Electron-transfer induced cleavage and formation of C—H-bonds in 17ē and 19ē platinum complexes

*M. G. Peterleitner,** *L. N. Morozova, T. A. Peganova, S. M. Peregudova,*
L. I. Denisovich, and N. A. Ustynuyk

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

The electrochemical behavior of platinum complexes $[Pt(\eta^4\text{-diene})(\eta^5\text{-}C_5R_5)]^+BF_4^-$ (1^+, diene = C_5Me_5H, R = H; 2^+, diene = C_5Me_5H, R = Me; 3^+, diene = C_6H_8, R = Me; 4^+, diene = C_8H_{12}, R = Me) was studied by cyclic voltammetry. Complexes 1^+ and 2^+ are shown to be capable of both oxidation and reduction. One-electron reduction of 2^+ gives a mixture of two neutral isomeric complexes **5a,b** of η^3-allylic and σ,π-olefinic type due to the cleavage of C—H bonds in the methyl groups of the pentamethylcyclopentadiene ligand of 19ē complexes 2^*. The preparative electrochemical oxidation of 2^+ results in cleavage of the C—H bond at the sp^3-hybridized pentamethylcyclopentadiene carbon atom in 17ē dication radical 2^{2+} to give the decamethylplatinocene dication $[Pt(\eta^5\text{-}C_5Me_5)_2]^{2+}(BF_4)_2$ (7^{2+}). It is shown that one-electron reduction of 7^{2+} and one-electron oxidation of **5a,b** is accompanied by the formation of C—H bonds to form 2^+.

Key words: electron-transfer induced reactions; cyclic voltammetry, platinum complexes.

It is known[1] that the cleavage and formation of C—H bonds in coordinated ligands can be induced by electron transfer that proceeds via 17ē or 19ē intermediates. However, there are no examples, if any exist, of 18ē compounds, in which activation of the C—H bond would be observed both during oxidation to 17ē compounds and reduction to 19ē complexes. In the present work, electrochemical reduction and oxidation of η^4-diene-η^5-cyclopentadienyl and related sandwich complexes of platinum together with processes of cleavage and formation of C—H bonds induced by electron transfer were studied. Interest in the investigation of these processes for the above mentioned compounds is due to a need for synthetic approaches to neutral 20ē platinocenes which are as yet unknown.

Results and Discussion

Electron-transfer properties of platinum complexes with the general molecular formula $[Pt(\eta^4\text{-diene})(\eta^5\text{-}C_5R_5)]^+BF_4^-$ (1^+, diene = C_5Me_5H, R = H, as a mixture of *exo-* and *endo*-H-isomers; 2^+, diene = C_5Me_5H, R = Me, in the form of *endo*-H-isomer; 3^+, diene = 1,3-cyclohexadiene, R = Me; 4^+, diene = 1,5-cyclooctadiene, R = Me) were studied by cyclic voltammetry (CVA).

As follows from the CVA data, complexes 1^+—4^+ are capable of both reduction (Fig. 1, peak *A*) and oxidation (peak *B*). This feature distinguishes them from structurally similar complexes $[Pt(\eta^4\text{-tetramethylcyclobutadiene})(\eta^5\text{-}Cp)]^+BF_4^-$ (Cp = C_5H_5, C_5H_4Me, C_5Me_5),[2] which exhibit only the ability to be reduced. The potentials of the peaks of diffusion controlled oxidation and reduction observed for 1^+—4^+ in various solvents are given in Table 1. One-electron reduction of compounds 1^+—4^+ proceeds irreversibly, as follows from comparison of the peaks corresponding to the reduction of 1^+—4^+ and the one-electron peak of the reduction of $[Co(\eta^5\text{-}C_5H_5)_2]^+BF_4^-$, along with the fact that a reverse scan of the potential reveals no peaks of the oxidation of 19ē radicals formed by the addition of one electron to the starting cations. The peak corresponding to the reduction of 2^+ is cathode-shifted by 0.23 V relative to the peak of complex 1^+, which is caused by the influence of the five methyl groups in the pentamethylcyclopentadienyl ligand. The nature of diene also affects the value of the reduction potential of the complexes shifting it to more negative values on going from 4^+ to 3^+. The processes of the reduction of complexes 1^+ and 2^+ were studied in more detail. It was found that the complete preparative reduction of 2^+ in THF at −1.80 V on a mercury cathode consumes 1 F mol^{-1} and results in a mixture of complexes **5a,b** (Scheme 1), which were isolated in 37 % yield after evaporation of the electrolysis solution and extraction of the oily residue with hexane. The structure of complexes **5a,b** was confirmed by the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1153—1157, June, 1995.

