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Redox-induced activation of C–H bonds in 1,2,3,4,5-pentamethylcyclopentadiene platinum complexes

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Abstract

The electrochemical behaviour of the platinum complexes $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5H_5)]^+BF_4^-$ (1^+) and $[Pt(\eta^4\text{-diene})(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (diene = C_5Me_5H (2^+) or 1,3-cyclohexadiene; (3^+) 1,5-cyclooctadiene(4^+)) has been studied by cyclic voltammetry. The complexes 1^+–4^+ are capable of both oxidation and reduction. The bulk electrolysis of 2^+ at the potential of its reduction gives a mixture of two neutral isomeric complexes **5a** and **5b**. These are assigned structures with η^3-allylic and of σ, π-bonding methylene cyclopentenyl $Me_3C_5H({=}CH_2)$ ligand. This is the proposed result from methyl C–H bond breakage in pentamethylcyclopentadiene ligand of an intermediate 19-electron complex $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^{\cdot}$ ($2^{\cdot}$). The same mixture of isomers **5a** and **5b** forms in interaction of 2^+ and ^{t}-BuOK in tetrahydrofuran. The preparative electrochemical oxidation of 2^+ proceeds with C–H bond scission at the pentamethylcyclopentadiene sp^3-hybridized carbon in an intermediate 17-electron dication radical $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^{\cdot 2+}$ ($2^{\cdot 2+}$) to give decamethylplatinacene dication $[Pt(\eta^5\text{-}C_5Me_5)_2]^{2+}(BF_4^-)_2$ (7^{2+}). The one-electron reduction of 7^{2+} regenerates 2^+.

Keywords: Platinum; Metallocenes; Cyclopentadienyl; Electrochemistry

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1. Introduction

C–H bond activation in coordinated ligands induced by electron transfer are well known [1], but examples of 18-electron complexes which can undergo C–H activation via both 17-electron and 19-electron intermediates remain rare. Here we report selective reductively and oxidatively induced C–H bond activation in η^4-pentamethylcyclopentadiene platinum complexes which have recently been prepared by us [2].

2. Results and discussion

The cyclic voltammetry study of $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5H_5)]^+BF_4^-$ (1^+) and $[Pt(\eta^4\text{-diene})(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (diene = C_5Me_5H, (2^+) or 1,3-cyclohexadiene (3^+), 1,5-cyclooctadiene (4^+)) was carried out on carbon glass electrode in CH_2Cl_2 solution with Bu_4NPF_6 as the supporting electrolyte.

It follows from the data (Table 1) obtained that 1^+–4^+ are able to undergo both oxidation and reduction, unlike the related complexes $[Pt(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}Cp)]^+$ (Cp = C_5H_5, C_5H_4Me, or C_5Me_5) for which oxidation was not observed [3].

The reduction of all four complexes 1^+–4^+ present one-electron irreversible processes. The values of the reduction potentials of 1^+–4^+ are close to reduction potentials found for $[Pt(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}Cp)]^+$ (Cp = C_5H_5, C_5H_4Me or C_5Me_5) [3]. The complex 1^+ is reduced at −1.34 V. The reduction peak of 2^+ is shifted to more negative values ($\Delta = 0.23$ V (Table 1)) because of the presence of five methyl groups in pentamethylcyclopentadienyl ligand. Methyl groups in the pentamethylcyclopentadiene ligand exert a similar influence on the reduction potential values, as can be seen from a comparison of reduction potentials of the 1,3-cyclohexadiene (3^+) (−1.44 V) and pentamethylcyclopentadiene (2^+) (−1.57 V) complexes. The 1,5-

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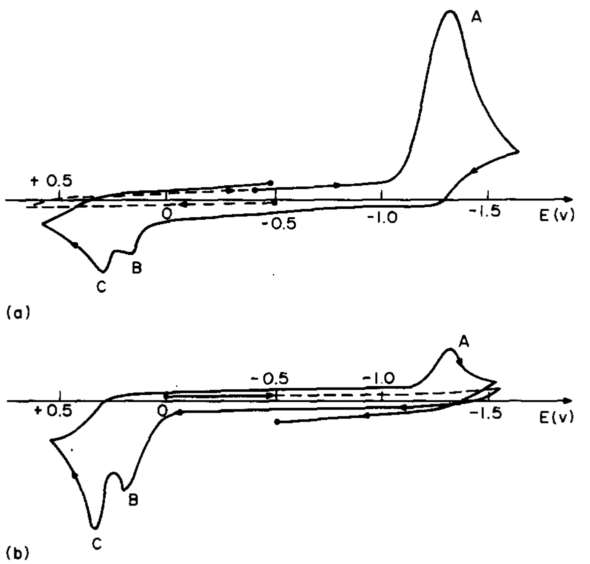


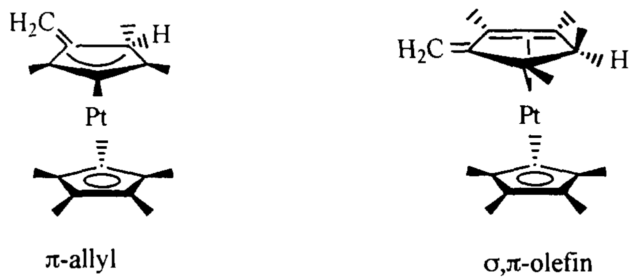
Fig. 1. Reduction of $[Pt(\eta^4-C_5Me_5H)(\eta^5-C_5Me_5)]^+ BF_4^-$ (2^+) as shown by cyclic voltammograms of 2^+; ($c = 4 \times 10^{-3}$ M l^{-1}; THF; Bu_4NPF_6; Hg electrode; $s = 200$ mV s^{-1}; with reference to a saturated calomel electrode): (a) before electrolysis; (b) after electrolysis.

cyclooctadiene complex (4^+) is reduced with slightly greater difficulty (−1.70 V).

