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Reductive electrocatalytic dehalogenation of nitrobenzyl halides: nitrophilic or halophilic attack?

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Electrochemical reduction of Cp_2TiCl_2 in the presence of benzylic halides results in their catalytic dehalogenation to form toluene derivatives. Possible schemes for the process were proposed on the basis of the results of electrochemical studies and digital simulation data. The catalytic scheme including the halophilic attack of the Ti^{III} complex to organic halide as a key step occurs for unsubstituted benzylic halides. In the case of nitro-substituted substrates, the reaction is strongly accelerated. In this case, an electron transfer from the reduced form of the catalyst to the NO_2 group of organic halide is possibly accompanied by the intramolecular charge transfer to the C—Hal bond, thus facilitating its cleavage. Thus, the nitro group in the starting benzylic halide acts as a "redox antenna," transferring an electron to the C—Hal bond. The proposed scheme is supported by semiempirical calculations of the geometry of molecular complexes with the Ti—Hal or Ti—NO_2 coordination.

Key words: titanocene dichloride, benzylic halides, reductive dehalogenation, electrocatalysis, semiempirical calculations.

Reactions of halogen substitution by hydrogen in organic compounds are well known and can be effected with various reagents and proceed *via* different mechanisms. A possible way is the reductive dehalogenation of benzylic halides ($ArCH_2X$) catalyzed by Ti^{III} complexes.[1] This reaction is of interest as a method for the selective dehalogenation in polyfunctional compounds. It can be used, in particular, as a synthesis of glycals from glycosyl halides.[2,3] The Ti^{III} complexes used as catalysts are generally synthesized from titanocene dichloride or other available Ti^{IV} complexes by the action of reducing agents, *e.g.*, metals (Zn, Mn, Al) or organometallic compounds (RMgX, RLi).[1,4] However, in recent works, the active form of the catalyst is prepared by electrochemical reduction of the Ti^{IV} complex,[5—8] and this form favors the reductive coupling of aldehydes to form pinacones[5] and the selective reduction of the nitro group.[6—8] The recent data[9,10] on the nature of active species produced by the electrochemical reduction of Cp_2TiCl_2 in solution show that these species undergo the subsequent electrocatalytic reactions with benzaldehyde or benzyl chloride.

It is known that electrocatalytic processes have several substantial advantages over common catalysis (high selectivity and ecological safety, no necessity for chemical oxidative or reducing agents in the reaction mixture, *etc.*). Therefore, it seems of special interest to develop new electrochemically activated reactions involving different types of transformations.

The purpose of the present work is to study the electrocatalytic dehalogenation of compounds of the $ArCH_2X$ series catalyzed by the reduced form of bis(η^5-cyclopentadienyltitanium) dichloride in solution.

Experimental

Instruments and electrodes. Cyclic voltammograms were recorded on IPC-Win and Autolab PGSTAT30 potentiostats (Ecochemie, Netherlands) at stationary platinum electrodes 3.8 and 0.8 mm in diameter in anhydrous organic solvents (THF, MeCN) with $Bu^n{}_4NPF_6$ as a supporting electrolyte at 20 °C. A special electrochemical cell connected by the three-electrode scheme was used, and the potential sweep rate was 100 mV s^{-1}. Electrolysis was carried out on a P-5827M potentiostat in a two-compartment electrolytic 10-mL cell. The working electrode was a graphite 1×1-cm tissue mounted on a platinum wire. In all cases, the counter electrode was platinum, and the reference electrode was Ag/0.01 *M* $AgNO_3$ in CH_3CN (the standard potential *vs.* Fc/Fc^+ in CH_3CN is –0.1 V). Peak potentials were recalculated taking into account ohmic losses.

Electrolysis products were analyzed on a Varian GC 3400 chromatograph equipped with a FID and HP1 silicone column (50 m × 0.32 mm) with a film thickness of 0.52 μm. The tem-

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perature of the detector and injector was 310 °C, and the temperature regime was 40 °C (3 min) → 300 °C, 10 deg min^{-1}.

Mass spectra were recorded on an MS-GC Finnigan MAT SSQ 7000 instrument with an ionization energy of 70 eV equipped with an HP-5 capillary silicone column (30 m).

Purification of solvents. Acetonitrile (pure) was stirred for 12 h above CaH_2 and distilled. Then it was refluxed above P_2O_5 for 2 h and distilled again, collecting a fraction with b.p. 81—82 °C (760 Torr).

Tetrahydrofuran (pure) was stirred above KOH, distilled above $LiAlH_4$, and stored above sodium benzophenone ketyl. A freshly distilled portion of the solvent was used in each experiment.

Argon was conveyed from a gas cylinder through a column filled with anhydrone and saturated with solvent vapor in an additional vessel. Dry argon saturated with solvent vapor was passed through the cell to remove oxygen from an electrolyte solution and for stirring.

Starting compounds. Titanocene dichloride (Acros), tetrabutylammonium hexafluorophosphate (Aldrich), benzyl chloride, benzyl bromide, and 4-methylbenzyl chloride (Merck) were used. Other halides were synthesized according to known procedures.

Preparative electrolysis (general procedure). Electrolysis was carried out in the corresponding solvent in the potentiostatic regime at the potential of Cp_2TiCl_2 reduction. A solution of Cp_2TiCl_2 (3 mmol L^{-1}) and organic halide (10 mmol L^{-1}) was used for electrolysis. The electrolysis was monitored by a digital voltmeter by changing the electrolysis current. After the end of electrolysis (2 F mol^{-1} of organic halide were passed), the solvent was evaporated *in vacuo* (~100 Torr), and the residue was extracted with benzene or diethyl ether and studied by GLC or GC-MS. The chemical and current yields were calculated in respect of the starting organic halide.

Semiempirical calculations were carried out by the PM3 method extended by including the parameters for all transition metals of the I Group and some II and III Group metals. This extended method (PM3(tm)) is included in the HyperChem 7.01 program package (HyperCube Inc., FL, USA). The geometry of molecules was optimized with the established convergence gradient not higher than 10 cal (Å $mol)^{-1}$. The systems with the close and open shells were calculated using the restricted and unrestricted Hartree—Fock methods, respectively.

Digital simulation of voltammograms in the framework of different kinetic schemes was performed by the DIGISIM program (Bioanalytical Systems) with an increment of 5 mV. The ohmic resistance was 1 kOhm.

Results and Discussion

Benzyl chloride, benzyl bromide, and their derivatives containing the methyl or nitro group in the benzene ring were chosen as objects of the study: $PhCH_2Cl$, $PhCH_2Br$, $4\text{-}MeC_6H_4CH_2Cl$, $4\text{-}NO_2C_6H_4CH_2Cl$, and $4\text{-}NO_2C_6H_4CH_2Br$. Several aryl halides ($4\text{-}NO_2C_6H_4Cl$, $4\text{-}NO_2C_6H_4Br$, $4\text{-}MeOC_6H_4Cl$) were also studied for comparison. The electrocatalytic reductive dehalogenation of these compounds was studied in THF or CH_3CN solutions by cyclic voltammetry (CV) and electrolysis methods using semiempirical calculation data.

