the height of the one-electron reduction wave of bis(diphenyl)chrome or with the additive height of the two one-electron reduction waves of $Cp_2Mo_2(CO)_4$[11] under other equal conditions. The A waves are diffusional because the limiting current of these waves (i_d) depends linearly on the height of the mercury column. The polarographic criterion of reversibility ($S = dE/d\lg(i/i_d - i)$) indicates the reversible or quasireversible character of these waves (Table 1). The reduction potentials of the complexes found by polarography ($E_{1/2}$) or CVA [$E_{1/2} = (E_c + E_a)/2$] are listed in Table 1.

We have no data on the quantum chemical orbital consideration of complexes of the **1^+**—**4^+** type, however, the A waves described above most likely relate to the carbocation center-directed reduction of the complexes. Actually, the potentials of these waves are almost independent of the nature of the metal (see Table 1). In addition, the reduction of the acetylene and methylacetylene (**5**) complexes, similar in structure to **1^+**—**4^+** but without carbocation center, occurs at more negative (by 1.3 V) potentials (Table 2), is irreversible, and is accompanied by Mo—Mo bond cleavage[11] (see below). One may propose that the absence of a strong Mo—C^+ interaction in **1^+**—**4^+** results in the existence of two sets of weakly interacting MO, one of which relates to the Mo_2C_2 fragment and another to the carbocation center. The redox-orbital of the carbocation center (the orbital to which the electron transfers) is lower than the LUMO of the Mo_2C_2 fragment. This fact causes the carbocationic center-directed reduction of **1^+**—**4^+**. In the case

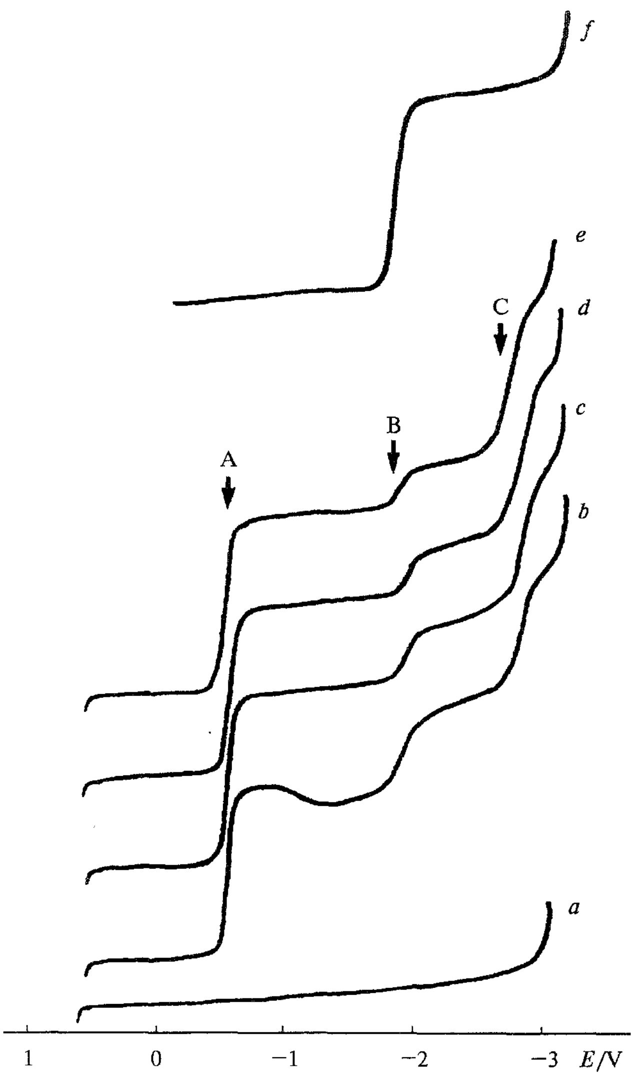


Fig. 1. Polarograms of $5 \cdot 10^{-4}$ *M* solutions of [$Cp_2Mo_2(CO)_4(HCCCR^1R^2)$]$^+BF_4^-$ (*b, c, d, e*) and [$Cp_2Mo_2(CO)_4$(HCCMe)] (*f*) complexes in THF/0.1 *M* Bu_4NBF_4 at 0 °C; SCE as reference electrode: base electrolyte (*a*); **1^+** (*b*); **2^+** (*c*); **3^+** (*d*); **4^+** (*e*).