Oxidation of 1^+–4^+ takes place at high positive potentials (Table 1). Only in the case of 2^+ is the oxidation peak quasi-reversible, while the other complexes, 1^+, 3^+ and 4^+, are oxidized irreversibly. The oxidation processes are of a one-electron native for 2^+ and 3^+ and of a two-electron native for 1 + and 4^+. It is proposed that decomposition of the first-formed 17-electron dication radicals $1^{\cdot 2+}$ and $4^{\cdot 2+}$ is followed by oxidation of decomposition products in the latter two instances.

2.1. Reduction of $[Pt(\eta^4-C_5Me_5H)(\eta^5-C_5R_5)]BF_4$ (R = H (1^+), Me (2^+))

After cathodic polarization of 1^+ and 2^+ at potentials of their reduction peaks new peaks were observed on anodic branch of cyclic voltammograms arising from oxidation of reduction products (Fig. 1(a)). The preparative electrochemical reduction of 1^+ and 2^+ was undertaken with the aim of establishing the structure of their reduction products.



5a,b

Scheme 1.

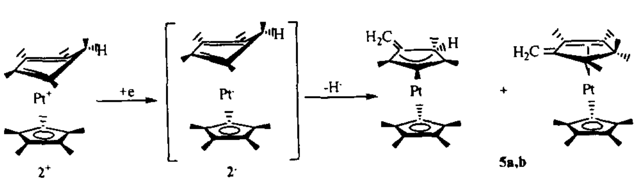
The bulk electrolysis of solution of $[Pt(\eta^4-C_5Me_5H)(\eta^5-C_5Me_5)]BF_4$ (2^+) in tetrahydrofuran (THF) was carried out on a mercury electrode at −1.8 V. After passing 1 F mol^{-1}, the solution showed no reduction peaks of 2^+ but did show oxidation peaks at +0.30 and +0.48 V (Fig. 1(b)). Evaporation of the solvent followed by extraction of the residue with hexane gave a mixture of two isomeric neutral complexes.

The ^1H NMR spectrum (C_6D_6) of this mixture showed strong singlets at $\delta = 1.93$ ($J_{Pt-H} = 18.3$ Hz) and 2.02 ($J_{Pt-H} = 24.4$ Hz) ppm arising from C_5Me_5 rings of different isomers, (the ratio is 1.3 : 1.0). In addition, six methyl resonances were observed at $\delta =$ 1.36 ($J_{Pt-H} = 44.0$ Hz), 1.47 ($J_{Pt-H} = 44.0$ Hz), 2.05 ($J_{Pt-H} = 26.4$ Hz), 1.42 ($J_{Pt-H} = 14.0$ Hz), 1.62 ($J_{Pt-H} = 14.0$ Hz) and 1.91 ppm. The presence of methyl doublets at 1.11 ($J = 6.9$ Hz) and 1.24 ($J = 7.4$ Hz) ppm as well as corresponding quartets at 2.96 ($J = 6.9$ Hz, $J_{Pt-H} = 48.4$ Hz) and 2.21 ($J = 6.9$, $J_{Pt-H} = 4.5$ Hz) ppm indicates that CHMe groups remain in each isomer. There are also two pairs of resonances in lower fields; 4.47 (s, 1H, $J_{Pt-H} = 24.7$ Hz), 4.68 (s, 1H, $J_{Pt-H} = 20.7$ Hz) and 2.65 (d, 1H, $J_{Pt-H} = 64.5$ Hz), 3.74 (d, 1H, $J_{Pt-H} = 62.3$ Hz) ppm. We therefore propose that the neutral complexes obtained in reduction are mixture of two isomers **5a** and **5b** one having η^3-allylic and the other a σ, π-olefin bonding (Scheme 1).

In the ^{13}C spectra, the C_5Me_5 rings exhibit two sets of signals, at 8.59 ($J_{Pt-C} = 3.4$ Hz), 99.73 ($J_{Pt-C} = 34.2$ Hz) and 10.63 ($J_{Pt-C} = 2.0$ Hz), 103.72 ($J_{Pt-C} = 35.4$ Hz) ppm. The resonance of quaternary carbon at 19.55 ($J_{Pt-C} = 442.0$ Hz) ppm is shifted upfield as is charac-

Table 1
Cyclic voltammetry data for 1^+–4^+ ($c = 2 \times 10^{-3}$; CH_2Cl_2; 0.1 M Bu_4NBF_4; $s = 200$ mV s^{-1}; with reference to a saturated calomel electrode)

Compound	E_{pa} V (V)	E_{pc} V (V)
$[Pt(\eta^4-C_5Me_5H)(\eta^5-C_5H_5)]^+BF_4^-$ (1^+)	+1.76 ($n = 2$)	−1.34 ($n = 1$)
$[Pt(\eta^4-C_5Me_5H)(\eta^5-C_5Me_5)]^+BF_4^-$ (2^+)	+1.35 ($n = 1$)	−1.57 ($n = 1$)
$[Pt(\eta^4-C_6H_8)(\eta^5-C_5Me_5)]^+BF_4^-$ (3^+)	+1.68 ($n = 1$)	−1.44 ($n = 1$)
$[Pt(\eta^4-C_8H_{12})(\eta^5-C_5Me_5)]^+BF_4^-$ (4^+)	+1.73 ($n = 2$)	−1.70 ($n = 1$)



Scheme 2.

terized for σ-bonded carbon atoms in σ,π-cycloenyl platinum complexes [4]. The resonances of secondary carbon atoms at 30.41 and 32.16 ppm do not show coupling to Pt, indicating the presence of uncoordinated *exo*-methylene groups. The two signals 50.58 ($J_{Pt-C} = 64.1$ Hz) and 52.29 ($J_{Pt-C} = 16.8$ Hz) ppm are due to the uncoordinated CHMe groups; the significant difference in Pt–C spin-coupling constants is probably due to different distances between those carbon atoms and the platinum Pt–C atom in the isomers **5a** and **5b**.