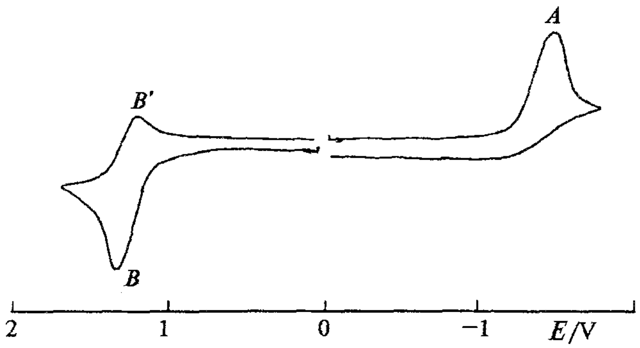


Fig. 1. Cyclic voltamperogram of complex 2^+ (glassy carbon electrode, THF, 0.2 *M* Bu_4NPF_6, 200 mV s^{-1}).

Table 1. Potentials of the peaks on the cyclic voltamperograms of the platinum complexes ($C = 2 \cdot 10^{-3}$ mol L^{-1}, 0.1 *M* Bu_4NBF_4, $V = 200$ mV s^{-1}, relative to saturated calomel electrode)

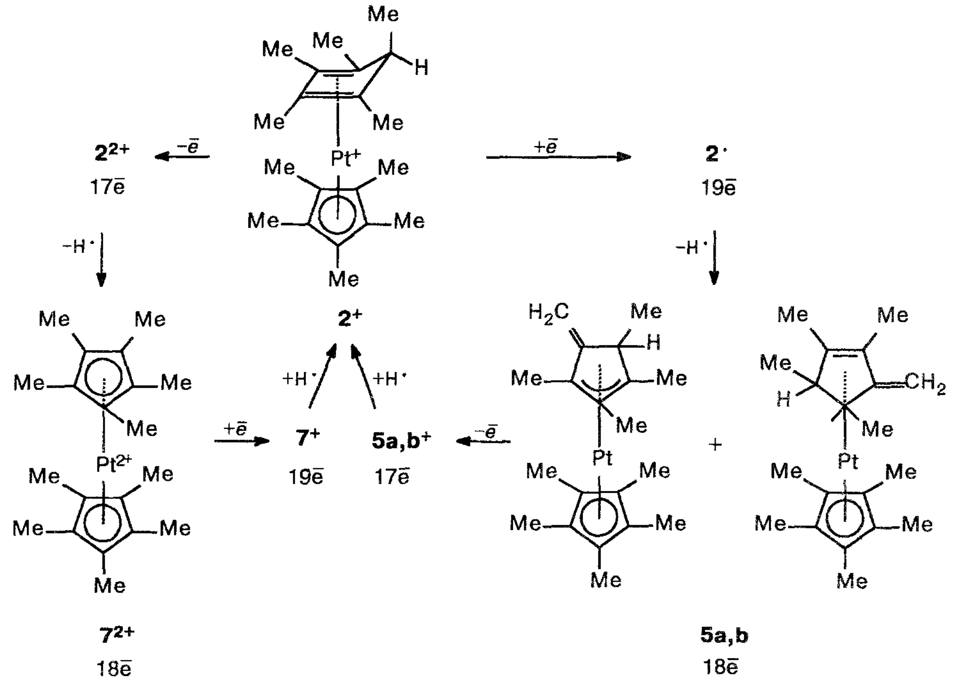
Compound	$-E_{c.p.}$/V			$E_{a.p.}$/V
	CH_2Cl_2	THF	Acetone	CH_2Cl_2
1^+	1.34	1.24	1.32	1.76*
2^+	1.57	1.44	1.54	1.35*
3^+	1.44	—	—	1.68
4^+	1.70	—	—	1.73
5a,b	—	2.35	—	0.20 0.32
6a—d	—	2.30	—	0.52 0.82
7^{2+}	—		0.60	—
8^{2+}	—		0.26	—

* Analogous potentials of the peaks are observed in acetone.