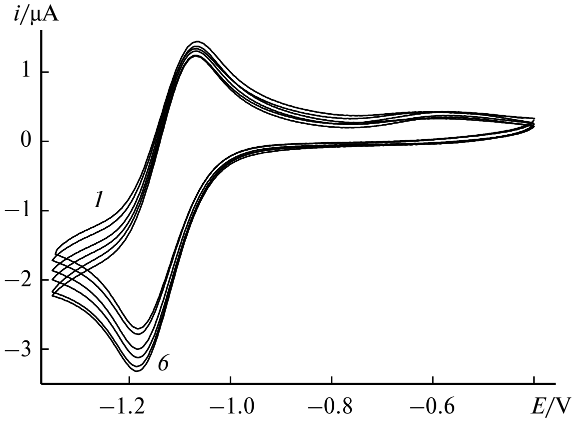


Fig. 1. Cyclic voltammograms for Cp_2TiCl_2 (1.1 mmol L^{-1}) in the presence of $PhCH_2Cl$: 0 (*1*), 10 (*2*), 20 (*3*), 50 (*4*), 80 (*5*), and 120 mmol L^{-1} (*6*). Experimental conditions: Pt, THF, 0.1 *M* Bu_4NPF_6, 100 mV s^{-1}.

Cyclic voltammetry and preparative electrolysis. The voltammogram for Cp_2TiCl_2 recorded at the Pt electrode in THF against 0.1 *M* Bu_4NPF_6 and its transforming obtained upon the addition of benzyl chloride to the solution are shown in Fig. 1. Additives of $PhCH_2Cl$ increase slightly the current of Cp_2TiCl_2 reduction, whereas the reverse peak of Ti^{III} complex reoxidation decreases, *i.e.*, the reduced form of titanocene dichloride is consumed in the presence of organic halide. A similar pattern only with more pronounced changes in the voltammograms was observed for $PhCH_2Br$.

The presence of the nitro group in the aromatic ring changes sharply the voltammetric pattern. Already in the presence of an equimolar amount of $4\text{-}NO_2C_6H_4CH_2Cl$, the peak of Ti^{III} complex reoxidation disappears completely, and an almost threefold increase in the cathodic current is observed (Fig. 2). This indicates a fast chemical reaction of the Ti^{III} complex in solution.

The results of potentiostatic electrolysis of the $ArCH_2X$ series in the presence of Cp_2TiCl_2 at the potential of Cp_2TiCl_2 reduction are presented in Table 1. The composition of the reaction mixtures obtained by electrolysis was analyzed by GLC and GC-MS. In all cases, the main reaction product was toluene or its derivative with the respective substituent; the corresponding dibenzyls were also formed in small amounts (<10%).

Electrolysis was carried out in the presence of approximately threefold (10 : 3) excess of benzyl halide over Cp_2TiCl_2 in the potentiostatic regime at the potential of Cp_2TiCl_2 reduction. The quantity of electricity passed was 2 F per mole of organic halide. In the case of nitrobenzyl halides, a high conversion (up to 70% calculated to the starting halide) is observed. This indicates that the catalyst is permanently regenerated during the reaction, *i.e.*, a catalytic cycle occurs. For nonactivated $PhCH_2Cl$, $PhCH_2Br$, and $4\text{-}MeC_6H_4CH_2Cl$, the reaction mixture contained a considerable amount of the start-

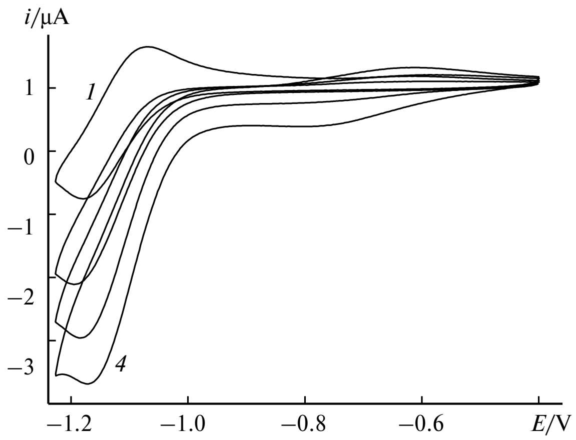


Fig. 2. Cyclic voltammograms for Cp_2TiCl_2 (0.92 mmol L^{-1}) in the presence of $4\text{-}NO_2C_6H_4CH_2Cl$: 0 (*1*), 1.1 (*2*), 2.2 (*3*), and 3.3 mmol L^{-1} (*4*). Experimental conditions: Pt, THF, 0.1 *M* Bu_4NPF_6, 100 mV s^{-1}.

ing halides. Aryl halides containing the $4\text{-}NO_2$ group are characterized by very low yields of the reductive dehalogenation products, and $4\text{-}MeOC_6H_4Cl$ is not dehalogenated at all (see Table 1).

Mechanism of catalysis. The electrochemical reduction of Cp_2TiCl_2 in solution produces radical anions $[Cp_2Ti^{III}Cl_2]^-$, which dissociate in part to the Cl^- anion and $Cp_2Ti^{III}Cl$ radical. The latter forms dimers $[Cp_2Ti^{III}Cl]_2$.[9,10] All of the three Ti^{III}-containing species are equilibrated and can act as mediators of the *outer-sphere* electron transfer from the electrode to $ArCH_2X$ to form the reductive dehalogenation products. This route is more probable for nitrobenzyl halides than for benzylic halides containing no nitro group. This is indicated, in particular, by the difference of potentials between the reduction peaks of the mediator and nitrohalide (for example, $E^p{}_{Cp_2TiCl_2} = -1.12$ V, $E^p{}_{NO_2C_6H_4CH_2Cl} = -1.42$ V; $\Delta E^p = 0.3$ V, *vs.* Ag/0.01 *M* $AgNO_3$ in MeCN), which is optimal, in this case, for efficient redox catalysis. However, the electrochemical gap for the $Cp_2TiCl_2/PhCH_2Cl$ pair is much broader ($E^p{}_{Cp_2TiCl_2} = -1.12$ V, $E^p{}_{PhCH_2Cl} = -2.39$ V; $\Delta E^p = 1.27$ V) that makes the mediator outer-sphere reduction is much less probable.

Table 1. Results of the potentiostatic electrolysis of Cp_2TiCl_2 ($C_0 = 3$ mmol L^{-1}, $E = -1.15$ V *vs.* Ag/$AgNO_3$ in MeCN) in the presence of $ArCH_2X$ or ArX ($C = 10$ mmol L^{-1})

Compound	Solvent	Additives	Yield (%)	Current efficiency(%)
$4\text{-}NO_2C_6H_4CH_2Cl$	THF	—	55—70	50
$4\text{-}NO_2C_6H_4CH_2Cl$	THF	Ph_3CH	60—72	55
$4\text{-}NO_2C_6H_4CH_2Cl$	MeCN	—	53—60	40
$4\text{-}NO_2C_6H_4CH_2Br$	THF	—	65—75	50
$4\text{-}MeC_6H_4CH_2Cl$	THF	Ph_3CH	15—24	13
$4\text{-}MeC_6H_4CH_2Cl$	MeCN	—	16—27	13
$PhCH_2Cl$	THF	—	8—12	6
$PhCH_2Br$	THF	—	25—30	20
$PhCH_2Br$	MeCN	Ph_3CH	25—32	20
$4\text{-}NO_2C_6H_4Cl$	MeCN	—	4—6	4
$4\text{-}NO_2C_6H_4Br$	MeCN	—	7—9	5
$4\text{-}MeOC_6H_4Cl$	MeCN	—	0	0