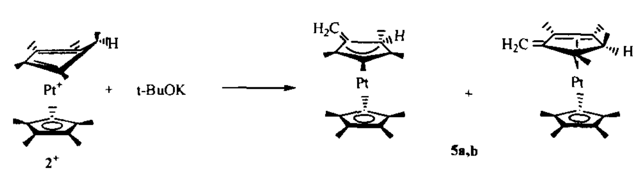
Although unequivocal assignment of all resonances of primary and quaternary carbon atoms cannot be made, the ^{13}C NMR spectrum (number of resonances, chemical shifts and values of Pt–C spin-coupling constants) agrees with the structures proposed for **5a** and **5b**. Elemental analysis also corresponds to those proposed for the compositions of **5a** and **5b**.

The results can be rationalized in terms of Scheme 2. The unstable 19-electron radical **2**˙ formed as a result of electrochemical reduction of $\mathbf{2}^+$ undergoes spontaneous homolysis of the C–H bonds in methyl groups attached to the coordinated carbons of the η^4-pentamethylcyclopentadiene ligand.

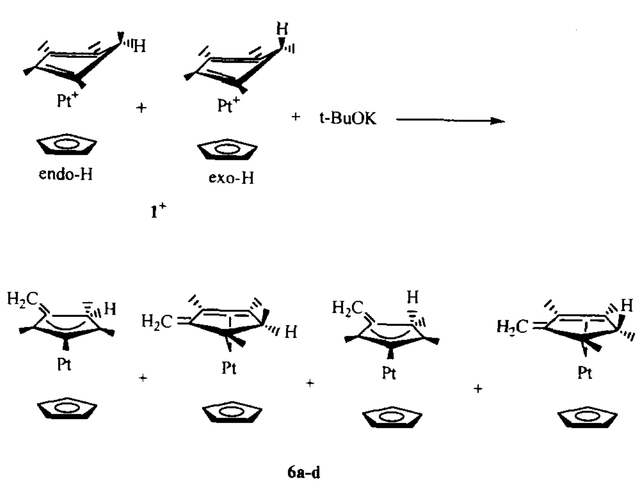
In this reaction no formation of products derived from breaking of C–H bonds at the sp^3 carbon atom of the η^4-ligand or in the methyl groups of the η^5-pentamethylcyclopentadienyl ligand has been observed.

The same mixture of **5a** and **5b** has been obtained by deprotonation of $\mathbf{2}^+$ with ^{t}BuOK in THF (Scheme 3).

The deprotonation of the mixture of *exo*-H and *endo*-H isomers of $\mathbf{1}^+$, which is phenomenologically very close to the process in Scheme 3, also leads to neutral isomeric complexes of platinum **6a–6d** (Scheme 4).



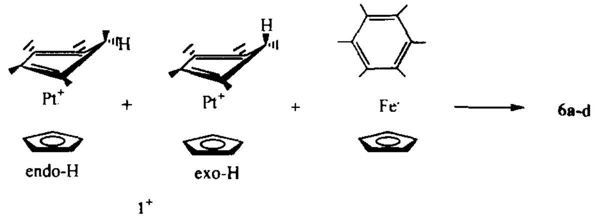
Scheme 3.



Scheme 4.

Unlike **5a** and **5b**, **6a–6d** proved to be rather unstable and were characterized only by the ^{1}H NMR spectrum and cyclic voltammetry data. Thus, in the ^{1}H NMR spectrum, three resonances of C_5H_5 rings have been observed at 5.58 ($J_{Pt-H} = 19.6$ Hz), 5.60 ($J_{Pt-H} = 20.1$ Hz) and 5.90 ($J_{Pt-H} = 28.6$ Hz) ppm. Three sets of *exo*-methylene signals are found at 4.58 (d, 1H, $J = 1.8$ Hz, $J_{Pt-H} = 25.6$ Hz), 4.93 (d, 1H, $J = 1.8$ Hz, $J_{Pt-H} = 20.6$ Hz), 4.60 (d, 1H, $J = 1.6$ Hz, $J_{Pt-H} = 27.2$ Hz), 4.89 (d, 1H, $J = 1.6$ Hz, $J_{Pt-H} = 23.4$ Hz), 2.71 (d, 1H, $J = 2.2$ Hz, $J_{Pt-H} = 110.1$ Hz), 4.25 (d, 1H, $J = 2.2$ Hz, $J_{Pt-H} = 61.0$ Hz) ppm. Resonances of the CHMe-group protons were also observed for two isomers 1.34 (d, 3H, CH_3, $J = 6.7$ Hz), 2.35 (q, 1H, $J = 6.7$ Hz), 1.04 (d, 3H, CH_3, $J = 7.1$ Hz), 3.23 (q, 1H, $J = 7.1$ Hz, $J_{Pt-H} = 52.0$ Hz) ppm; part of the resonances of the third minor isomer has not been observed owing to a low concentration and to overlap of signals with those of the major isomers. Nevertheless, the NMR data allow one to propose that the reduction of $\mathbf{1}^+$ proceeds analogously to the reduction of $\mathbf{2}^+$.