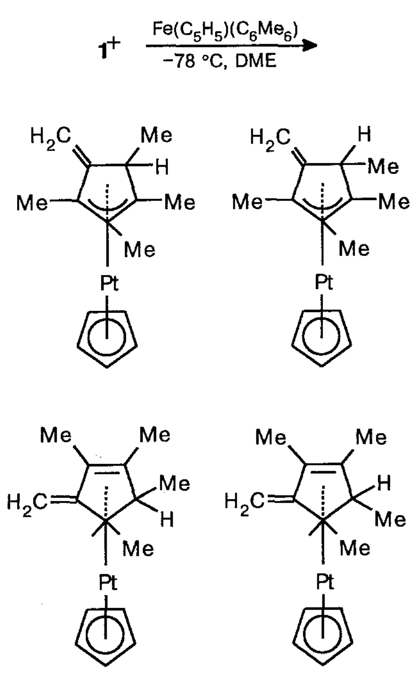
data of ^1H and ^{13}C NMR and elemental analysis.[3] The preparative electrolysis of complex 1^+ in THF on a mercury cathode (E of electrolysis = −1.50 V) proceeds with the consumption of 2 F mol^{-1} and the precipitation of platinum metal. This attests to the decomposition of the reduction products under the conditions of electrolysis, giving electroactive compounds that cause the additional expenditure of electricity. Only the reduction of 1^+ at −78 °C under the action of a one-electron reducing agent, viz., $19\bar{e}$ complex $Fe(C_5H_5)(C_6Me_6)$ (oxidation potential is −1.55 V),[4] allowed us to obtain the mixture of complexes **6a—d** (in 13 % yield), which are the *exo*- and *endo*-H-isomers of the η^5-cyclopentadienyl analogs of **5a,b** (Scheme 2). The structure of complexes **6a—d**, which proved to be less stable than **5a,b**, was confirmed by ^1H NMR spectral data.[3]

Two oxidation peaks are present on the cyclic voltamperogram of complexes **5a,b** of σ,π-olefin and allyl type, which is in agreement with the presence of two complexes of different structure in the mixture.* As