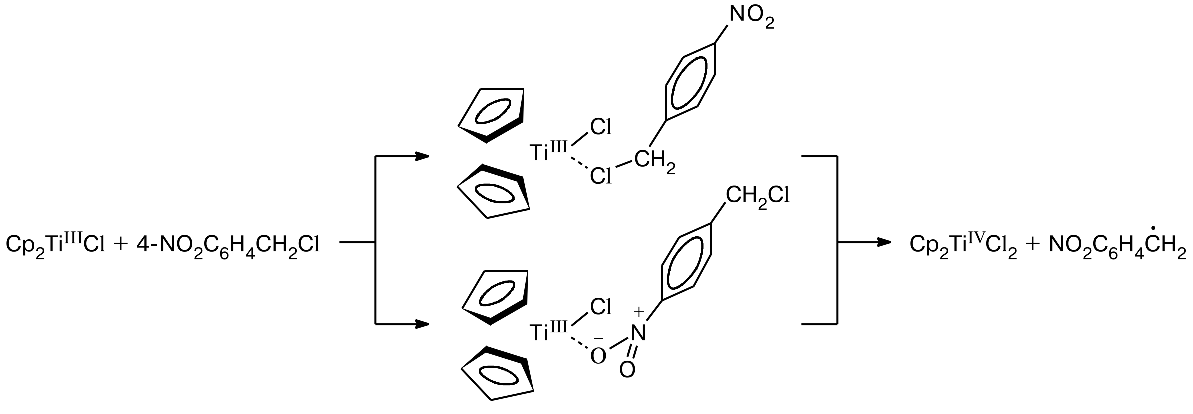
When considering the outer-sphere mediator reduction, we inevitably conclude that the probability of the outer-sphere redox process involving the $[Cp_2Ti^{III}Cl_2]^-$ radical anion as a mediator is low. It can be assumed that the energies of an electron in this radical anion and in the electrode at the potential of radical anion formation are the same (because the free Gibbs energies of the initial (Cp_2TiCl_2 and the electron in the electrode) and final states $(Cp_2TiCl_2)^-$ should become equal after equilibration). The probability of direct reduction at the "electrode" is much higher. The more so, any steric or other hindrance for the electron transfer to $ArCH_2X$ can hardly be discussed. A gain in the rate is possible only due to the elimination of two-dimensional restrictions on going from the heterogeneous electron transfer from the electrode to homogeneous redox catalysis in solution, if the process is diffusionally controlled. As for $Cp_2Ti^{III}Cl$ or $[Cp_2Ti^{III}Cl]_2$, their reducing ability, according to the data in Ref. 9, is lower than that of the radical anion and, therefore, these species can hardly pretend to be outer-sphere mediators.

The second opportunity is to perform an inner-sphere electron transfer, *i.e.*, the process during which an organic substrate incorporates into the coordination sphere of the metal to form a coordination bond with the latter. Since the inner-sphere electron transfer rate is usually several orders of magnitude higher than the outer-sphere transfer rate (at close ΔG)[11] and the probability of the outer-sphere electron transfer seems to be very low in the case, then an inner-sphere electron transfer is possible for coordinately unsaturated $Cp_2Ti^{III}Cl$.

It is reasonable to assume that the coordinately unsaturated (if ignoring coordination with the solvent) $Cp_2Ti^{III}Cl$ radical reacts first of the three species considered ($[Cp_2Ti^{III}Cl_2]^-$, $Cp_2Ti^{III}Cl$, $[Cp_2Ti^{III}Cl]_2$). The $[Cp_2Ti^{III}Cl_2]^-$ radical anion with the coordination number 8 cannot coordinate to an organic substrate, because the coordination number 9 is rather improbable for Ti due to its small atomic size. The same is valid for the eight-coordinate dimeric molecule $[Cp_2Ti^{III}Cl]_2$, whose Ti atoms are bonded through the chloride bridges.

In the case of simple benzylic halides, $[Cp_2Ti^{III}Cl]$ can be coordinated only through the halogen atom, and an organic molecule is reduced *via* the halogen *atom transfer* (*halophilic mechanism*). However, the case of nitrobenzyl halide (Scheme 1) provides the second possibility: coordination through the NO_2 group. Then the long-range electron transfer to the σ*-C—Hal bond followed by the cleavage of this bond becomes possible (*nitrophilic mechanism*).

Scheme 1



The catalytic cycle presented in Scheme 2 can be proposed for an inner-sphere process with significant coordination. This scheme takes into account a possibility of coordination of the $Cp_2Ti^{III}Cl$ radical to both the starting nitrobenzyl chloride and reaction product (nitrotoluene).

Scheme 2 can be applied to both halophilic and nitrophilic reactions.

A solvent or special additives, for instance, Ph_3CH, can be used as a source of H atoms.

Further transformations of the benzylic radicals that formed can be described by different schemes. The benzylic radicals can dimerize

$$2\,ArCH_2^{\bullet} \rightarrow (ArCH_2)_2, \qquad (1)$$

the reaction with the paramagnetic Ti^{III} complex can occur

$$ArCH_2^{\bullet} + Cp_2TiCl \rightarrow Cp_2TiCl(ArCH_2) \qquad (2)$$

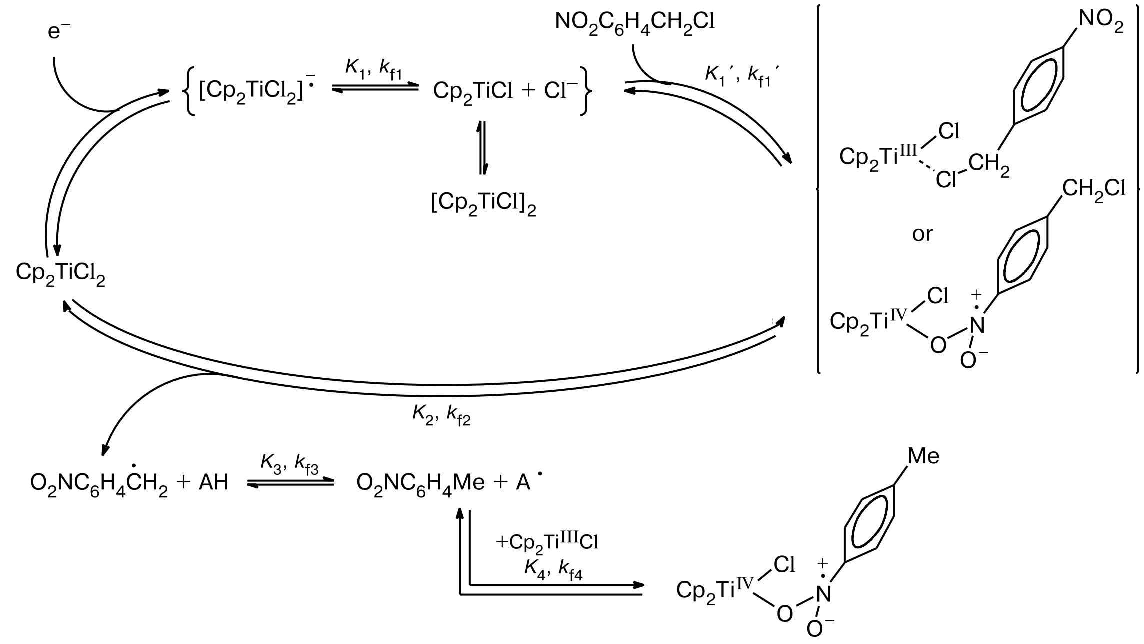
and a hydrogen atom can be eliminated from a solvent molecule or other specially added substances (for example, Ph_3CH, as in our case)

$$ArCH_2^{\bullet} + AH \rightarrow ArCH_3 + A^{\bullet}. \qquad (3)$$

Dimeric compounds can be formed *via* the following scheme:

$$Cp_2TiCl(ArCH_2) + ArCH_2Cl \rightarrow Cp_2TiCl_2 + (ArCH_2)_2. \qquad (4)$$

Scheme 2



AH is the source of H atoms in solution.