The bulk electrolysis of solution of *exo*- and *endo*-H isomers of complex $\mathbf{1}^+$ was carried out in THF on an Hg cathode at −1.5 V. After passing 1 F mol^{-1} through the electrolyzed solution, the appearance of new oxidation peaks of low intensity at +0.52 and +0.82 V was observed on the anode branch of cyclic voltammogram. At the same time, reduction peaks of $\mathbf{1}^+$ with 50% of original intensity were observed for the solution. After passing 2 F mol^{-1} the initial current dropped from 25 to 3 μA, and the reduction peak of $\mathbf{1}^+$ had completely



Scheme 5.

Table 2
Cyclic voltammetry data for $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5R_5)]^+BF_4^-$ (R ≡ H (1^+) or Me (2^+)) and the products of their reduction ($c = 2 \times 10^{-3}$; THF; 0.1 M Bu_4NBF_4; $s = 200$ mV s^{-1}; with reference to a saturated calomel electrode)

Compound	E_{pc} (V)	E_{pa} [a] (V)	E_{pa} (V)	E_{pc} [b] (V)
1^+	−1.24 ($n = 1$)	+0.46 +0.60		
6a–bd	−2.30		+0.52 +0.82	−1.15
2^+	−1.44 ($n = 1$)	+0.19 +0.32		
5a, 5b	−2.35		+0.20 +0.32	−1.40

[a] Peaks were observed after cathodic polarization only.
[b] Peaks were observed after anodic polarization only.

disappeared while the intensity of oxidation peak had not changed. Electrolysis was accompanied by the deposition of platinum metal. All attempts to isolate **6a–6d** proved unsuccessful.

Chemical reduction of 1^+ by the 19-electron radical iron complex $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]^{\cdot}$, which has an oxidation potential of −1.55 V [5], gave mixture of isomers **6a–6d** with 12% yield (Scheme 5).

Cyclic voltammograms of isomeric complexes **5a**, **5b** and **6a–6d** (Table 2) show the presence of oxidation peaks coinciding with those observed on cyclic voltammograms of solution obtained after electrolysis of the complexes mentioned. After preliminary anodic polarization the appearance of reduction peaks of respectively 1^+ and 2^+ on polarograms of deprotonation products was observed, indicating that the latter were probable products of oxidation of **6a–6d** and of **5a** and **5b**.

Table 3
Cyclic voltammetry data for $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5R_5)]^+BF_4^-$ (R=H (1^+) or Me (2^+)) and $[Pt(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5R_5)]^{2+}(BF_4^-)_2$ (R = Me (7^{2+}) or H (8^{2+})) ($c = 2 \times 10^{-3}$; acetone; 0.1 M Bu_4NBF_4; $s = 200$ mV s^{-1}; with reference to a saturated calomel electrode)

Compounds	E_{pa} (V)	E_{pc} [a] (V)	E_{pc} (V)	E_{pa} [b] (V)
1^+	+1.76 ($n = 1$)	−0.24 −1.26	−1.32 ($n = 1$)	+0.52 +0.82
7^{2+}			−0.26 ($n = 1$) −1.28	+1.68
2^+	+1.32 ($n = 1$)	−0.60 −1.28	−1.54 ($n = 1$)	+0.20 +0.30
8^{2+}			−0.60 ($n = 1$) −1.46	+1.30

[a] Peaks were observed after anodic polarization only.
[b] Peaks were observed after cathodic polarization only.

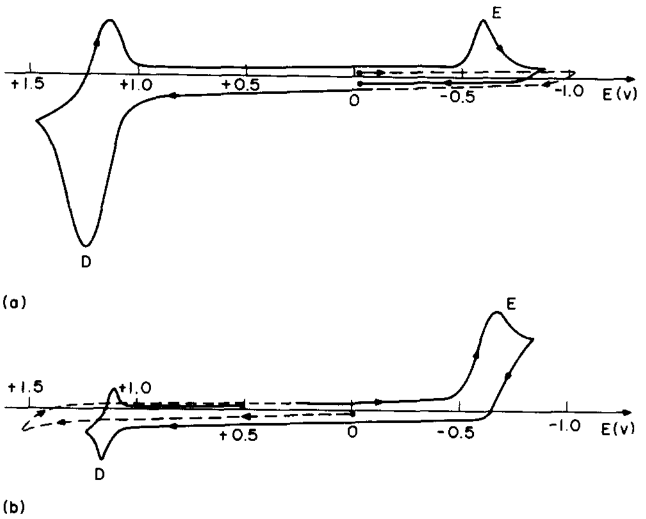
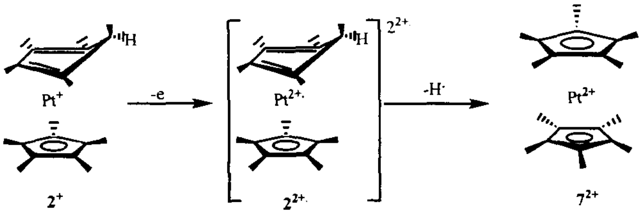


Fig. 2. Oxidation of $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (2^+) as shown by cyclic voltammograms of 2^+ ($c = 4 \times 10^{-3}$ M l^{-1}; acetone; $NaBF_4$, carbon-glass electrode; $s = 200$ mV^{+1} s^{-1}; with reference to a saturated calomel electrode): (a) before electrolysis; (b) after electrolysis.