Scheme 1



Scheme 2



6a—d

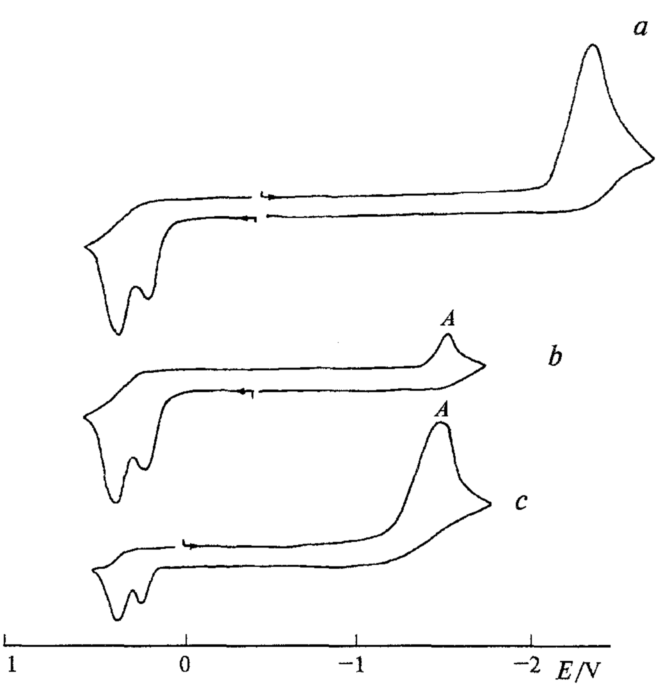


Fig. 2. Cyclic voltamperograms of the complexes (glassy carbon electrode, THF, 0.2 *M* Bu_4NPF_6, 200 mV s^{-1}). *a* — **5a,b**, the peaks of oxidation and reduction; *b* — **5a,b**, the peaks of oxidation and the corresponding cathodic answer (peak *A*); *c* — $\mathbf{2}^+$, the peak of reduction (*A*) and the corresponding anodic answers.

expected, on the voltamperograms of complexes **6a—d** the oxidation peaks are observed at the more positive potentials than those for **5a,b** due to the presence of non-metallated η^5-cyclopentadienyl ligand in **6a—d**. The oxidation peaks of complexes **5a,b** and **6a—d** are irreversible. On the reversed scan of the potential, the reduction peaks are observed on the cathode branch of the voltamperograms of complexes **5a,b** and **6a—d** (see Fig. 2, *b*, peak *A*). The potentials of these peaks are close to the reduction potentials of $\mathbf{2}^+$ and $\mathbf{1}^+$, which allowes one to propose that $\mathbf{2}^+$ and $\mathbf{1}^+$ are the products of the oxidation of **5a,b** and **6a—d**. It should be noted that the anode peaks of complexes **5a,b** and **6a—d** are observed on the anode branches of the cyclic voltamperograms of $\mathbf{2}^+$ and $\mathbf{1}^+$ only after preliminary cathode polarization of these compounds (see Fig. 2, *c*, for $\mathbf{2}^+$), which indicates a rather high reaction rate of the cleavage of C—H bonds in $\mathbf{2}^*$ and $\mathbf{1}^*$ to form **5a,b** and **6a—d**.

The data obtained indicate that the addition of an electron to $\mathbf{1}^+$ and $\mathbf{2}^+$ leads to the reactive $19\bar{e}$ radicals $\mathbf{1}^*$ and $\mathbf{2}^*$, which are stabilized by the homolytic cleavage of the C—H bonds in the methyl groups located at the α- and β-positions to the sp^3-hybridized carbon atom of η^4-pentamethylcyclopentadienyl ligand coordinated to the metal. This process gives $18\bar{e}$ complexes **5a,b** and **6a-d**. The oxidation of the latter probably results in the generation of $17\bar{e}$ cation radical species, which abstract hydrogen atom from the solvent to form the C—H bond and, thus, to regenerate the pentamethylcyclopentadiene structure of the ligand. These processes are shown in Scheme 1 taking complex $\mathbf{2}^+$ as an example.

The oxidation of complexes $\mathbf{1}^+$—$\mathbf{4}^+$ in various solvents occurs at high positive potentials (see Table 1). Decamethyl complex $\mathbf{2}^+$ is oxidized most readily (peak *B*, Fig. 1 and 3, *a*) with the elimination of one electron to give the most stable $17\bar{e}$ dication radical. The peak of the reduction of the latter can be detected during reversed scanning of the potential in CH_2Cl_2 and acetone (see Fig. 3, *a*, peak *B'*). However, $i_{c.p.} < i_{a.p.}$, which indicates a rather high reactivity of the dication radical. At more negative potentials (−0.6 V), a peak corresponding to the reduction of the product of the conversion of dication radical appears (see Fig. 3, peak *C*). In order to identify this product, we carried out the preparative oxidation of $\mathbf{2}^+$ in acetone on a carbon-glass electrode at a potential of +1.7 V using $NaBF_4$ as the background electrolyte. Dication of dimethylplatinocene $\mathbf{7}^{2+}$ was isolatied in 49 % yield as the electrolysis product, and its structure

---

[*] The peaks of reduction on the cyclic voltamperograms of complexes **5a,b** (see Fig. 2, Table 1) and **6a—d** (Table 1), which are observed at more negative potentials than those of the peaks of reduction of $\mathbf{1}^+$ и $\mathbf{2}^+$, were not specially studied in the present work.