The further reduction of the benzyl radicals both at the electrode

$ArCH_2^{\bullet} + e \rightarrow ArCH_2^-$, (5)

$ArCH_2^- + H^+ \rightarrow ArCH_3$,

and in solution

$ArCH_2^{\bullet} + [Cp_2TiCl_2]^- \rightarrow Cp_2TiCl_2 + ArCH_2^-$, (6)

$ArCH_2^- + H^+ \rightarrow ArCH_3$.

cannot be excluded.

Analysis of the reduction potentials of the benzylic radicals (E_{Bn/Bn^-} = −1.215 V (SCE, DMF),[12] $E_{NO_2C_6H_4CH_2/NO_2C_6H_4CH_2^-} = -0.45$ V (SCE, DMF)[13]) indicates that the substantial contribution from reactions (5) and (6) can be expected only in the case of nitrobenzyl halides.

Since the main electrolysis product is RH in our case, reactions (1) and (4) affording dibenzyls can hardly contribute substantially to the overall process.

Step K_4 in Scheme 2 takes into account a possibility of the reaction product (nitrotoluene) to coordinate to the coordinately unsaturated Cp_2TiCl complex. To check this hypothesis by the CV method, we studied mixtures of solutions of Cp_2TiCl_2 and 4-$NO_2C_6H_4CH_3$, *viz.*, the dehalogenation product of 4-nitrobenzyl halides. The addition of 4-nitrotoluene to titanocene dichloride does not result in the catalytic increase in the current of Cp_2TiCl_2 reduction; however, the peak of Ti^{III} reoxidation disappears completely (Fig. 3). This suggests that the proposed reaction of the Ti center with the nitro group of the reaction product (nitrotoluene), *viz.*, K_4 and k_{f4} (Scheme 2), is possible and can be a reason for the fast disappearance of the peak of Ti^{III} reoxidation.

To verify the correspondence of the process under study to Scheme 2, we performed the digital simulation of the process for unsubstituted benzylic halides and nitrobenzyl chloride. Step K_4 was ignored for unsubstituted benzylic halides, and Cp_2TiCl can coordinate only to the halogen atom of the starting organic halide. For unsubstituted benzylic halides, the CV curves calculated by Scheme 2 agree well with the experimental curves (*cf.* Figs. 1 and 4) at the following rate and equilibrium constants indicated in Scheme 2: k_{f1} = 1000 s^{-1}, K_1 = 0.001 mol L^{-1}, k_{f2} =10 L (mol s)$^{-1}$, K_2 = 0.005, k_{f3} = 1 s^{-1}, $K_3 \geq 100$ (step $k1'$ was not considered separately).

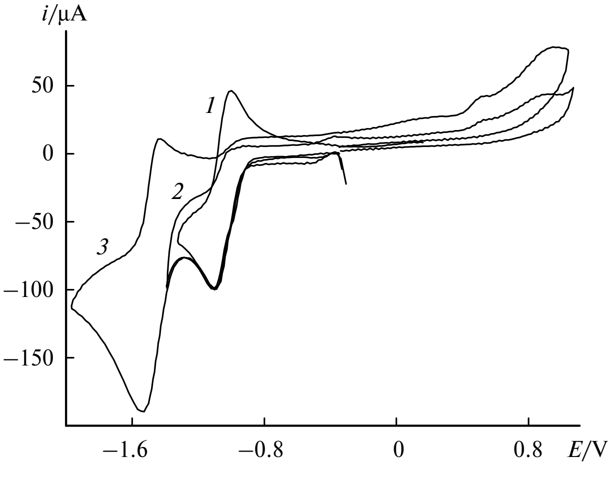


Fig. 3. Cyclic voltammograms for Cp_2TiCl_2 (1 mmol L^{-1}) (*1*) and its mixture with 4-$NO_2C_6H_4Me$ (1.2 mmol L^{-1}) (*2*, *3*). Experimental conditions: Pt, THF, 0.1 *M* Bu_4NPF_6, 100 mV s^{-1}.

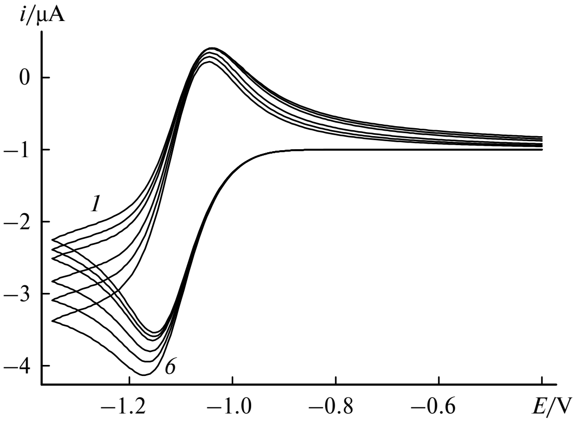


Fig. 4. Digital simulation of the electrocatalytic reaction of Cp_2TiCl_2 with $PhCH_2Cl$ according to Scheme 2 ($PhCH_2Cl$: 0 (*1*), 10 (*2*), 20 (*3*), 50 (*4*), 80 (*5*), and 120 mmol L^{-1} (*6*)). Calculated rate constants: k_{f1} = 1000 s^{-1}, K_1 = 0.001 mol L^{-1}, k_{f2} = 10 L (mol s)$^{-1}$, K_2 = 0.005, k_{f3} = 1 s^{-1}, $K_3 \geq 100$).

Scheme 2, being confirmed by the data of digital simulation of the voltammetric curves for unsubstituted $ArCH_2X$, assumes the halophilic attack of the reduced form of titanocene dichloride to the organic substrate. This assumption was also advanced earlier[10] along with possible structures of the intermediates with the Cl atom as a bridge between the reactants.

However, for 4-$NO_2C_6H_4CH_2Cl$, digital simulation by Scheme 2 ignoring the subsequent coordination of the product formed ($NO_2C_6H_4CH_3$) with Cp_2TiCl (step K_4 including a possible subsequent fast step, for example, the rearrangement shown above) gave an explicit discrepancy: an increase in the cathodic current for Cp_2TiCl_2 and a decrease in the reverse peak of reoxidation of the Ti^{III} complexes in solution are much faster in the experimental curve than in the theoretical one.