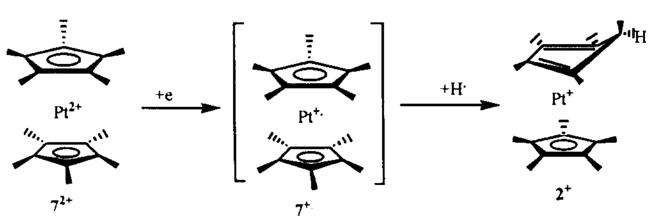
2.2. Oxidation of $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (2^+)

According to the cyclic voltammetry data, oxidation of 2^+ in CH_2Cl_2 or acetone solutions gives a new complex as evidenced by the appearance of reduction peak at −0.43 V (CH_2Cl_2) or −0.60 V (acetone) (Table 3 and Fig. 2(a)). The preparative electrolysis of $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+BF_4$- ($2^+$) was carried out in acetone solution on a carbon–glass anode at +1.7 V using $NaBF_4$ as the supporting electrolyte. The completion of the process was determined by the disappearance of the oxidation peak of the starting complex at +1.30 V and the appearance of the reduction peak at −0.60 V (Fig. 2(b)). Decamethylplatinocene dication (7^{2+}) was isolated with 49% yield after electrolysis (Scheme 6).

The oxidation of 2^+ is thought to lead to unstable 17-electron dication radical $2^{\cdot 2+}$ which undergoes C–H bond scission at the sp^3-hybridized carbon atom of the η^4-cyclopentadiene ligand to give the dication 7^{2+}. An analogous process has been observed on oxidation of η^4-pentamethylcyclopentadiene rhodium complexes [6].



Scheme 6.



Scheme 7.

We have recently prepared decamethylplatinocene dication $[Pt(\eta^5\text{-}C_5Me_5)_2]^{2+}$ (7^{2+}) by interaction of $[Pt_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Br)_3]^{3+}$ with $AgBF_4$ in the presence of pentamethylcyclopentadiene [7]. The electrochemical method of synthesis of 7^{2+} has the advantage of not requiring the difficult-to-make $[Pt_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Br)_3]^{3+}$ [8] as starting material. The complex 7^{2+} is reduced at −0.60 V, i.e. its reduction potential is shifted to the cathodic region by comparison with $[Ni(\eta^5\text{-}C_5Me_5)_2]^{2+}$ [9]. The reduction peak of 7^{2+} is irreversible even at −60°C, indicating that fast chemical transformation of the first-formed 19-electron cation radical $7^{\cdot+}$ occurs; by comparison the isostructural 19-electron cation radical $[Ni(\eta^5\text{-}C_5Me_5)_2]^{\cdot+}$ is sufficiently stable and can be isolated [9]. It should be noted that the reduction potential of 7^{2+} is more negative than was found for the Pt(II) sandwich complex $[Pt(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_6Me_6)]^{2+}$ [3].

The cyclic voltamogram of 7^{2+} exhibits reduction peaks at −1.50 V and an oxidation peak at +1.30 V (Table 3), both latter peaks belonging to 2^+. The fact that the oxidation peak at +1.30 V is not observed without preliminary cathodic polarization shows that 2^+ arises owing to reduction of the dication 7^{2+}. In accordance with this hypothesis, preparative electrochemical reduction of 7^{2+} in acetone, obtained by oxidation of 2^+ at −0.8 V, resulted in regeneration of 2^+ (Scheme 7).

In the latter process the formation of the 19-electron cation radical of decamethylplatinocene $7^{\cdot+}$ is followed by hydrogen abstraction from the medium in exactly the same manner as was found to occur on reduction of the decamethylrhodocenium cation [10].

Preparative electrochemical oxidation of isomers 1^+ could not be carried out owing to the high potential (+1.7 V) required as well as their limited solubility. Nevertheless the cyclic voltammetry data obtained for monocationic complexes 1^+ and pentamethylplatinocene dication 8^{2+} (Table 3) allow the proposition to be made that 1^+ and 8^{2+} are interconverted during the redox cycle similar to the analogous interconversions of decamethyl derivatives 2^+ and 7^{2+}.

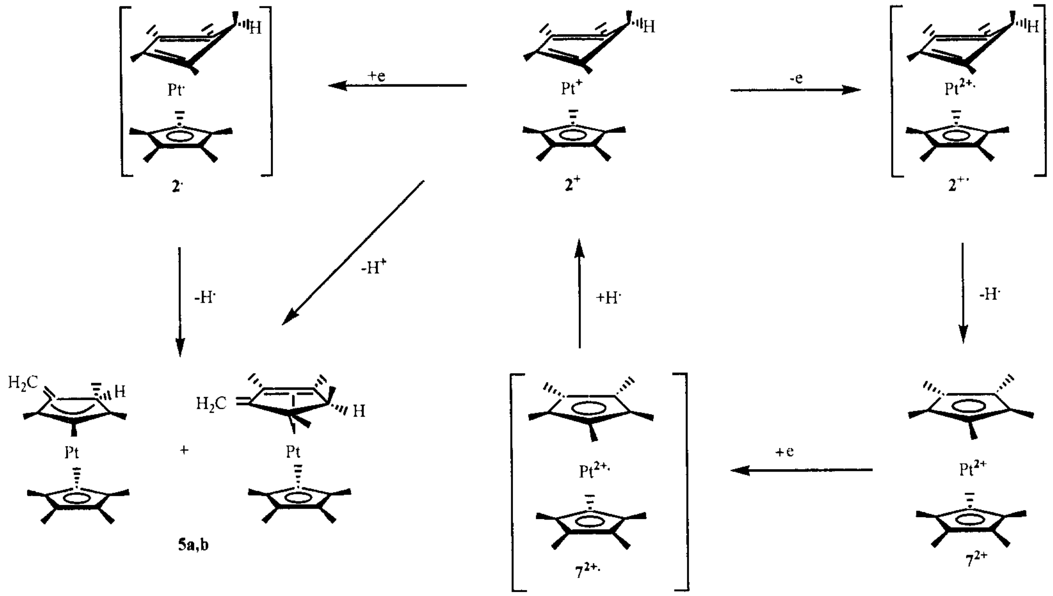
The results of this study can be summarized by Scheme 8.