Table 1. ^{13}C NMR data, constants of substituents (R^1, R^2), and polarographic parameters of two-electron A waves of the reduction of [$Cp_2M_2(CO)_4(HCCCR^1R^2)$]$^+$ cations ($C_0 = 5 \cdot 10^{-4}$ *M*) in THF/0.1 *M* Bu_4NBF_4 at 0 °C. SCE as reference electrode

Complex	M	R^1, R^2	$-\Sigma\sigma^*$	$-\Sigma E_s^0$	$E_{1/2}$/V	S^*/mV	δ $R^1R^2C^+$
1^+	Mo	H, H	0	0	−0.450	36	+75.37
2^+	Mo	H, Me	0.49	0.25	−0.465	35	+101.15
3^+	Mo	Me, Me	0.98	0.50	−0.490	34	+148.68
4^+	Mo	H, Pr^i	0.68	1.10	−0.530	40	
$1a^+$	W	H, H			−0.490	35	+72.72
$2a^+$	W	H, Me			−0.505	32	+99.13
$3a^+$	W	Me, Me			−0.500	35	+153.56

* $dE/d\lg(i/i_d - i)$.

Table 2. Polarographic parameters of the reduction waves for $[Cp_2Mo_2(CO)_4(HCCCR^1R^2)]^+$ cations and related complexes ($C_0 = 5 \cdot 10^{-4}$ *M*) in THF/0.1 *M* Bu_4NBF_4 at 0 °C. SCA as reference electrode

Complex	$E_{1/2}^A$/V	i_d^A/μA	$E_{1/2}^B$/V	i_d^B/μA	$E_{1/2}^C$/V	i_d^C/μA
1^+	−0.45*	7.4	−1.85	3.1	−2.71	4.6
2^+	−0.46*	7.7	−1.88	2.4	−2.74	5.2
3^+	−0.49*	7.8	−1.88	2.0	−2.82	5.7
4^+	−0.53*	7.4	−1.90	1.8	−2.79	5.8
5	−1.81	8.2				
$Cp_2Mo_2(CO)_4(C_2H_2)$	−1.84	8.3				
$Cp_2W_2(CO)_4(C_2H_2)$	−1.95	8.4				

* Reversible waves.

of $\mathbf{1a}^+$—$\mathbf{3a}^+$, the reduction is also center-directed because, first, these complexes are reduced almost at the same potentials as their dimolybdenum analogs, and, secondly, the reduction of $[Cp_2W_2(CO)_4(C_2H_2)]$ without a carbocation center occurs at more negative (by 1.45 V) potentials (see Table 2).