When we introduced the step of interaction of the $Cp_2Ti^{III}Cl$ radical with nitrotoluene (K_4 and k_{f4}) into the calculation kinetic scheme, the digital simulation of the process for 4-$NO_2C_6H_4CH_2Cl$ by complete Scheme 2 gave a good coincidence of the theoretical and experimental curves (*cf.* Figs 5 and 2) at the following rate constants: k_{f1} = 1000 s^{-1}, K_1 = 0.001 mol L^{-1}, $k_{f2} = 4 \cdot 10^5$ L (mol s)$^{-1}$, K_2 = 1000, k_{f3} > 100 s^{-1}, K_3 = 1000 mol L^{-1}, $k_{f4} = 4 \cdot 10^5$ L (mol s)$^{-1}$, $K_4 = 10^6$ L mol^{-1} (as in the case

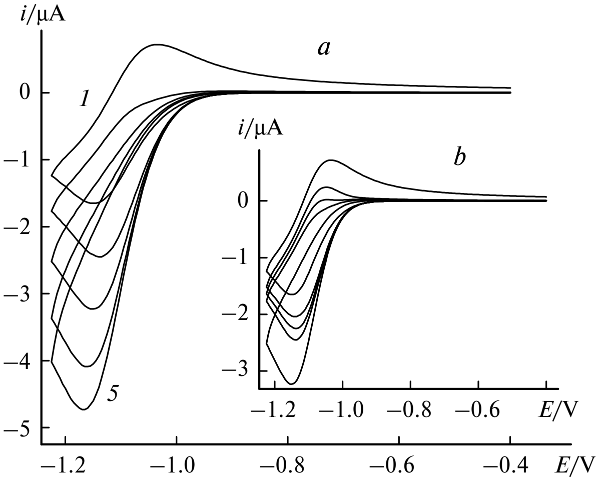


Fig. 5. *a*. Digital simulation of the electrocatalytic reaction of Cp_2TiCl_2 (0.92 mmol L^{-1}) with $4\text{-}NO_2C_6H_4CH_2Cl$ according to Scheme 2. *b*. Results obtained by the addition of small amounts of $4\text{-}NO_2C_6H_4CH_2Cl$: 0 (*1*), 0.3 (*2*), 0.4 (*3*), 0.5 (*4*), and 1.1 mmol L^{-1}. Calculated rate constants: k_{f1} = 1000 s^{-1}, K_1 = 0.001 mol L^{-1}, $k_{f2} = 4 \cdot 10^5$ L (mol s)$^{-1}$, K_2 = 1000, k_{f3} > 100 s^{-1}, K_3 = 1000 mol L^{-1}, $k_{f4} = 4.10^5$ L (mol s)$^{-1}$, $K_4 = 10^6$ L mol^{-1}.

of unsubstituted benzylic halides, the complexation step with the starting 4-nitrobenzyl halide (K_1' and k_{f1}') was not separately considered).

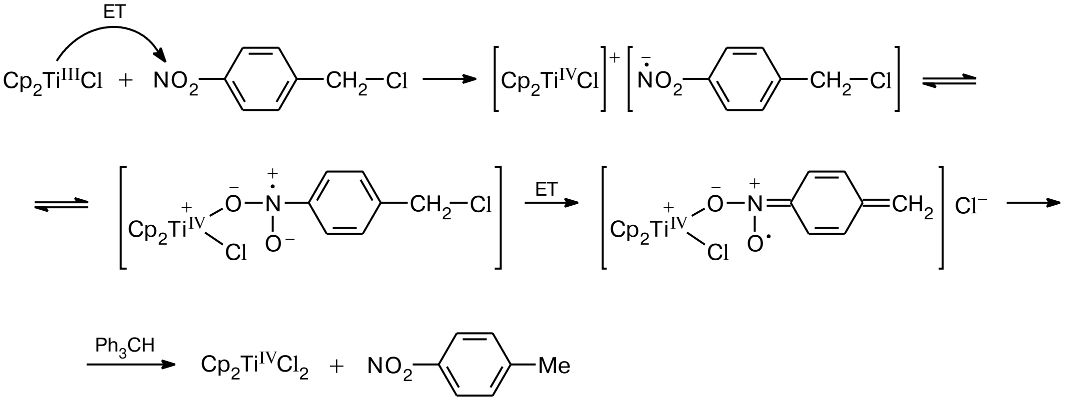
As shown in Scheme 2, for nitrobenzyl halides, coordination with the O atom of the nitro group can be an alternative of the halophilic attack for the coordinately unsaturated Cp_2TiCl complex. In our opinion, the reaction between the electrochemically reduced form Cp_2TiCl_2 and $4\text{-}NO_2C_6H_4CH_2Cl$ proceeds, more probably, as an inner-sphere electron transfer (ET) from the Ti^{III} atom to the nitro group rather than the halophilic attack. This inner-sphere ET is accompanied by the intramolecular electron transfer to the C—Cl bond, resulting in the elimination of the halide ion. In this case, the NO_2 group acts as a "redox antenna" facilitating the electron transfer from the reduced form of the Ti complex to an organic substrate, thus accelerating the reaction substantially (Scheme 3).

Analogies to the proposed scheme are presented in Refs 14 and 15 along with the proofs that the easily reducible NO_2 group can serve as an electron carrier to the kinetically impeded part of the molecule. The coordination of the nitro group is additionally favored by the fact[16] that the nitroxyl anion substitutes readily the Cl^- anion in the $CpTiCl_3$ complex, *i.e.*, coordination with the oxygen atom is more preferential.

We also attempted to carry out reductive dehalogenation for a series of halobenzenes under similar conditions. However, the reaction does not occur for $4\text{-}MeOC_6H_4Cl$, and although the replacement of the methoxy group by the nitro group affords the reductive dehalogenation product, its amount is very low (see Table 1). Perhaps, in this case, the presence of the NO_2 group makes it possible to transfer an electron (outer- or inner-sphere ET) from the reduced form of titanocene dichloride to nitrophenyl halide, thus facilitating the elimination of the halogen atom. However, the elimination of halogen in the halobenzene radical anion is much more difficult than that in the benzyl halide radical anion. This is indicated by the data on the rate of dissociation of the σ-C—Hal bond in radical anions of the nitrophenyl[17] and nitrobenzyl[18] types to form the halide anion and organic radical. For $4\text{-}NO_2C_6H_4CH_2Hal$, log*k* = 3.9 (Cl) and 5.7 (Br), whereas for $4\text{-}NO_2C_6H_4Hal$, log*k* = −6.0 (Cl) and −2.9 (Br). As can be seen from these data, the difference in stability of the phenylic and benzylic type radical anions is very high. This results in the situation when even the presence of the NO_2 group in a halobenzene molecule affords no significant amount of the reductive dehalogenation product.