Thus the ability of 1^+ and 2^+ to be both reduced and oxidized allows comparison to be made of the influence of various electron transfer processes on C–H bond activation in these compounds.

The reduction of 2^+ leads to the 19-electron radical which undergoes C–H bond activation at the methyl groups attached to coordinated carbon atoms of the $\eta^4\text{-}C_5Me_5H$ ligand giving **5a** and **5b**.

Oxidation of 2^+ to the 17-electron dication radical $2^{\cdot 2+}$ is accompanied by C–H activation (at the sp^3-hybridized carbon atom of the pentamethylcyclopentadiene ligand), resulting in the formation of the decamethylplatinocene dication 7^{2+}.

It should be emphasized that, although 1^+ and 2^+ contain several different C–H bonds, their activation



Scheme 8.

processes are selective both for 17- and 19-electron intermediates. The driving force of the processes is the formation of 18-electron compounds.

3. Experimental details

All experiments were performed under argon in solvents purified by standard methods. Complexes 1^+–4^+ were prepared by the method described in [2]. Polarography measurements were made with a PI-50-1 potentiostat and peak potentials were recorded with reference to a saturated calomel electrode. Coulometric measurements were made with an OH-404 Radelkis coulometer. Bulk electrolysis were made with a P-5827M potentiostat. ^{1}H and ^{13}C NMR spectra were obtained with Bruker-WP-200-SY and Varian VXR-400 spectrometers. All chemical shifts are reported with reference to tetramethylsilane.

3.1. Electrochemical reductions of $[Pt(\eta^4\text{-}C_5M_5H)(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (2^+)

The reduction of $\mathbf{2}^+$ (111 mg, 0.2 mmol) was carried out at a stirred Hg electrode (-1.8 V) in THF (50 cm^3) (0.2 M Bu_4NPF_6); after consumption of $19.6Q$ ($Q_{\text{theor}} = 19.4$; $n = 1$) the current decreased from 20 to 3 mA. A cyclic voltammogram of the solution obtained showed the disappearance of reduction peak of $\mathbf{2}^+$ and the appearance of two new oxidation peaks at $+0.30$ and $+0.48$ V; electrolysis was stopped. The solution was decanted and the THF removed in vacuo, to leave a residue which was extracted by hexane (3×20 cm^3). Combined hexane solution was filtered and evaporated; then the residue was dried in vacuo (yield of **5a** and **5b**, 63 mg (68%)). Anal. Found: C, 51.92; H, 6.26. $C_{20}H_{30}Pt$ Calc.: C, 51.53; H, 6.49%.

^{1}H NMR (C_6D_6): δ (first isomer) 1.11 (d, 3H, CH*Me*, $J = 6.9$ Hz); 1.36 (s, 3H, CH_3, $J_{\text{Pt-H}} = 44.0$ Hz); 1.47 (s, 3H, CH_3, $J_{\text{Pt-H}} = 44.0$ Hz); 1.93 (s, 15H, C_5Me_5, $J_{\text{Pt-H}} = 18.2$ Hz); 2.05 (s, 3H, CH_3, $J_{\text{Pt-H}} = 26.4$ Hz); 2.96 (q, 1H, C*H*Me, $J = 6.9$ Hz, $J_{\text{Pt-H}} = 48.4$ Hz); 4.47 (s, 1H, =C*H*H, $J_{\text{Pt-H}} = 24.7$ Hz); 4.68 (s, 1H, =CH*H*, $J_{\text{Pt-H}} = 20.7$ Hz); δ (second isomer) 1.24 (d, 3H, CH*Me*, $J = 7.4$ Hz); 1.62 (s, 3H, CH_3, $J_{\text{Pt-H}} = 14.0$ Hz); 1.91 (s, 3H, CH_3); 2.02 (s, 15H, C_5Me_5, $J_{\text{Pt-H}} = 24.4$ Hz); 2.21 (q, 1H, C*H*Me, $J = 7.4$ Hz, $J_{\text{Pt-H}} = 4.5$ Hz); 2.66 (d, 1H, C*H*H, $J = 2.2$ Hz, $J_{\text{Pt-H}} = 64.5$ Hz); 3.74 (d, 1H, CH*H*, $J = 2.2$ Hz, $J_{\text{Pt-H}} = 62.3$ Hz). ^{13}C NMR (C_6D_6); δ (primary) 8.59 (C_5*Me*$_5$, $J_{\text{Pt-C}} = 3.4$ Hz); 10.63 (C_5*Me*$_5$, $J_{\text{Pt-C}} = 2.0$ Hz); 11.19 (CH_3, $J_{\text{Pt-C}} = 45.8$ Hz); 12.40 (CH_3, $J_{\text{Pt-C}} = 110.2$ Hz); 12.93 (CH_3, $J_{\text{Pt-C}} = 26.6$ Hz); 14.45 (CH_3, $J_{\text{Pt-C}} = 11.9$ Hz); 14.61 (CH_3, $J_{\text{Pt-C}} = 20.2$ Hz); 14.89 (CH_3, $J_{\text{Pt-C}} = 14.6$ Hz); 18.05 (CH_3, $J_{\text{Pt-C}} = 54.4$ Hz); 20.80 (CH_3, $J_{\text{Pt-C}} = 72.7$ Hz); δ (secondary) 30.41 (=CH_2, $J_{\text{Pt-C}} = 34.3$ Hz); 32.16 (=CH_2, $J_{\text{Pt-C}} = 34.0$ Hz); δ (tertiary) 50.58 (*CH*Me, $J_{\text{Pt-C}} = 64.1$ Hz); 52.29 (*C*HMe, $J_{\text{Pt-C}} = 16.8$ Hz); δ (quaternary) 19.55 ($J_{\text{Pt-C}} = 422.0$ Hz); 80.38 ($J_{\text{Pt-C}} = 144.0$ Hz); 89.81 ($J_{\text{Pt-C}} = 36.3$ Hz); 99.73 ($J_{\text{Pt-C}} = 34.2$ Hz); 103.72 ($J_{\text{Pt-C}} = 35.4$ Hz); 132.98 ($J_{\text{Pt-C}} = 32.2$ Hz); 140.92 ($J_{\text{Pt-C}} = 13.1$ Hz); 163.50 ($J_{\text{Pt-C}} = 82.2$ Hz).