The collection of the data obtained allows us to propose that the reversible two-electron reduction of $\mathbf{1}^+$—$\mathbf{4}^+$ and $\mathbf{1a}^+$—$\mathbf{3a}^+$ results in the carbon-centered $[Cp_2M_2(CO)_4(HCCCR^1R^2)]^-$ anions ($\mathbf{1}^-$—$\mathbf{4}^-$, $\mathbf{1a}^-$—$\mathbf{3a}^-$). Basically, the reduction can occurs *via* both *EE*- and *ECE*-schemes (*E* is the electron transfer stage, *C* is the chemical stage) with the intermediate formation of the corresponding radical (or radical-like) particles $[Cp_2M_2(CO)_4(HCCCR^1R^2)]^\cdot$ ($\mathbf{1}^\cdot$—$\mathbf{4}^\cdot$; $\mathbf{1a}^\cdot$—$\mathbf{3a}^\cdot$). The *EE*-scheme results in the reduction of radicals ($R^\cdot$) to anions (R^-) at potentials not more than 150 mV more negative than $E^0(R^+/R^\cdot)$. In this case, the slope of the wave A(*S*) is close to 30—42 mV.[13—17] In the *ECE*-scheme the *C* stage results in the transformation of radicals into particles that are more easily reduced than R^+. The slope of the A wave in this case is 30 mV.[13,14] The chemical transformation of the radical in the *C* stage, *e.g.*, its solvation, structural, or conformational changes due to the change in the bond lengths, angles, *etc.*, is reversible and fast in the time scale of the CVA method, because only in this case can the reduction be electrochemically reversible. Thus, in any considered scheme, the *S* or ΔE_r values ($\Delta E_r = E_c - E_a$ is the criterion of reversibility for the CVA method, where E_c, E_a are the potentials of the cathodic and anodic peaks, respectively) for $(\mathbf{1}$—$\mathbf{4})^{+/\cdot}$ or $(\mathbf{1a}$—$\mathbf{3a})^{+/\cdot}$ are close to 30—40 mV,[13—17] which corroborates the experimental data (see Table 1). In our opinion the *ECE* scheme should be preferred, because the difference $E^0(R^+/R^\cdot) - E^0(R^\cdot/R^-)$ is 1.5—2 V for benzyl type compounds,[18] and therefore two one-electron waves would be observed on polarograms for the *EE*- (or *EEC*-) scheme.

The influence of the R^1 and R^2 substituents on the reduction potentials of $\mathbf{1}^+$—$\mathbf{4}^+$ complexes (wave A) was studied in order to qualitatively estimate the contribution of the alkyl substituents at the carbenium center as well as the M_2C_2 fragment to the delocalization of the carbocation center positive charge. For this purpose, the two-parameter Taft equation with purely inductive Taft constants σ^* and steric Palm constants $E^0{}_s$ was chosen as the correlation equation. This equation is usually used for the analysis of aliphatic compounds with direct spatial interaction between the substituents and the reaction center

$$E^R = E^H + \rho^*\Sigma\sigma^* + \delta\Sigma E_s^0,$$

where E^R and E^H are the $E_{1/2}$ values for complexes containing and not containing alkyl substituents, respectively, and ρ^* and δ are the inductive and steric constants, respectively.[13] The values obtained for aliphatic substrates were used for ρ^* and δ.[19] It can be seen from Fig. 2, *a* that the electronic effects of the substituents have almost no effect on the reduction potentials ($\rho^* = 0.0024$; $\delta = 0.071$), but the influence of steric effects is predominant (Fig. 2, *b*). In other words, the inductive effects of the substituents do not play a noticeable role in the reduction process, and the potentials are satisfactorily described by the one-parameter equation

$$E^R = E^H + \delta\Sigma E_s^0$$

with correlation coefficient $R^2 = 0.997$ and $\delta = 0.074$. The positive sign of δ indicates that the increase in steric hindrances makes the reduction difficult.

The absence of the inductive effect of the substituents on the reduction potentials of complexes $\mathbf{1}^+$—$\mathbf{4}^+$ indicates that the delocalization of the positive charge of the carbocation center occurs mainly with the participation of the M_2C_2 fragment. In principle, the predominant influence of the steric effects of the substituents may be indicative of steric hindrances to the interaction between the carbocation center and the M_2C_2 fragment created by the substituents. The values of the Mo—C^+ distances, 2.439 and 2.75 Å for $\mathbf{1}^+$ and $\mathbf{3}^+$, respectively,[9] can serve as evidence. Steric hindrances created by the substituents to the transfer of an electron from the electrode to the substrate also cannot be excluded. The influence of these effects on the reduction potentials is the opposite: steric hindrances must make the electron transfer difficult but must increase the positive charge at the carbocation center due to "exclusion" of the participa-