Semiempirical calculations. We performed the quantum-chemical calculations of the d^0 complexes of the $[Cp_2Ti^{IV}Cl]^+$ cation with *p*-nitrobenzyl chloride coordinated to the Ti atom through the oxygen atom of the nitro group *viz*., $[Cp_2Ti^{IV}(Cl)\text{—}ON(O)C_6H_4CH_2Cl\text{-}p]^+$,

Scheme 3

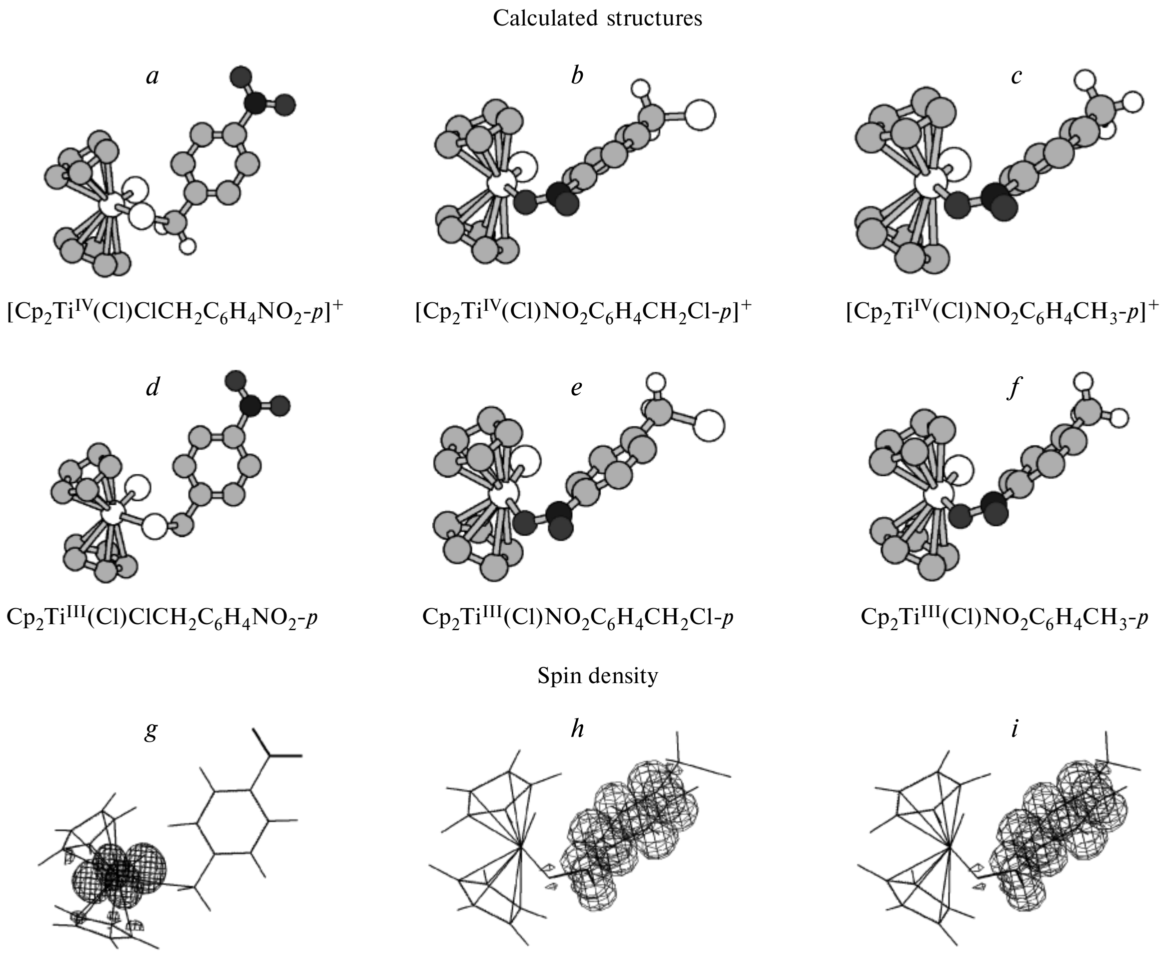


and through the benzyl chlorine atom, *viz.*, $[Cp_2Ti^{IV}(Cl)ClCH_2C_6H_4NO_2\text{-}p]^+$, as well as the d^0 complex with *para*-nitrotoluene coordinated through the nitro group, *viz.*, $[Cp_2Ti^{IV}(Cl)—ON(O)C_6H_4Me\text{-}p]^+$. In addition, we also calculated the reduced forms of these complexes, which are the uncharged radical species of the d^1 type: $[Cp_2Ti^{III}(Cl)—ON(O)C_6H_4CH_2Cl\text{-}p]$, $[Cp_2Ti^{III}(Cl)ClCH_2C_6H_4NO_2\text{-}p]$, and $[Cp_2Ti^{III}(Cl)—ON(O)C_6H_4Me\text{-}p]$.

The geometry of the complexes coordinated to the NO_2 group differs from that of the complexes coordinated to the Cl atom (Fig. 6): in the first case, the benzene ring of the "guest" (organic molecule) is unfolded in such a way that it is projected on the horizontal plane passing through the Ti atom between the Cp rings and C_6 face, and in the second case, it is projected by the edge.

Note that the geometry of the cationic Ti^{IV} d^0 complexes differs slightly from the geometry of the radical Ti^{III} d^1 complexes, *i.e.*, the $Ti^{IV} \rightarrow Ti^{III}$ reduction leads to an insignificant structural reorganization of the molecule. The difference in the geometries of the NO_2- and Cl-coordinated complexes is related, probably, to the difference in orbital Ti—donor atom interactions.

According to the theoretical concepts,[19] the d^0 fragment of the Cp_2Ti^{IV} complex has three unoccupied orbitals lying in the interring plane of the fragment. When ignoring a possibility of rotation of the Cp rings about the normals passing through the Ti atom, due to which they can exist in eclipsed or inhibited conformations, then the symmetry of the Cp_2Ti fragment is C_{2v}, and the orbitals can be classified according to this point group using designations *a* and *b*. The unoccupied orbitals and the origin of their shapes from the hybridization of the canonical orbitals of the metal are presented in Fig. 7, *a*—*c*.[19] The orbitals of the a_1 symmetry are hybrid, and the b_2 orbital is non-hybrid, *i.e.*, an almost pure d_{xy} orbital. The three lowest unoccupied orbitals obtained by the calculation of the $[Cp_2Ti^{IV}]^{2+}$ d^0 dication correspond to the theoretically predicted orbitals (see Fig. 7, *d*—*f*).