3.2. Electrochemical oxidation of $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (2^+)

The electrolysis of $\mathbf{2}^+$ (103 mg, 0.2 mmol) was carried out at a carbon glass electrode ($+1.7$ V) in acetone (50 cm^3) (0.1 M $NaBF_4$). Monitoring of the electrolysis was provided by cyclic voltammetry. The resulting solution was evaporated to dryness, and the residue was dissolved in water (30 cm^3). The addition of a solution of NH_4PF_6 in water led to precipitation of white solid, which was filtered, dried in vacuo and reprecipitated from CH_2Cl_2–Et_2O (yield of $\mathbf{7}^{2+}$, 70 mg (49%)). Anal. Found: C, 31.48; H, 3.74. $C_{20}H_{30}F_{12}P_2Pt$ Calcd.: C, 31.77; H, 4.00%.

^{1}H NMR (acetone-d_6): 2.39 (s, 2 C_5Me_5, $J_{\text{Pt-H}} = 19.2$ Hz). ^{13}C NMR (acetone-d_6): 8.03 (s, C_5Me_5, $J_{\text{Pt-C}} = 9.0$ Hz); 114.6 (s, C_5Me_5, $J_{\text{Pt-C}} = 69.1$ Hz).

The oxidation of $\mathbf{2}^+$ (64 mg, 0.018 mmol) in acetone (50 cm^3) (0.1 M Bu_4NPF_6) at $+1.4$ V using a carbon glass electrode required $13.3Q$ ($Q_{\text{theor}} = 11.2$; $n = 1$). The cyclic voltammogram of the resulting solution shows a cathodic peak at -0.60 V, characteristic for ($[Pt(\eta^5\text{-}C_5Me_5)_2]^{2+}(PF_6^-)_2$). Reduction of the solution at -0.8 V ($Q_{\text{exp}} = 9.2$) led to regeneration of $\mathbf{2}^+$ ($E_{\text{pc}} = -1.44$ V).

^{1}H NMR (acetone-d_6): 2.39 (s, 2C_5Me_5, $J_{\text{Pt-H}} = 19.2$ Hz).

3.3. Interaction of $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ *with* ^{t}*BuOK*

Sodium tert-butoxide (34 mg; 0.3 mmol) was added to a suspension of $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (118 mg; 0.2 mmol) in THF (10 cm^3) at -78 °C. The mixture was stirred for 10 min, and allowed to warm to room temperature; then the solvent was evaporated in vacuo (yield of **5a** and **5b**, 76 mg (82%)). Anal. Found: C, 51.92; H, 6.26. $C_{20}H_{30}Pt$ Calcd.: C, 51.53; H, 6.49%.

^{1}H NMR (C_6D_6): δ (first isomer) 1.11 (d, 3H, 3H*Me*, $J = 6.9$ Hz); 1.36 (s, 3H, CH_3, $J_{\text{Pt-H}} = 44.0$ Hz); 1.47 (s, 3H, CH_3, $J_{\text{Pt-H}} = 44.0$ Hz); 1.93 (s, 15H, C_5Me_5, $J_{\text{Pt-H}} = 18.2$ Hz); 2.05 (s, 3H, CH_3, $J_{\text{Pt-H}} = 26.4$ Hz); 2.96 (q, 1H, C*H*Me, $J = 6.9$ Hz, $J_{\text{Pt-H}} = 48.4$ Hz); 4.47 (s, 1H, =C*H*H, $J_{\text{Pt-H}} = 24.7$ Hz); 4.68 (s, 1H, =CH*H*, $J_{\text{Pt-H}} = 20.7$ Hz); δ (second isomer) 1.24 (d, 3H, CH*Me*, $J = 7.4$ Hz); 1.62 (s, 3H, CH_3, $J_{\text{Pt-H}} = 14.0$ Hz); 1.91 (s, 3H, CH_3); 2.02 (s, 15H, C_5Me_5, $J_{\text{Pt-H}} = 24.4$ Hz); 2.21 (q, 1H, C*H*Me, $J = 7.4$ Hz, $J_{\text{Pt-H}} = 4.5$ Hz); 2.66 (d, 1H, C*H*H, $J = 2.2$ Hz, $J_{\mathrm{Pt-H}} = 64.5$ Hz); 3.74 (d, 1H, CH*H*, $J = 2.2$ Hz, $J_{\mathrm{Pt-H}} = 62.3$ Hz).

3.4. Interaction of $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5H_5)]^+BF_4^-$ (1^+) with ^{t}BuOK

Sodium tert-butoxide (34 mg; 0.3 mmol) was added to a suspension of $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5H_5)]^+BF_4^-$ (100 mg; 0.2 mmol) in THF at −78°C. The mixture was stirred for 10 min and allowed to warm to room temperature; then the solvent was evaporated in vacuo. A solid was extracted by hexane (20 cm^3); the resulting solution was filtered and evaporated in vacuo (yield of **6a–6d**, 51 mg (65%)).