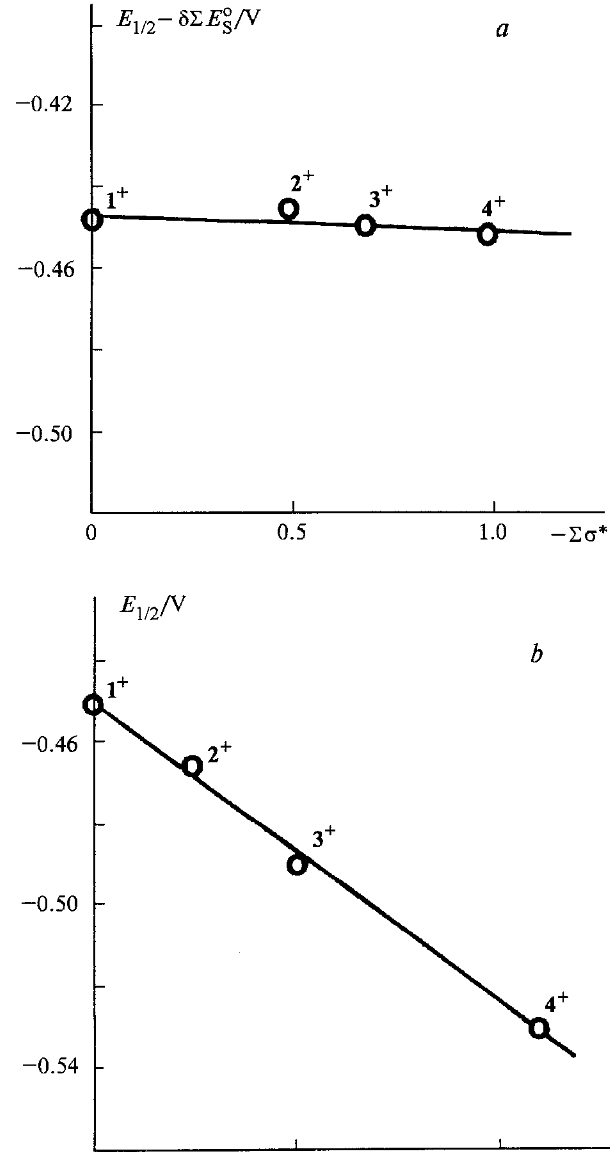


Fig. 2. Dependence of $E_{1/2}$ of the A wave for 1^+—4^+ on the inductive and steric constants (*a*) and only the steric constants (*b*) of the substituents. Numeration of points corresponds to that of the compounds in Table 1.

tion of the M_2C_2 fragment in the charge delocalization and, hence, facilitate the reduction. Therefore, the observed shift of the reduction potentials to the negative region as the steric stress of the reaction center increases (see Fig. 2) counts in favor of the influence of the substituent on the electron transfer. This influence may be determined, for example, by the increase in the reorganization energy when going from a primary to a ternary carbocation.

The anionic complexes $[Cp_2M_2(CO)_4(HCCCR^1R^2)]^-$ generated by the two-electron reduction of the corresponding original cations seem to be sufficiently strong bases and are protonated either by trace amounts of moisture in the solvent or by the Bu_4N^+ cation as the proton donor (see, *e.g.*, Ref. 6). This explains the smaller height of the corresponding anodic responses on the cyclic voltammograms of $\mathbf{1}^+$—$\mathbf{4}^+$ at room temperature, that can be seen in Fig. 2, *a* for $\mathbf{3}^+$. The anions generated become stable in the time scale of CVA (the existence of cathodic and anodic peaks equal in height on the cyclic voltammograms) only at low temperatures (see Fig. 2, *a*). The attempt to study the protonation of electrogenerated anions by water failed, because the original cationic complexes react with it. The reactivity of the electrogenerated anions towards other proton donors was not studied.