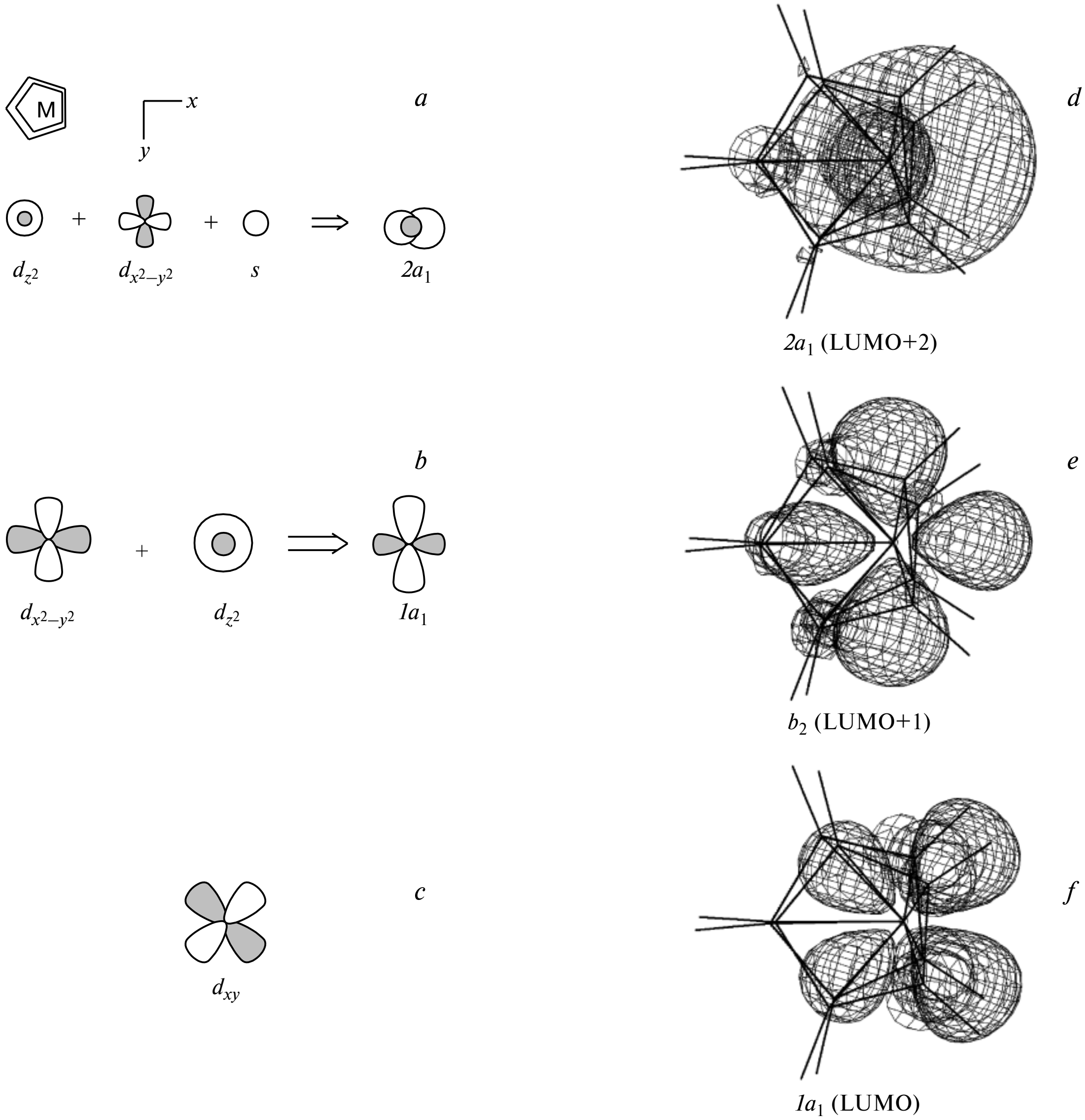

Calculated structures

$[Cp_2Ti^{IV}(Cl)ClCH_2C_6H_4NO_2\text{-}p]^+$ $[Cp_2Ti^{IV}(Cl)NO_2C_6H_4CH_2Cl\text{-}p]^+$ $[Cp_2Ti^{IV}(Cl)NO_2C_6H_4CH_3\text{-}p]^+$

$Cp_2Ti^{III}(Cl)ClCH_2C_6H_4NO_2\text{-}p$ $Cp_2Ti^{III}(Cl)NO_2C_6H_4CH_2Cl\text{-}p$ $Cp_2Ti^{III}(Cl)NO_2C_6H_4CH_3\text{-}p$

Spin density

Fig. 6. Geometry calculated by the PM3(tm) method for the $[Cp_2Ti^{IV}Cl]^+$ and $Cp_2Ti^{III}Cl$ molecular complexes with *p*-nitrobenzyl chloride for coordination at the chlorine atom and nitro group and with *p*-nitrotoluene for coordination at the nitro group (*a*—*f*) and the localization of the total spin density in the $Cp_2Ti^{III}ClX$ complexes (*g*—*i*).



$2a_1$ (LUMO+2)

b_2 (LUMO+1)

$1a_1$ (LUMO)

Fig. 7. Theoretically predicted (*a—c*) and calculated (*d—f*) three lowest free orbitals of the Cp_2Ti^{2+} cation.

The orbitals of the $2a_1$ and b_2 symmetry are used for bonding the Lewis lone electron pairs of the Cl and O donating atoms (Fig. 8, *a*).

The $1a_1$ orbital in symmetry is suitable for bonding of the p(π) orbital of a donor if this orbital is plane, *i.e.*, lies in the plane of the $1a_1$ orbital (Fig. 8, *b*).

Coordination to the NO_2 group uses the non-hybrid 2p(O) orbital rather than π(O=N), because the energy of the pure p orbital is higher than that of p(π) (Fig. 8, *c*).

In this case, in the preferential geometry the benzene ring is projected to the interring plane by its planar face.

For coordination to the Cl atom, both p orbitals are almost degenerate and, therefore, one can choose between the "plane" and "edge" orientations. It is most likely that an organic molecule prefers, in this case, the "edge" orientation for steric reasons (Fig. 8, *d*).

For the "plane" orientation, a charge transfer is possible between Cp_2Ti and nitrobenzyl halide "through bonds" and "through space." This is favored by the close arrangement of the benzene ring to the Ti atom. According to the calculations, the distance between the Ti atom and benzene ring is rather short: 3.29 Å for the $[Cp_2Ti^{IV}(Cl)—ON(O)C_6H_4CH_2Cl\text{-}p]^+$ d^0 complex and 3.24 Å for the $[Cp_2Ti^{III}(Cl)—ON(O)C_6H_4Me\text{-}p]$ d^1 complex. This distance is much longer (3.8 Å) in the $[Cp_2Ti^{IV}(Cl)ClCH_2C_6H_4NO_2\text{-}p]^+$ complex coordinated to the chlorine atom, *i.e.*, the charge transfer "through space" is less probable.

On going from the $[Cp_2Ti^{IV}ClX]^+$ d^0 cations to the reduced $[Cp_2Ti^{III}ClX]^0$ d^1 radicals for the complexes coordinated to the NO_2 group, we obtain no changes in the orientation of the benzene ring (in both cases,