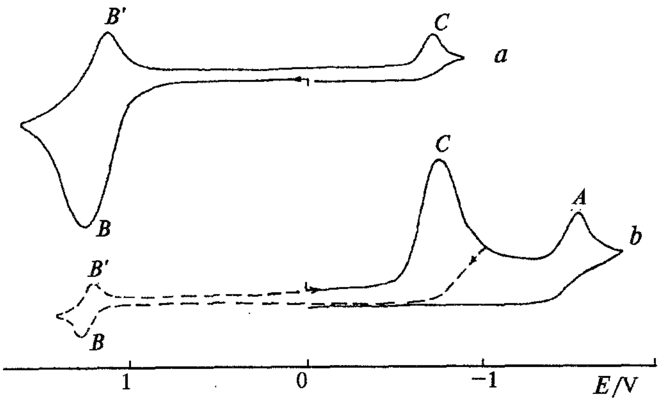


Fig. 3. Cyclic voltamperograms of the complexes (glassy carbon electrode, acetone, 0.2 *M* Bu_4NPF_6, 200 mV s^{-1}). *a* — 2^+, the peak of oxidation (*B*), the peak of reduction 2^{++} (*B'*), and the corresponding cathodic answer (peak *C*); *b* — 7^{2+}, the peaks of reduction (*A*, *C*) and the corresponding anodic answer (*B*, *B'*).

was confirmed by the data of ^1H and ^{13}C NMR and element analysis.[3] This compound was previously obtained by the reaction of $[Pt_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Br)_3]^+$ with $AgBF_4$ in the presence of cyclopentadiene.[5] The advantage of the electrochemical preparation of 7^{2+} from 2^+ is that the use of hardly accessible $[Pt_2(C_5Me_5)_2(\mu\text{-}Br)_3]$ is not neccesary.[5]

Thus, the oxidation of 2^+ results in the formation of the reactive 17ē dication radical, wherein the C—H bond at the sp^3-carbon atom of the pentamethylcyclopentadiene ligand is cleaved to form dicationic platinocene 7^{2+} (see Scheme 1).

Unlike the decamethylbiscyclopentadienyl complexes of nickel which are known as three redox forms, *viz.*, $(C_5Me_5)_2Ni^{n+}$, n = 0, 1, 2 (18ē, 19ē and 20ē, respectively), 7^{2+} is the first stable 18ē biscyclopentadienyl platinum complex. The investigation of its redox properties showed that 7^{2+} cannot be oxidized, but can be rather easily reduced (see Fig. 1, *b*, peak *C*). The dication of pentamethylplatinocene 8^{2+} prepared by a chemical method[5] behaves analogously. The reduction peaks of 7^{2+} and 8^{2+} are monoelectronic and irreversible even at −60 °C, which indicates the high reactivity of the 19ē cation radicals formed. The appearance of the peaks characteristic of 2^+, *viz.*, a cathode peak (see Fig. 3, *b*, peak *A*) at high values of the cathode potential, and a pair of peaks *BB'* (see Fig. 3, *b*) that arise after preliminary reduction of 7^{2+}, testify that 2^+ is the product of the stabilization of 17ē cation 7^+. This is also confirmed by the data on the preparative reduction of 7^{2+} on a glassy carbon electrode in aceton at −0.80 V. The voltamperogram of the solution obtained after electrolysis exhibits only the peaks of complex 2^+, which is formed due to the addition of hydrogen to 7^+ and formation of the C—H bond at the sp^3-hybridized carbon atom of the pentamethylcyclopentadiene ligand. It should be noted that the potential of the reduction peak of 7^{2+} ($E_{c.p.}$ = −0.60 V) is of a more negative value than the potential of the pair $(C_5Me_5)_2Ni^{2+/+}$ ($E_{c.p.}$ = +0.31 V),[6] while 19ē cation $(C_5Me_5)_2Pt^+$ is more reactive than the rather stable 19ē cation $(C_5Me_5)_2Ni^+$, which can be further reduced to 20ē complex $(C_5Me_5)_2Ni$. A similar conclusion can be done when comparing the reactivities of 19ē complexes $Co(C_5R_5)_2$ and $Rh(C_5R_5)(C_5Me_5)$, where R = H, Me. The latter complexes, unlike $Co(C_5R_5)_2$, are stabilized either via dimerisation of the ligand-ligand type (R = H) or by the formation of the C—H bond to give $Rh(\eta^5\text{-}C_5R_5)(\eta^4\text{-}C_5Me_5H)$ (R = Me).[7] A similar reaction is also observed for 19ē cation 7^{+*}.