The different behavior of the complexes studied on Hg- and Pt-electrodes is also of interest (Fig. 3). The form of the cyclic voltammograms and reduction potentials are almost the same at both electrodes for the ternary carbocationic complex $\mathbf{3}^+$, whereas they differ considerably for $\mathbf{1}^+$, $\mathbf{2}^+$, and 4^+, which contain C—H bonds at the carbon atom of the carbocation center. This is shown in Fig. 3, *b*, *c* for the example of $\mathbf{4}^+$ (the different heights of the peaks are caused by the different areas of the Hg- and Pt-electrodes). The influence of the electrode material on the direction of the electrode reactions has been discussed previously.[20,21] For the complexes studied, this problem demands a special consideration that is not a subject of this work. Nevertheless, it can be noted that, as it has been shown,[21] platinum tends to be an acceptor of H atoms from potential donors of H atoms. In principle, the radical intermediates $\mathbf{1}^\cdot$, $\mathbf{2}^\cdot$, and $\mathbf{4}^\cdot$ are such donors for the corresponding $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{4}^+$ complexes. One may propose that platinum detaches the H atom from them in the stage of the generation of these intermediates. Perhaps the explanation suggested is not the only one possible, however, in any case, the reduction of $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{4}^+$ on the Pt-electrode is irreversible and the $E_{1/2}$ values differ from those obtained for the Hg-electrode due to the participation of the electrode material in the electrode reaction. Thus, the voltammograms at the Hg-electrode reflect the real redox behavior of complexes $\mathbf{1}^+$—$\mathbf{4}^+$.

If the two-electron reduction of $\mathbf{1}^+$—$\mathbf{4}^+$ at the potentials of the A wave is accompanied by the formation of the carboanionic complexes $\mathbf{1}^-$—$\mathbf{4}^-$, which are partially protonated in the time scale of the electrochemical measurements, at least one of more cathodic waves (B and C) on the polarograms (see Fig. 1) must correspond to the reduction of the complexes $[Cp_2M_2(CO)_4(HCCCHR^1R^2)]$. Actually, it can be seen from Fig. 1, *b*, *f* and the data of Table 2 for $\mathbf{1}^+$ and the model methylacetylenic complex **5** that the values of $E_{1/2}$ of the B wave for $\mathbf{1}^+$ and of the single wave for **5** are close. (Some difference in the values of $E_{1/2}$ is due to the irreversible character of these waves, which results in a shift of $E_{1/2}$ of the wave to the region of cathodic potentials as the complex concentration, including near-

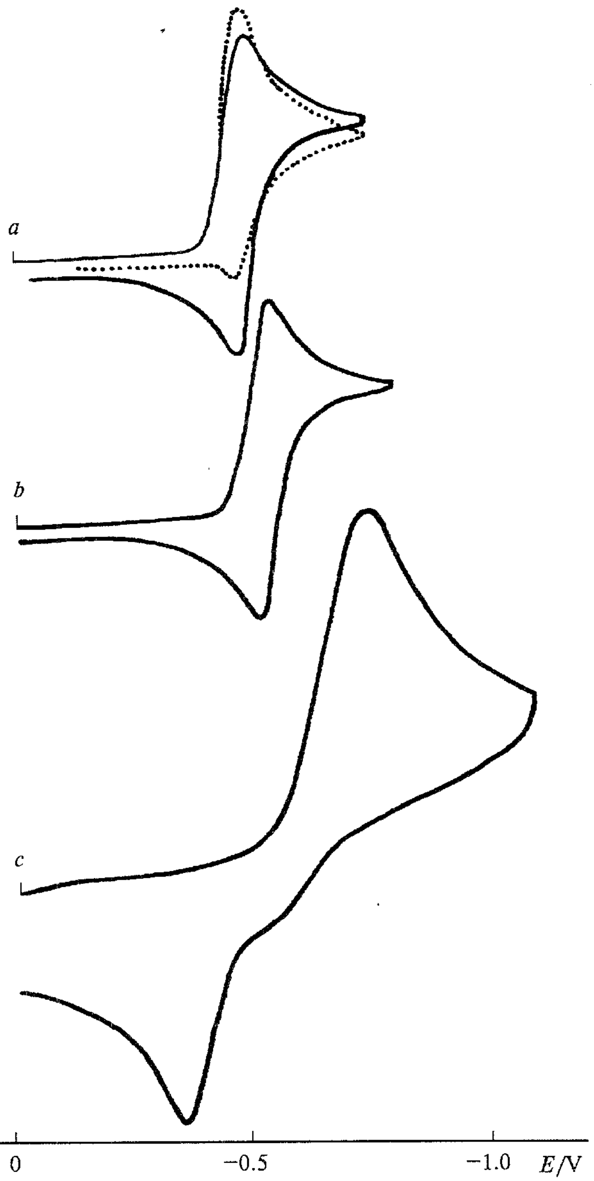
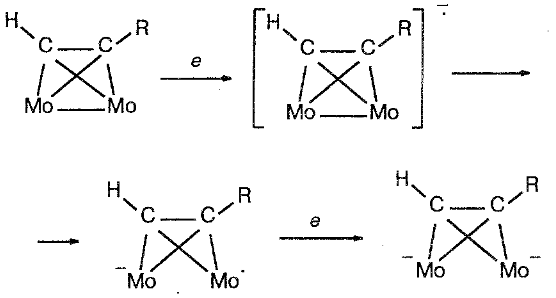