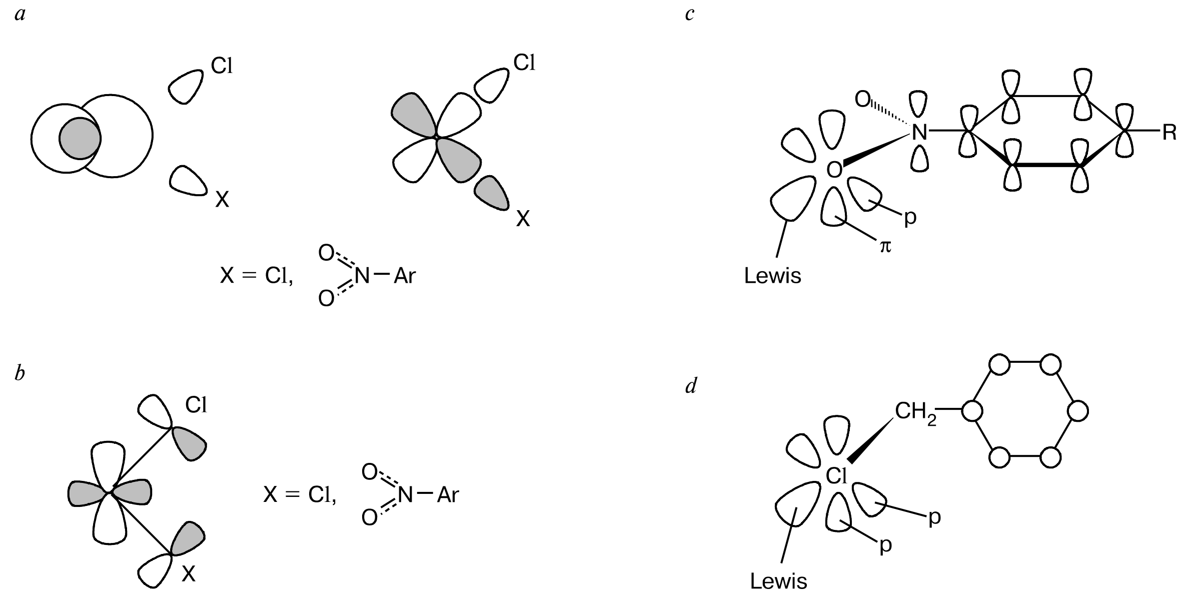


Fig. 8. Theoretical consideration of bonding in the Cp_2TiXCl molecules: (*a*) orbitals of the $2a_1$ and b_2 symmetry used for bonding of the Lewis lone electron pairs of the donating Cl and O atoms; (*b*) orbital $1a_1$ bonding the p(π)-orbitals of the donor if this orbital is plane; (*c*) non-hybrid 2p-orbital of the O atom used for coordination at the NO_2 group; and (*d*) edge orientation for coordination at the Cl atom.

the "plane" orientation with respect to the interring Cp_2Ti plane is observed). However, the Ti—ON(O) bond in the d^1 radical shortens (by approximately 0.3 Å) compared to that in the d^0 cation. The calculated Ti—O bond lengths in $[Cp_2Ti^{IV}(Cl)—ON(O)C_6H_4CH_2Cl\text{-}p]^+$ and $[Cp_2Ti^{IV}(Cl)—ON(O)C_6H_4Me\text{-}p]^+$ are 2.32—2.33 Å, whereas those in the corresponding radicals are 2.02—2.03 Å. This implies that the charge transfer from Cp_2Ti to $NO_2C_6H_4R$ in the radical d^1 complexes should be more efficient. It should be mentioned for comparison that the X-ray diffraction data**[20]** for the compounds with the coordination type of the Ti—O bond, for instance, for the $[Cp_2Ti^{III}(EtOEt)_2]^+[(C_6F_5)_3BH]^-$ complexes, give 2.26 Å. For the $Cp_2Ti(ONO_2)_2$ complex containing nitrate anions as ligands, the Ti—O bond is shorter and equal to 2.15 Å according to the X-ray diffraction data.**[21]**

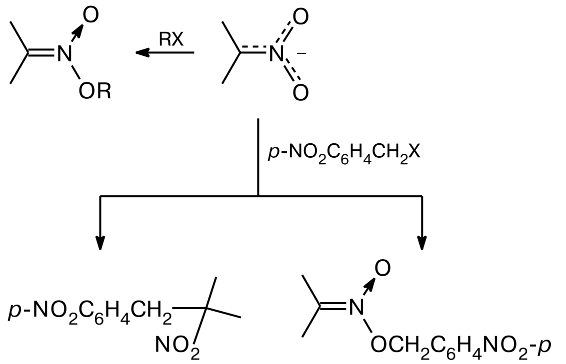
In the radical d^1 complexes, the spin density is localized on the aromatic ligand if the latter is coordinated by the nitro group (see Fig. 6). For coordination to the chlorine atom, the spin density remains on the Ti atom of the Cp_2Ti $3d^1$ fragment. Actually, the NO_2-coordinated d^1 complexes can be considered as complexes of the nitroarene radical anion with the $Cp_2Ti^{IV}Cl$ d^0 cation.

Thus, the semiempirical calculations show that in the radical $[Cp_2Ti^{III}(Cl)—ON(O)C_6H_4CH_2Cl\text{-}p]$ d^1 complex the nitroarene ligand can act, in fact, as a "redox antenna" withdrawing electrons from the reduced form of titanocene dichloride. Due to vibrations, the symmetry of nitroarene changes and the π and σ*(C—Cl) orbitals are mixed to result in the C—Cl bond cleavage. When $NO_2C_6H_4CH_2Cl$ is coordinated to the chlorine atom, no charge transfer is observed. For example, in the case of unsubstituted benzylic halide, the reaction occurs as an inner-sphere Cl atom transfer (see Scheme 2).

* * *

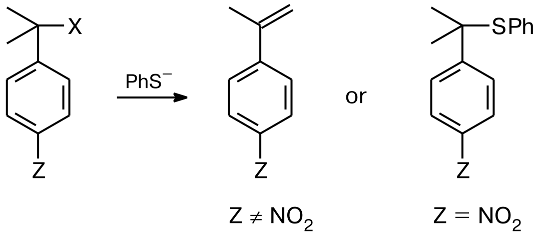
Thus, the results obtained in this work indicate that the reductive dehalogenation of benzylic halides in the presence of Cp_2TiCl_2 gives rise to the corresponding toluene derivatives. Possible schemes of the catalytic process were proposed on the basis of electrochemical studies, digital simulation data, and semiempirical calculations. The catalytic scheme, whose key step is the halophilic attack of the Ti^{III} complex to the organic halide, takes place, most likely, for unsubstituted benzylic halides. The introduction of the nitro group into the aromatic ring considerably accelerates the reaction. In this case, the process can pass through the electron transfer from the reduced form of the catalyst to the NO_2 group of organic halide and is accompanied by the intramolecular charge transfer to the C—Hal bond, thus favoring its cleavage. The nitro group in the starting benzyl halide acts, therefore, as a "redox antenna" transferring an electron to the C—Hal bond.

Other examples for changing the reaction mechanism by the introduction of the nitro group as a substituent are published. The classical example is the alkylation of the nitroalkane anions. The ambidentate 2-nitropropane anion reacts, as a rule, with different alkylating agents to the oxygen atom. The only exception are the *para*-nitrobenzyl derivatives producing both the O- and C-alkylation products, whose ratio depends on the nature of the alkylating agent[22,23]:

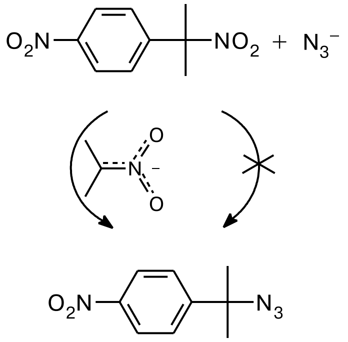


The mechanism including the primary electron transfer from the 2-nitropropane anion to *para*-nitrobenzyl halide was proposed for this reaction.[24]

p-Nitrobenzyl halides undergo substitution instead of elimination even in the case of tertiary compounds[25]:



α,*p*-Dinitrocumene does not react with the azide ion. However, in the presence of the reducing agent (2-nitropropane anion), the substitution product is formed in 97% yield[26]:



Thus, reactions proceeding through electron transfer become very probable in the presence of NO$_2$ groups.

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