Thus, the results of our study (Scheme 1) attest to the fact that the oxidation and reduction of 2^+ induce two types of reactions. During these redox cycles, the cleavage of C—H bonds is observed for the methyl groups located in the α- and β-positions to the sp^3-carbon atom of the ligand in the case of 19ē complex 2^* and for those at the sp^3-carbon atom of the pentamethylcyclopentadiene ligand in the case of 17ē cation 2^{2+}. These selective processes give rise to new complexes **5a,b** and 7^{2+}. The oxidation of **5a,b** or reduction of 7^{2+} proceed rather easily and involve the generation of the corresponding odd-electron complexes. The further reactions of the latter result in the formation of C—H bonds and the regeneration of complex 2^+, which is probably the most thermodynamically stable.

Experimental

Cyclic voltamperograms were recorded using a high-speed potentiostat PI-50-1. The working electrodes were glassy carbon and platinum, the auxillary electrode was a platinum plate, and the reference electrode was an aqueous saturated calomel electrode. The measurements were carried out in acetone, tetrahydrofuran, and methylene chloride solutions using a 0.1 *M* solution of tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The concentration of the starting compounds was $2 \cdot 10^{-3}$ mol L^{-1}. The sweep rate of the potential was 200 mV s^{-1}. The preparative electrolyses were carried out using a P-5827M potentiostat in an electrolyzer of 50 cm^3 in volume with the cathode and anode areas separated by a porous membrane. Coulometric measurements were done using a Radelkis digital integrator.

The studied platinum complexes were synthesized according to the procedures described previously.[8] The compounds obtained by preparative electrolyses were isolated and characterized by element analysis and ^1H and ^{13}C NMR spectroscopy.

This work was carried out with financial support from the Russian Foundation for Basic Research (Project No. 94-03-08598).

References

1. D. Astruc, *New J. Chem.*, 1992, **16**, 305.
2. G. E. Herberich, U. Englert, and F. Marken, *J. Chem. Soc. Dalton Trans.*, 1993, 1979.
3. O. V. Gusev, L. N. Morosova, T. A. Peganova, M. G. Peterleitner, S. M. Peregudova, L. I. Denisovich, P. V. Petrovskii, Y. F. Oprunenko, and N. A. Ustynyuk, *J. Organomet. Chem.*, 1995 (in press).
4. J. R Hamon, D. Astruc, E. Roman, and P. Michaud, *J. Am. Chem. Soc.*, 1981, **103**, 758.
5. O. V. Gusev, T. A. Peganova, M. G. Peterleitner, S. M. Peregudova, L. I. Denisovich, N. A. Ustynyuk, and P. M. Maitlis, *J. Organomet. Chem.*, 1994, **480**, C16.
6. J. L. Robbins, N. Edelstein, B. Spencer, and J. C. Smart, *J. Am. Chem. Soc.*, 1982, **104**, 1882.
7. O. V. Gusev, L. I. Denisovich, M. G. Peterleitner, A. Z. Rubezhov, N. A. Ustynyuk, and P. M. Maitlis, *J. Organomet. Chem.*, 1993, **452**, 219.
8. O. V. Gusev, L. N. Morozova, T. A. Peganova, P. V. Petrovskii, N. A. Ustynyuk, and P. M. Maitlis, *J. Organomet. Chem.*, 1994, **472**, 359.

Received February 2, 1995