Fig. 3. Cyclic voltammograms of $5\cdot10^{-4}$ *M* solutions of $[Cp_2Mo_2(CO)_4(HCCCMe_2)]^+BF_4^-$ (3^+, *a*; dotted line at 20 °C) and $[Cp_2Mo_2(CO)_4(HCCCHPr^i)]^+BF_4^-$ (4^+, *b, c*) complexes in THF/0.1 *M* Bu_4NBF_4 on Pt- (*a, c*) and Hg-electrodes (*b*) at 0 °C and scanning velocity of potential 0.2 V s^{-1}. SCE as reference electrode.

electrode concentration decreases.) Complex **5** is irreversibly reduced by the two-electron transfer (the comparison with the height of the one-electron wave of the cation of bis(diphenyl)chrome) due to the transfer of an electron to the antibonding orbital of the Mo—Mo bond. The radical anion formed is unstable and is cleaved at the metal—metal bond with the subsequent transfer of the second electron to the radical center.

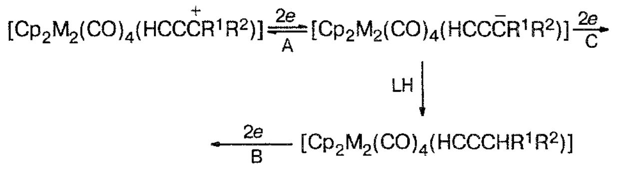


This *ECE*-mechanism is typical of the reduction of complexes with a single metal—metal bond and is realized, *e.g.*, for the reduction of $[CpMo(CO)_3]_2$.[12,22]

In this case, the third and the most cathodic wave on the polarograms for $\mathbf{1}^+$—$\mathbf{4}^+$ (see Fig. 1, Table 2) should be related to the two-electron reduction of the nonprotonated forms of the $\mathbf{1}^-$—$\mathbf{4}^-$ carbanions probably realized according to the *ECE*-scheme, which is similar to that for the deprotonated forms (see above). In fact, the total limiting current of the B and C waves equals the limiting current of the A wave; in addition, increasing the temperature to room temperature is accompanied by a decrease in the C wave due to the increase in the B wave, while the additive two-electron character of the B and C waves is retained. Of course, this analysis of the waves based only on the polarographic data should be treated with caution, however, another logical scheme is unlikely in our view.

The data obtained allows one to present the mechanism of the reduction of $\mathbf{1}^+$—$\mathbf{4}^+$ at the Hg-electrode as Scheme 1 (LH is the proton donor).