^{1}H NMR (C_6D_6): δ (first isomer) 1.34 (d, 3H, CH_3, $J = 6.7$ Hz); 1.54 (s, 3H, CH*Me*, $J_{\mathrm{Pt-H}} = 6.8$ Hz); 1.81 (s, 3H, CH_3, $J_{\mathrm{Pt-H}} = 46.7$ Hz); 2.21 (s, 3H, CH_3, $J_{\mathrm{Pt-H}} = 46.7$ Hz); 2.35 (q, 1H, C*H*Me, $J = 6.8$ Hz); 4.58 (d, 1H, C^HH, $J = 1.8$ Hz, $J_{\mathrm{Pt-H}} = 25.6$ Hz); 4.93 (d, H, CH*H*, $J = 1.8$ Hz, $J_{\mathrm{Pt-H}} = 20.6$ Hz); 5.58 (s, 5H, C_5H_5, $J_{\mathrm{Pt-H}} = 19.6$ Hz), δ (second isomer) 1.04 (d, 3H, CH*Me*, $J = 7.1$ Hz); 1.68 (s, 3H, CH_3, $J_{\mathrm{Pt-H}} = 6.0$ Hz); 1.84 (s, 3H, CH_3, $J_{\mathrm{Pt-H}} = 47.4$ Hz); 2.14 (s, 3H, CH_3, $J_{\mathrm{Pt-H}} = 34.7$ Hz); 3.23 (q, 1H, C*H*Me, $J = 7.1$ Hz, $J_{\mathrm{Pt-H}} = 52.0$ Hz); 4.60 (d, 1H, C*H*H, $J = 1.6$ Hz, $J_{\mathrm{Pt-H}} = 27.2$ Hz); 4.89 (d, 1H, CH*H*, $J = 1.6$ Hz, $J_{\mathrm{Pt-H}} = 23.4$ Hz); 5.60 (s, 5H, C_5H_5, $J_{\mathrm{Pt-H}} = 20.1$ Hz); δ (third isomer) 2.70 (d, 1H, C*H*H, $J = 2.2$ Hz, $J_{\mathrm{Pt-H}} = 110.1$ Hz), 4.25 (d, 1H, CH*H*, $J = 2.2$ Hz, $J_{\mathrm{Pt-H}} = 61.0$ Hz); 5.90 (s, 5H, C_5H_5, $J_{\mathrm{Pt-H}} = 28.6$ Hz).

3.5. Reduction $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5H_5)]^+BF_4^-$ (1^+) by $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$

A solution of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]^\cdot$ (130 mg, 0.46 mmol) in dimethoxyethane (DME) (40 cm^3) was added to suspension of **1**$^+$ (200 mg, 0.41 mmol) in DME (10 cm^3) at −78°C. The resulting mixture was allowed to warm to room temperature and stirred for 1.5 h. The solution was filtered and evaporated in vacuo. Residue oil was extracted by pentane (3 × 10 cm^3). Pentane solution was filtered and evaporated in vacuo. The solid residue obtained was dried in vacuo (yield of **6a–6d**, 19 mg (12%).

^{1}H NMR (C_6D_6): δ (first isomer) 1.34 (d, 3H, CH_3, $J = 6.7$ Hz); 1.54 (s, 3H, CH*Me*, $J_{\mathrm{Pt-H}} = 6.8$ Hz); 1.81 (s, 3H, CH_3, $J_{\mathrm{Pt-H}} = 46.7$ Hz); 2.21 (s, 3H, CH_3, $J_{\mathrm{Pt-H}} = 46.7$ Hz); 2.35 (q, 1H, C*H*Me, $J = 6.8$ Hz); 4.58 (d, 1H, C_HH, $J = 1.8$ Hz, $J_{\mathrm{Pt-H}} = 25.6$ Hz); 4.93 (d, H, CH*H*, $J = 1.8$ Hz, $J_{\mathrm{Pt-H}} = 20.6$ Hz); 5.58 (s, 5H, C_5H_5, $J_{\mathrm{Pt-H}} = 19.6$ Hz); δ (second isomer) 1.04 (d, 3H, CH*Me*, $J = 7.1$ Hz); 1.68 (s, 3H, CH_3, $J_{\mathrm{Pt-H}} = 6.0$ Hz); 1.84 (s, 3H, CH_3, $J_{\mathrm{Pt-H}} = 47.4$ Hz); 2.14 (s, 3H, CH_3, $J_{\mathrm{Pt-H}} = 34.7$ Hz); 3.23 (q, 1H, C*H*Me, $J = 7.1$, $J_{\mathrm{Pt-H}} = 52.0$ Hz); 4.60 (d, 1H, C*H*H, $J = 1.6$ Hz, $J_{\mathrm{Pt-H}} = 27.2$ Hz); 4.89 (d, 1H, CH*H*, $J = 1.6$ Hz, $J_{\mathrm{Pt-H}} = 23.4$ Hz); 5.60 (s, 5H, C_5H_5, $J_{\mathrm{Pt-H}} = 20.1$ Hz); δ (third isomer) 2.70 (d, 1H, C_HH, $J = 2.2$ Hz, $J_{\mathrm{Pt-H}} = 110.1$ Hz), 4.25 (d, 1H, CH*H*, $J = 2.2$ Hz, $J_{\mathrm{Pt-H}} = 61.0$ Hz); 5.90 (s, 5H, C_5H_5, $J_{\mathrm{Pt-H}} = 28.6$ Hz).

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