Scheme 1



$$[Cp_2M_2(CO)_4(HCC\overset{+}{C}R^1R^2)] \underset{A}{\overset{2e}{\rightleftharpoons}} [Cp_2M_2(CO)_4(HCC\overset{-}{C}R^1R^2)] \xrightarrow[C]{2e}$$

$$\downarrow LH$$

$$\xleftarrow[B]{2e} [Cp_2M_2(CO)_4(HCCCHR^1R^2)]$$

It should be mentioned in conclusion that in the analysis of the waves given above, it is of interest to use the increase in the limiting current of the C wave in the series $\mathbf{1}^+ < \mathbf{2}^+ < \mathbf{3}^+$ and the decrease in the limiting current of the B wave in the opposite sequence for the qualitative estimation of the kinetic basicity of the generated carbanionic complexes $\mathbf{1}^-$—$\mathbf{3}^-$. For such an approach, the basicity of the carbanions increases in the series $\mathbf{3}^- < \mathbf{2}^- < \mathbf{1}^-$, *i.e.*, in the same sequence as the height of the B wave. This wave (see Scheme 1) relates to the fraction of the protonated product formed within the lifetime of a drop. Of course, this suggestion needs to be experimentally verified.

The increase in the basicity of the electrogenerated carbanionic complexes in the series $\mathbf{3}^- < \mathbf{2}^- < \mathbf{1}^-$ is in indirect accord with the positive charge density at the carbocation center in the original cations. This follows from the values of the chemical shifts of the carbon atom of the carbocationic center[23] in the ^{13}C NMR spectra (see Table 2). In this case, the order of the change in the carbanion basicity is likely to be considered as a measure of the negative charge density at the carbanion center, which decreases in the same series as the basicity. This allows one to propose that the M_2C_2 fragment manifests donor properties towards the carbocationic/carbanionic center to a greater extent than acceptor properties.

Experimental

Tetrafluoroborates of cations $\mathbf{1}^+$—$\mathbf{4}^+$ and $\mathbf{1a}^+$—$\mathbf{3a}^+$ of the general formula $[Cp_2M_2(CO)_4(HCCCR^1R^2)]^+$ (M = Mo, W; R^1, R^2 = H, Me, Pr^i) were obtained according to the previously described procedure[4,5] including the cross-addition of $Cp_2M_2(CO)_4$ to the corresponding acetylenes $HC{\equiv}CCR^1R^2OH$ with the subsequent protonation of the adducts $[Cp_2M_2(CO)_4$-μ-$(HC{\equiv}CCR^1R^2OH)]$ with an ether solution of aqueous HBF_4 in CH_2Cl_2.

The units of a "PAR 370" electrochemical system were used for the electrochemical measurements in anhydrous THF preliminarily purified by the ketyl method: the solvent was distilled directly into a cell that had been evacuated and then filled with dry argon according to the previously described procedure.[21,24] A 0.1 *M* solution of Bu_4NBF_4 in THF was used as the base electrolyte. In order to remove trace amounts of moisture, a weighted sample of Bu_4NBF_4 was melted *in vacuo* immediately prior to the preparation of the solution of the base electrolyte. The low-temperature electrochemical measurements were performed while the electrochemical cell was cooled with a mixture of EtOH with liquid nitrogen in a Dewar flask.

A dropping Hg-electrode with forced detachment of the drop (the period of dropping was 1 s) was used as the working electrode for the polarographic measurements. "Hanging drop" Hg-electrode and Pt-disk (1 mm in diameter) stationary electrodes were used for cyclic voltammometry. A Pt-wire served as the accessory electrode. The measurements were performed with the compensation of ohmic losses by the method of positive feedback. All potentials are presented relative to an aqueous saturated calomel electrode (SCE). For this purpose, the potential of the reference electrode (Ag/AgCl/4 *M* aqueous LiCl), which was separated from the studied solution in the cell by a bridge filled with the solution of the base electrolyte, was referred to the potential of the redox-transition bis(diphenyl)chrome$^{0/+}$ (E^0 = −0.68 V, SCE). The accuracy of the potential measurement was ± 5 mV.

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